

4-[4-(Dimethylamino)benzylidene-  
amino]-3,5-bis(2-pyridyl)-4H-1,2,4-  
triazoleGiuseppe Bruno, Francesco Nicoló,\* Fausto Puntoriero,  
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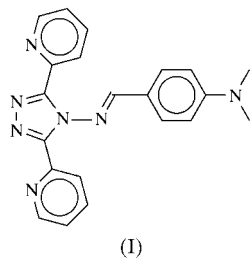
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The title compound,  $C_{21}H_{19}N_7$ , is a polypyridine ligand that is suitable for assembling complex metal systems capable of photoinduced electron transfer. The solid-state structure has been determined at room temperature by single-crystal X-ray diffraction. The molecule is not flat and both the bis(pyridyl)-triazole and the benzylideneamine fragments show significant distortions from planarity.

## Comment

The design of new polypyridine ligands containing redox-active sites is an important research field, since these species can be used to build multicomponent systems for photoinduced electron transfer upon metal coordination (Venturi *et al.*, 1998). In this field, the structural organization of multicomponent arrays is of interest, since many factors that determine the rate constants of the electron-transfer process are related to geometric parameters. Bis(pyridyl)triazole ligands have proved to be well suited to these applications, and many luminescent and redox-active  $Ru^{II}$  and  $Os^{II}$  complexes based on this class of ligand have been reported (Balzani *et al.*, 1996; Giuffrida *et al.*, 1996; Serroni *et al.*, 1996; Di Pietro *et al.*, 2002).



We report here the synthesis and crystal structure of a new ligand, (I), based on the bis(pyridyl)triazole moiety and bearing a dimethylamine moiety as the redox-active compo-

nent. The coordinating and redox-active subunits are connected by an aromatic spacer (Fig. 1), which controls the distance between the sites and allows suitable electronic coupling.

In the crystal structure, the bis(pyridyl)triazole fragment of the ligand is not flat, and the C3/N4/C4–C7 and C8/N9/C10–C13 pyridyl rings make dihedral angles of 40.16 (6) and 22.78 (7)°, respectively, with the mean plane of the triazole ring. The different rotations of the two rings are mainly due to hydrogen-bonding interactions between the disordered *ortho* CH group on the C8/N9/C10–C13 ring and either atom N2 or atom N5, depending on the positions of the disordered N atoms in the ring (see Table 2). However, the C2–C3 and C1–C8 bonds have almost the same length, both being slightly shorter than the typical single-bond value, thus confirming the absence of important conjugation effects. An almost flat disposition of the three rings has been observed in similar 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole derivatives (Mernari *et al.*, 1998; Sueur *et al.*, 1991), in which the  $C_{\text{triazole}}-C_{\text{pyridine}}$  single-bond lengths are comparable to the values in (I), despite the coplanar arrangement. However, the triazole ring has the same planar geometry in all the similar fragments reported in the Cambridge Structural Database (Allen, 2002) and shows comparable bond lengths and angles (Table 1).

Despite the possible large electronic delocalization, the 4-(dimethylamino)benzylideneamine substituent is not planar, as evidenced by the torsion angles involving the N5=C14 double bond. The N1–N5=C14–C15 methylamine system is slightly distorted from planarity [torsion angle =  $-174.5(1)^\circ$ ] and its mean plane makes dihedral angles of 62.7 (1) and 21.1 (1)° with the planes of the triazole and phenyl rings, respectively. The N5=C14 bond is significantly shorter than the corresponding bonds in the conjugated C1=N2–N3=C2

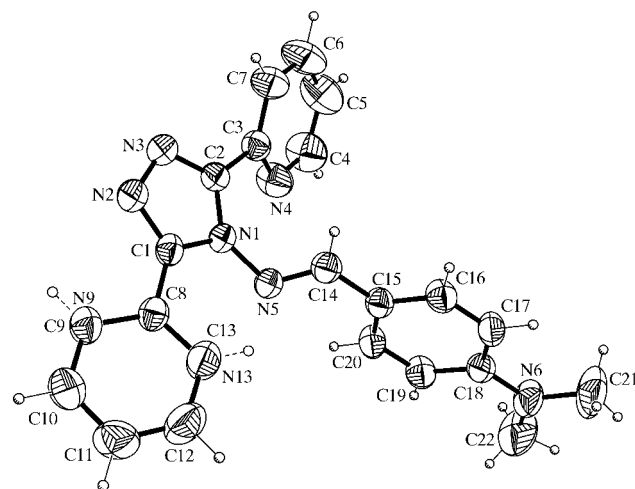


Figure 1

A perspective view showing the atomic numbering scheme of the asymmetric unit of (I). Dashed C–H bonds represent the two conformations of the disordered pyridyl ring, in which the CH group is interchanged with the N atom. Displacement ellipsoids have been drawn at the 50% probability level, while the H-atom sizes are arbitrary.

system of the triazole ring [mean value = 1.365 (3) Å], while the C14—C15 distance is not significantly shorter than a typical  $Csp^2-Csp^2$  single bond, as expected. However, comparable bond lengths have been observed in the flat conformation of the same fragment in a similar compound (Akkurt & Hiller, 1993), which confirms that the reduced delocalization is not caused by the distortion from planarity.

