

C—H...N contacts in 4-phenyl-3-(4-pyridyl)-  
4H-1,2,4-triazoleLiliana Mazur,<sup>a</sup> Anna E. Koziol<sup>a\*</sup>  
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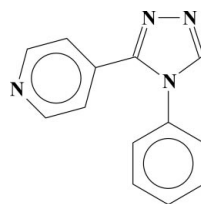
## Key indicators

Single-crystal X-ray study  
T = 293 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$   
R factor = 0.057  
wR factor = 0.126  
Data-to-parameter ratio = 14.4For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title compound,  $\text{C}_{13}\text{H}_{10}\text{N}_4$ , is a disubstituted 1,2,4-triazole derivative. The pyridyl and phenyl rings form dihedral angles of  $46.7(3)$  and  $55.9(4)^\circ$ , respectively, with the central triazole ring. The molecules in the crystal structure form two types of centrosymmetrically related dimers through hydrophobic C—H...N and  $\pi$ – $\pi$  intermolecular interactions.

## Comment

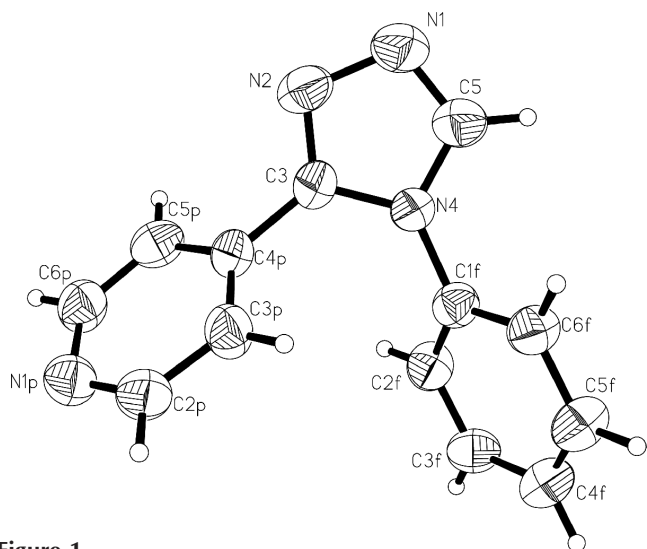
Extensive studies have been carried out in recent years on substituted 1,2,4-triazoles. The immense interest in this class of compounds results from their chemical, biological and pharmacological significance. 1,2,4-Triazole and its derivatives are starting materials for the synthesis of many heterocycles (Milcent & Redeuilh, 1979; Milcent *et al.*, 1983). They are also very useful ligands in coordination chemistry. Some complexes containing 1,2,4-triazole ligands have specific magnetic and optical properties (Kahn & Martinez, 1998; Groeneveld *et al.*, 1982; Vos *et al.*, 1983; Koningsbruggen *et al.*, 1995, 1998). Apart from their chemical significance, 1,2,4-triazole derivatives have been found to be associated with diverse pharmacological properties, such as anti-inflammatory, antifungal and antiviral (Massa *et al.*, 1992; Mahomed *et al.*, 1993; Mullican *et al.*, 1993). Some of them are also known to exhibit analgesic, anticonvulsant, tranquilizing, antidepressant, anxiolytic (Bradbury & Rivett, 1991; Sughen & Yoloye, 1978; Stillings *et al.*, 1986; Kane *et al.*, 1988) or even antitumour activities (Hatheway *et al.*, 1978) and are applied in therapy (*e.g.* Alprazolam, Estazolam, Triazolam and Adinazolam; Budavari *et al.*, 1996). There are many structures of 1,2,4-triazole derivatives described in the scientific literature, but to date no crystal structure of a simple 3-(4-pyridyl)-1,2,4-triazole derivative, unsubstituted in position C5, has been reported (Cambridge Structural Database, Version 5.25; Allen, 2002). The nature of the substituents and the type of their substitution have a significant impact on the chemical and pharmacological properties of compounds. In view of these important factors, the crystal structure determination of 3-(4-pyridyl)-4-phenyl-4H-1,2,4-triazole, (I), has been undertaken.



