

2-(3-Pyridyl)-1,3,8-triazanaphthalene,  
a product of the catalytic transfor-  
mation of 3-cyanopyridine

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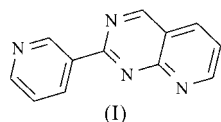
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The title compound,  $C_{12}H_8N_4$ , was obtained by thermal treatment of 3-cyanopyridine in the presence of magnesium phthalocyanine as catalyst. The X-ray structure analysis, in direct contrast to molecular orbital calculations corresponding to the gas phase, shows the molecule to be non-planar in the solid state, with an interplanar angle between the pyridine and 1,3,8-triazanaphthalene rings of  $13.33$  ( $9$ )°. Molecules related to one another by cell translation, and positioned at intervals consistent with  $\pi$ - $\pi$  intermolecular interactions, form stacks in the  $b$  direction.

## Comment

The present study continues our investigations of the compounds formed during the transformation of organic cyano compounds in the presence of magnesium phthalocyanine as catalyst. In this context and to increase our understanding of the function of magnesium phthalocyanine (MgPc) during the transformation process, we have investigated the reactions of the 2- and 4-cyanopyridine isomers, finding that during thermal treatment in the presence of magnesium phthalocyanine a trimerization process takes place, resulting in the formation of 2,4,6-tris(2-pyridyl)-1,3,5-triazine and 2,4,6-tris(4-pyridyl)-1,3,5-triazine, respectively (Janczak *et al.*, 2003). We now present the solid-state structure of 2-(3-pyridyl)-1,3,8-triazanaphthalene, (I), the product of the transformation of 3-cyanopyridine in the presence of magnesium phthalocyanine, and compare the result with that predicted for an isolated molecule by a density functional theory (DFT) fully optimized geometry calculation.



The molecule of (I), with the labelling scheme used in the X-ray structure analysis, is shown in Fig. 1. Selected geometric

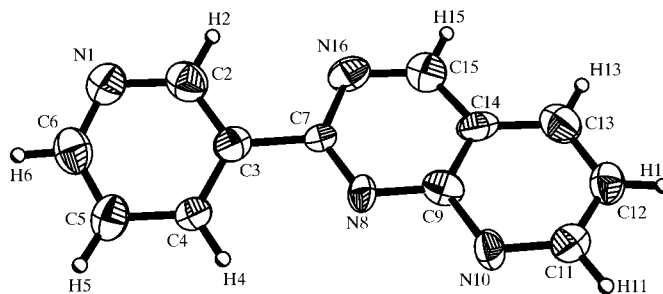


Figure 1

The molecule of (I), showing the atom-labelling scheme. Non-H atoms are shown as 50% probability displacement ellipsoids and H atoms are shown as spheres of arbitrary radii.

parameters for this model, together with those corresponding to fully optimized geometry calculations at the B3LYP/6-31G( $d,p$ ) level (Frisch *et al.*, 1995) for an isolated (gas phase) molecule, are given in Table 1.

As revealed by X-ray structure analysis, the C—C and N—C bond lengths in (I) are entirely consistent with those found for other molecules of this type (Allen, 2002). Furthermore, the pyridine and 1,3,8-triazanaphthalene ring systems, although planar, exhibit significant angular distortions. In both cases, the internal C—N—C and N—C—C angles are, respectively, less than and greater than  $120^\circ$ . These angular differences have been attributed to the steric effect of lone-pair electrons at the ring N atoms and are in agreement with the valence-shell electron-pair repulsion theory, which predicts the need for more space for non-bonding lone-pair electrons than for bonding electrons (Gillespie, 1963, 1992).

The optimized geometry of the molecule calculated by DFT methods gives values similar to those found in the crystal; however, the variation in the internal C—N—C and N—C—C

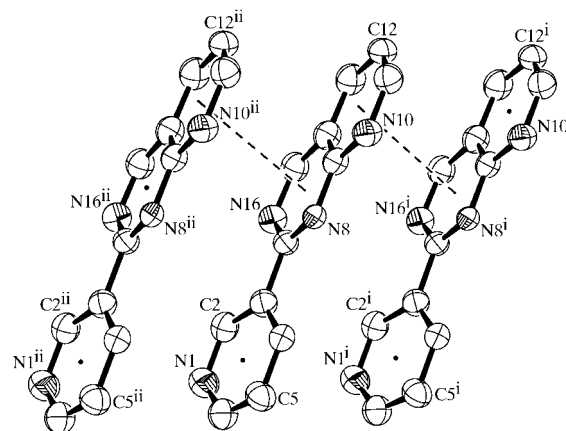


Figure 2

Part of a stack of molecules of (I), propagated in the  $b$  direction (left to right across the page). Non-H atoms are shown as 50% probability displacement ellipsoids and H atoms have been omitted for clarity; selected atoms are labelled. Dashed lines indicate two of the shorter contacts between ring centroids, which are themselves shown as small dots. [Symmetry codes: (i)  $x, y + 1, z$ ; (ii)  $x, y - 1, z$ .]