## Experimental

An excess of  $SOCl_2$  (2 ml) was added to  $C_6H_{10}(COOH)_2$  (200 mg) dissolved in benzene (25 ml). After refluxing for 30 min, the solution was distilled to eliminate the excess  $SOCl_2$ . The isolated species  $C_6H_{10}C(O)Cl$  was added to a solution of 4-(dimethylamino)benzoic acid (383.2 mg, 2.32 mmol) in benzene (50 ml; all reagents from Aldrich). After refluxing for 1 h, the reaction mixture was cooled to room temperature and the white precipitate was filtered off, washed ten times with  $Et_2O$  and recrystallized from  $EtOH/Et_2O$  (1:2,  $v/v$ ) (yield 82%). Analysis calculated for  $C_{21}H_{19}N_7$ : C 68.28, H 5.18, N 26.54%; found: C 67.99, H 5.24, N 26.77%.

### Crystal data

|                               |   |
|-------------------------------|---|
| $C_{21}H_{19}N_7$             | $D_x = 1.276 \text{ Mg m}^{-3}$           |
| $M_r = 369.43$                | Mo $K\alpha$ radiation                    |
| Monoclinic, $C_2/c$           | Cell parameters from 31 reflections       |
| $a = 26.300$ (4) Å            | $\theta = 6.3-13.6^\circ$                 |
| $b = 9.469$ (2) Å             | $\mu = 0.08 \text{ mm}^{-1}$              |
| $c = 17.440$ (2) Å            | $T = 298$ (2) K                           |
| $\beta = 117.69$ (1) $^\circ$ | Regular prism, colourless                 |
| $V = 3846$ (1) Å <sup>3</sup> | $0.20 \times 0.19 \times 0.10 \text{ mm}$ |
| $Z = 8$                       |   |

### Data collection

|  |                          |
|--|--------------------------|
| Siemens P4 diffractometer              | $h = -7 \rightarrow 31$  |
| $\omega$ -2 $\theta$ scans             | $k = -1 \rightarrow 11$  |
| 4041 measured reflections              | $l = -20 \rightarrow 18$ |
| 3413 independent reflections           | 3 standard reflections   |
| 2023 reflections with $I > 2\sigma(I)$ | every 197 reflections    |
| $R_{int} = 0.010$                      | intensity decay: none    |
| $\theta_{max} = 25.1^\circ$            |                          |

### Refinement

|                                 |   |
|---------------------------------|---|
| Refinement on $F^2$             | $w = 1/[\sigma^2(F_o^2) + (0.0440P)^2]$             |
| $R[F^2 > 2\sigma(F^2)] = 0.032$ | where $P = (F_o^2 + 2F_c^2)/3$                      |
| $wR(F^2) = 0.076$               | $(\Delta/\sigma)_{max} = 0.004$                     |
| $S = 0.79$                      | $\Delta\rho_{max} = 0.14 \text{ e } \text{Å}^{-3}$  |
| 3413 reflections                | $\Delta\rho_{min} = -0.14 \text{ e } \text{Å}^{-3}$ |
| 255 parameters                  | Extinction correction: <i>SHELXL97</i>              |
| H-atom parameters constrained   | Extinction coefficient: 0.0011 (1)                  |

Reflection intensities were evaluated by profile fitting of a 96-step peak scan among 2 $\theta$  shells (Diamond, 1969) and were then corrected for Lorentz and polarization effects. Standard uncertainties were estimated from counting statistics. In one 2-pyridyl fragment, it was not possible to identify the N atom in one of the two *ortho* positions, and it was necessary to treat the ring as the overlap of two rotated conformations, with the occupancy of the N atom split over both *ortho* positions of the ring. H atoms were located in idealized positions and allowed to ride on their parent C atoms, with isotropic displacement parameters related to the refined values of the corresponding parent atoms. In the final Fourier maps, the electron-density residuals were not significant.

Data collection: *P3/V* (Siemens, 1989); cell refinement: *P3/V*; data reduction: *SHELXTL-Plus* (Siemens, 1990); program(s) used to

**Table 1**

Selected geometric parameters (Å,  $^\circ$ ).

|              |           |                |            |
|--------------|-----------|----------------|------------|
| N1—C2        | 1.362 (2) | C2—C3          | 1.476 (2)  |
| N1—C1        | 1.369 (2) | N5—C14         | 1.275 (2)  |
| N1—N5        | 1.423 (1) | C14—C15        | 1.443 (2)  |
| C1—N2        | 1.315 (2) | C18—N6         | 1.364 (2)  |
| C1—C8        | 1.471 (2) | N6—C22         | 1.433 (2)  |
| N2—N3        | 1.383 (2) | N6—C21         | 1.435 (2)  |
| N3—C2        | 1.318 (2) |                |            |
|              |           |                |            |
| C2—N1—C1     | 106.0 (1) | C2—N3—N2       | 107.6 (1)  |
| C2—N1—N5     | 126.8 (1) | N3—C2—N1       | 109.4 (1)  |
| C1—N1—N5     | 126.9 (1) | C14—N5—N1      | 112.3 (1)  |
| N2—C1—N1     | 109.3 (1) | N5—C14—C15     | 121.7 (1)  |
| C1—N2—N3     | 107.7 (1) |                |            |
|              |           |                |            |
| N1—C2—C3—N4  | 40.7 (2)  | N1—N5—C14—C15  | -174.5 (1) |
| N1—C1—C8—N13 | 22.3 (2)  | N5—C14—C15—C20 | 17.7 (2)   |

**Table 2**

Hydrogen-bonding geometry (Å,  $^\circ$ ).

| $D-H \cdots A$      | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|---------------------|-------|--------------|--------------|----------------|
| C9—H9 $\cdots$ N2   | 0.93  | 2.57         | 2.864 (2)    | 99             |
| C13—H13 $\cdots$ N5 | 0.93  | 2.38         | 2.959 (2)    | 120            |

solve structure: *SIR93* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XPW* (Siemens, 1996); software used to prepare material for publication: *PARST97* (Nardelli, 1995) and *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1615). Services for accessing these data are described at the back of the journal.

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