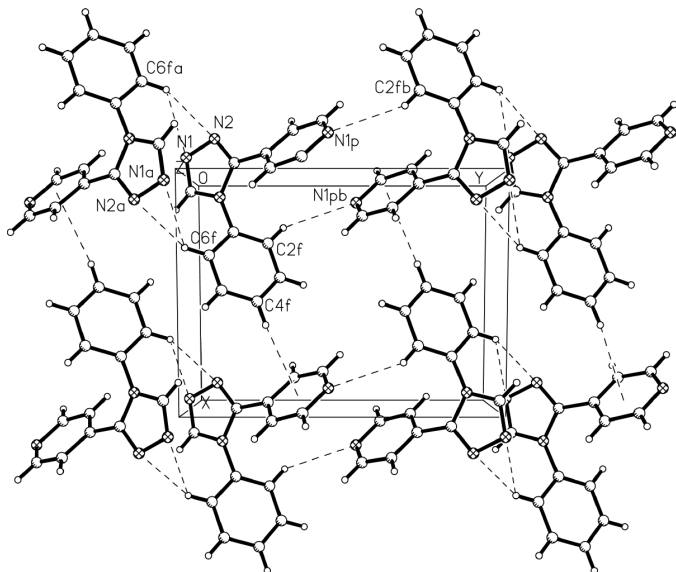
(I)

The title molecule (Fig. 1) consists of three aromatic rings, *viz.* triazole, pyridyl and phenyl, which are each essentially

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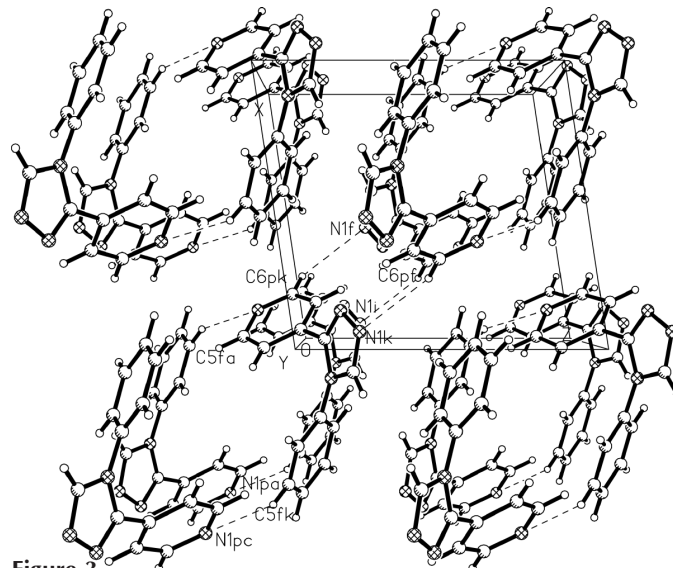
**Figure 1**  
The molecular structure of (I), with the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.



**Figure 2**  
The packing arrangement of (I), viewed along the *c* axis. Dashed lines indicate C—H...N hydrogen bonds and C—H... $\pi$  contacts.

planar, but are not coplanar. The N2—C3—C4<sub>p</sub>—C3<sub>p</sub> and C5—N4—C1<sub>f</sub>—C2<sub>f</sub> torsion angles, describing the orientation of the pyridyl and phenyl rings with respect to the 1,2,4-triazole ring, are  $-130.7(4)^\circ$  and  $-121.9(4)^\circ$ , respectively. The dihedral angle between the pyridyl and phenyl planes is  $63.8(4)^\circ$ . The bond lengths and angles in (I) are comparable with those observed in related compounds (Chinnakali *et al.*, 1999; Rogers *et al.*, 1990). The N1=C5 and N2=C3 bonds display double-bond character, with bond distances of  $1.304(4)$  and  $1.318(3)$  Å, respectively, whereas the N4—C3 and N4—C5 bonds have an intermediate character (Table 1).

The molecule of (I) has no H atoms bonded to heteroatoms, and thus the molecular packing is determined by a combination of C—H...N (Taylor & Kennard, 1982), C—H... $\pi$  and  $\pi$ - $\pi$  interactions (Figs. 2 and 3, and Table 2). In the crystal