angles is now less marked. Thus, the distortion of the rings is perceived to result mainly from the steric effect of lone-pair electrons at the ring N atoms and in the crystal, augmented, to some extent, by  $\pi$ - $\pi$  intermolecular interactions and the crystal packing.

In complete contrast to the results of the crystal structure analysis, where the molecule is found to exhibit an angle of  $13.33(9)^\circ$  between the planes of the pyridine ring and the 1,3,8-triazanaphthalene moiety by rotation about the C3—C7 bond joining them, the optimized molecule is completely planar. This geometry was confirmed by calculating potential energies for a series of conformations in which the pyridine ring was rotated in steps of  $5^\circ$  about the C3—C7 bond, while keeping the other optimized parameters, except the length of the C3—C7 bond, fixed. This process revealed a global minimum on the potential energy surface at  $0^\circ$  rotation (the planar equivalent of Fig. 1) and a further minimum,  $1.5 \text{ kJ mol}^{-1}$  higher than the first, at  $180^\circ$ , together with two equivalent energy maxima at  $90^\circ$  and  $270^\circ$ , both  $34.84 \text{ kJ mol}^{-1}$  higher than the energy at  $0^\circ$ . The energy value at the maxima is higher than the value at room temperature ( $2.5 \text{ kJ mol}^{-1}$ ) and thus, at ambient temperature, the change in the conformation from that at the rotation angle of  $0^\circ$  to that at  $180^\circ$  is hindered. The energy barrier is nearly equivalent to the hydrogen-bond energy (Pauling, 1967). The  $35 \text{ kJ mol}^{-1}$  difference between the energy of the conformations of the molecule at  $0$  and  $90^\circ$  can be assigned to the  $\pi$ -delocalization energy of the  $\pi$ -electrons that are delocalized not only in the rings but also, at  $0^\circ$ , over the inter-ring C3—C7 bond; at the rotation angle of  $90^\circ$ , the delocalization of the  $\pi$ -electrons over the inter-ring bond is impossible because of the symmetry of the orbitals. The lengthening of the C3—C7 inter-ring bond from  $1.483$  (at  $0^\circ$ ) to  $1.504 \text{ \AA}$  (at  $90^\circ$ ) supports this hypothesis. Thus, in the molecule with lower energy, the inter-ring C3—C7 bond possesses a slight double-bond character as a result of delocalization of the  $\pi$ -electrons between the rings and along the bond (Allen *et al.*, 1987).

In the crystal structure of (I), a major feature is the face-to-face stacking of molecules related to one another by a cell translation, thus forming columns that propagate in the  $b$  direction (Fig. 2). Taking account of the tilt of the planes relative to the  $b$  cell edge, of the order of  $66^\circ$ , the repeat distance of  $3.804(1) \text{ \AA}$  corresponds to an interplanar separation of  $\sim 3.5 \text{ \AA}$ , which is consistent with the requirements of  $\pi$ - $\pi$  stacking and clearly accommodates the distance of  $3.4 \text{ \AA}$  required for overlapping  $\pi$ -aromatic ring systems (Pauling, 1967).

## Experimental

Crystals of (I) were obtained directly during the thermal annealing of 3-cyanopyridine in the presence of magnesium phthalocyanine as catalyst at  $453$ – $473 \text{ K}$ . Below  $453 \text{ K}$ , the (4+1)-coordination complex of magnesium phthalocyanine, in which a 3-cyanopyridine molecule is axially coordinated to the central Mg atom, is stable (Janczak *et al.*, 2003). Above  $453 \text{ K}$ , the 3-cyanopyridine molecules are released from the  $[\text{MgPc}\{3\text{-CN}(\text{C}_5\text{H}_4\text{N})\}]$  complex in an activated state and

the title complex forms from two 3-cyanopyridine molecules. In one of the molecules, the H atom *ortho* to both the CN group and the pyridine N atom is transferred to the C atom of the CN group, and then the activated 3-cyanopyridine molecules react and form crystalline (I).