**Figure 3**  
Packing of the molecules, viewed along the *b* axis. Dashed lines indicate hydrogen bonds.

structure, the molecules are associated into centrosymmetric hydrogen-bonded dimers of two types. The first type of dimer is formed *via* a bifurcated C6<sub>f</sub>—H6<sub>f</sub>...N1/N2( $1-x, 1-y, 1-z$ ) hydrogen bond and is additionally stabilized by  $\pi$ - $\pi$  stacking between triazole rings, with a distance of  $3.637(4)$  Å between the ring centroids and a perpendicular distance of  $3.595(4)$  Å. Interactions *via* C2<sub>f</sub>—H2<sub>f</sub>...N1<sub>p</sub>( $1-x, -y, 1-z$ ) hydrogen bonds and  $\pi$ - $\pi$  stacking of pyridyl rings form the second type of dimer. The perpendicular distance between two of these pyridyl rings is  $3.480(4)$  Å, while the distance between the centers of the rings is  $3.889(4)$  Å. Screw-related molecules have C5<sub>f</sub>—H5<sub>f</sub>...N1<sub>p</sub> and C6<sub>p</sub>—H6<sub>p</sub>...N1 short contacts down the *b* axis (Fig. 3). In addition to these interactions, the crystal structure is also stabilized by C—H... $\pi$  contacts involving the C4<sub>f</sub>—H4<sub>f</sub> atoms of one molecule and the pyridyl ring of a second molecule translated along the *a* axis (Fig. 2). The geometry of these contacts is given in Table 2.

## Experimental

The title compound, (I), was synthesized by reaction of an N3-substituted amidrazone with diethylethoxymethylene malonate as reported by Modzelewska (1991–1992). Crystals were obtained by recrystallization from methanol at room temperature. The melting point (determined on a Boëtius microscope) was 475 K. The orange single crystal selected for X-ray diffraction measurements was a very thin, soft plate.

### Crystal data

C<sub>13</sub>H<sub>10</sub>N<sub>4</sub>  
*M<sub>r</sub>* = 222.25  
 Monoclinic,  $P2_1/n$   
*a* =  $9.165(2)$  Å  
*b* =  $12.030(4)$  Å  
*c* =  $9.812(4)$  Å  
 $\beta$  =  $98.69(3)^\circ$   
*V* =  $1069.4(6)$  Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* =  $1.380$  Mg m<sup>-3</sup>  
 Cu K $\alpha$  radiation  
 Cell parameters from 58 reflections  
 $\theta$  =  $6-15^\circ$   
 $\mu$  =  $0.70$  mm<sup>-1</sup>  
*T* =  $293(2)$  K  
 Plate, orange  
 $0.54 \times 0.21 \times 0.02$  mm

## Data collection

Kuma KM-4 four-circle diffractometer  
 $\omega$ -2 $\theta$  scans  
 Absorption correction: numerical (KM-4 Software; Kuma, 1998)  
 $T_{\min} = 0.706$ ,  $T_{\max} = 0.988$   
 2210 measured reflections  
 2210 independent reflections

702 reflections with  $I > 2\sigma(I)$   
 $\theta_{\max} = 75.1^\circ$   
 $h = -11 \rightarrow 11$   
 $k = 0 \rightarrow 15$   
 $l = 0 \rightarrow 12$   
 3 standard reflections every 100 reflections  
 intensity decay: 3.0%

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.057$   
 $wR(F^2) = 0.126$   
 $S = 0.96$   
 2210 reflections  
 154 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.046P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.18 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

N1—C5	1.304 (4)	N4—C5	1.360 (3)
N1—N2	1.404 (3)	N4—C1f	1.448 (3)
N2—C3	1.318 (3)	N1P—C6p	1.333 (4)
C3—N4	1.367 (3)	N1P—C2p	1.338 (3)
C5—N1—N2	106.1 (3)	C5—N4—C3	104.6 (2)
C3—N2—N1	107.3 (2)	C5—N4—C1f	125.9 (3)
N2—C3—N4	110.2 (3)	N1—C5—N4	111.9 (3)
N2—C3—C4p	124.3 (3)		
N2—C3—C4p—C3p	-130.7 (3)	C5—N4—C1f—C2f	-121.9 (3)

Table 2

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C5—H5 $\cdots$ N1p <sup>i</sup>	0.93	2.93	3.534 (4)	124
C6f—H6f $\cdots$ N2 <sup>ii</sup>	0.93	2.63	3.486 (4)	154
C6f—H6f $\cdots$ N1 <sup>iii</sup>	0.93	2.96	3.580 (4)	126
C2f—H2f $\cdots$ N1p <sup>iii</sup>	0.93	2.84	3.563 (4)	136
C5f—H5f $\cdots$ N1p <sup>iv</sup>	0.93	2.69	3.554 (4)	155
C6p—H6p $\cdots$ N1 <sup>v</sup>	0.93	2.72	3.464 (4)	137
C4f—H4f $\cdots$ $\pi$ <sup>vi</sup>	0.93	2.94	3.782 (4)	151

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

All H atoms were positioned geometrically and a riding model was applied, with a C—H distance of 0.93  $\text{\AA}$  for the triazole, pyridyl and

phenyl H atoms. The displacement parameters of the H atoms were set at  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

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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