## Crystal data

$\text{C}_{12}\text{H}_8\text{N}_4$   
 $M_r = 208.22$   
 Orthorhombic,  $Pna2_1$   
 $a = 21.627(4) \text{ \AA}$   
 $b = 3.8040(10) \text{ \AA}$   
 $c = 11.605(2) \text{ \AA}$   
 $V = 954.7(3) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.449 \text{ Mg m}^{-3}$   
 $D_m = 1.445 \text{ Mg m}^{-3}$   
 $D_m$  measured by flotation in dichloroethylene/dibromethylene

Mo  $K\alpha$  radiation  
 Cell parameters from 1322 reflections  
 $\theta = 2.6$ – $27.9^\circ$   
 $\mu = 0.09 \text{ mm}^{-1}$   
 $T = 293(2) \text{ K}$   
 Parallelepiped, colourless  
 $0.38 \times 0.12 \times 0.08 \text{ mm}$

## Data collection

Kuma KM-4 CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: analytical face-indexed (SHELXTL; Sheldrick, 1990)  
 $T_{\min} = 0.959$ ,  $T_{\max} = 0.984$   
 5415 measured reflections

2107 independent reflections  
 1322 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.036$   
 $\theta_{\text{max}} = 27.9^\circ$   
 $h = -27 \rightarrow 27$   
 $k = -4 \rightarrow 4$   
 $l = -15 \rightarrow 14$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.051$   
 $wR(F^2) = 0.075$   
 $S = 0.99$   
 2107 reflections  
 145 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.025P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.002$   
 $\Delta\rho_{\text{max}} = 0.15 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$   
 Absolute structure: Flack (1983), 928 Friedel pairs  
 Flack parameter =  $0.2(2)$

**Table 1**

Selected X-ray structural and molecular orbital (MO) calculated geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (I).

	X-ray	MO		X-ray	MO
N1—C6	1.307 (3)	1.321	C8—C9	1.348 (3)	1.354
N1—C2	1.378 (4)	1.320	C9—N10	1.359 (3)	1.349
C2—C3	1.389 (4)	1.391	C9—C14	1.407 (3)	1.402
C3—C4	1.377 (3)	1.390	N10—C11	1.323 (4)	1.315
C3—C7	1.488 (3)	1.483	C11—C12	1.380 (4)	1.408
C4—C5	1.380 (4)	1.379	C12—C13	1.374 (4)	1.356
C5—C6	1.368 (4)	1.386	C13—C14	1.426 (4)	1.412
C7—N8	1.301 (3)	1.306	C14—C15	1.380 (4)	1.413
C7—N16	1.384 (3)	1.359	C15—N16	1.343 (3)	1.289
C6—N1—C2	113.8 (3)	117.9	N8—C9—N10	116.0 (2)	117.5
N1—C2—C3	123.9 (3)	123.6	N8—C9—C14	122.2 (2)	120.5
C4—C3—C2	118.1 (3)	117.7	N10—C9—C14	121.9 (3)	121.9
C4—C3—C7	121.1 (2)	120.9	C11—N10—C9	114.8 (3)	115.8
C2—C3—C7	120.8 (2)	121.5	N10—C11—C12	128.1 (3)	125.1
C5—C4—C3	119.0 (3)	118.9	C13—C12—C11	118.4 (3)	118.1
C6—C5—C4	117.5 (3)	118.3	C12—C13—C14	116.0 (3)	118.6
N1—C6—C5	127.5 (3)	123.6	C15—C14—C9	115.2 (3)	115.8
N8—C7—N16	127.2 (2)	125.6	C13—C14—C9	120.8 (3)	119.1
N8—C7—C3	117.4 (2)	118.0	C15—C14—C13	124.0 (3)	125.1
N16—C7—C3	115.4 (2)	116.3	N16—C15—C14	124.8 (3)	122.8
C7—N8—C9	117.0 (2)	118.2			

The Friedel equivalents were not merged; however, in the absence of significant anomalous scattering, the value of the Flack (1983) parameter was at best only weakly indicative of the correct orientation of the structure relative to the polar axis (Flack & Bernardinelli, 1999, 2000). In the final stages of refinement, H atoms were introduced in calculated positions (C–H = 0.93 Å) and refined using a riding model [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ].

Data collection: *KM-4 Software* (Kuma, 2000); cell refinement: *KM-4 Software*; data reduction: *KM-4 Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1264). Services for accessing these data are described at the back of the journal.

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