

**(1R)-6,9,15,18,21-Pentaazapentacyclo-
[12.7.0.0^{1,18}.0^{2,7}.0^{8,13}]henicosa-2,4,6,-
8(13),9,11,14-heptaene****Long Lin, Yong-Cai Qiu,
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Key indicators

Single-crystal X-ray study

 $T = 273$ KMean $\sigma(\text{C}-\text{C}) = 0.002$ Å R factor = 0.038 wR factor = 0.117

Data-to-parameter ratio = 12.6

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

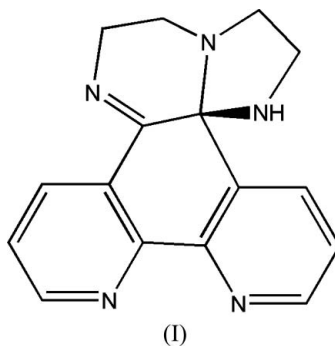
The reaction of 1,10-phenanthroline-5,6-dione and diethylenetriamine unexpectedly yielded the title compound, $\text{C}_{16}\text{H}_{15}\text{N}_5$, which is a non-planar and chiral fused-ring system composed of two pyridine rings and three non-aromatic rings. Crystal symmetry results in a racemic mixture of enantiomers. Aromatic π - π stacking interactions exist between adjacent molecules and weak bifurcated $\text{N}-\text{H}\cdots(\text{N},\text{N})$ hydrogen bonds lead to dimeric associations of molecules, generated by inversion.

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Comment

1,10-Phenanthroline-5,6-dione is a useful intermediate for preparing further ring-fused ligands by reacting the α -dione groups with compounds containing amino groups. The product is dependent on the other reactant: when aromatic diprimary amines were used, their facile Schiff base condensations with the dione resulted in extended aromatic systems (Yamada *et al.*, 1992; Hiort *et al.*, 1993; Yam *et al.*, 1995). The reaction of the dione with aldehydes in the presence of ammonium acetate and acetic acid has yielded a number of imidazo[4,5-*f*]-[1,10]phenanthroline derivatives (Wu *et al.*, 1996, 1997, 2005; Ji *et al.*, 2001; Kurth *et al.*, 2001). However, reaction of the dione in ethanol with such tetraamines as *N,N'*-bis(3-amino-propyl)ethylenediamine, triethylaminetetramine and tris(2-aminoethyl)amine afforded only the reduced product 1,10-phenanthroline-5,6-diol, while the corresponding reaction with another tetraamine, *N,N'*-bis(2-aminophenyl)ethylenediamine, gave a non-planar and chiral multi-ring product (Coyle *et al.*, 2003). The reaction between the dione and urea in toluene resulted in bipyridine-glycoluril (Elemans *et al.*, 1998, 2002).



We report here the crystal structure of the title compound, (I), a novel five-ring fused molecule, which was obtained from the reaction of an ethanolic solution of the dione with diethylenetriamine. As shown in Fig. 1, the molecule is non-

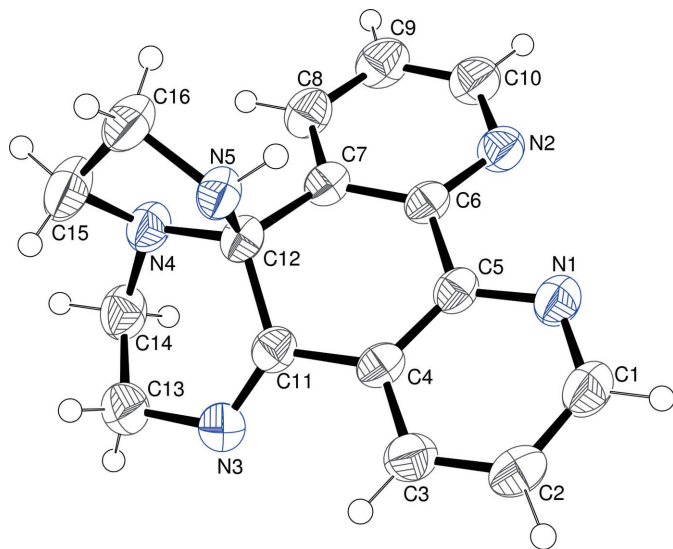


Figure 1
The structure of (I), showing 50% probability displacement ellipsoids (arbitrary spheres for the H atoms).

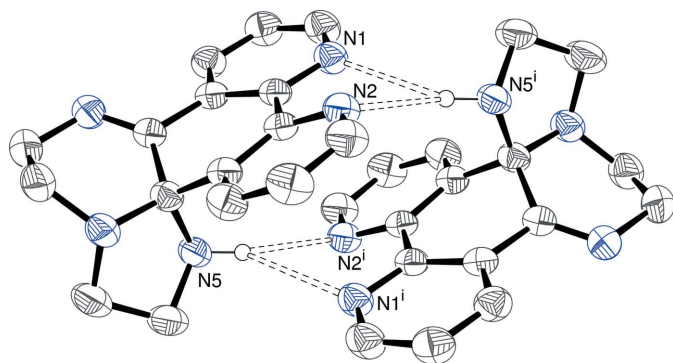


Figure 2
The dimeric association of two molecules of (I) via two bifurcated N—H...N(N) bonds (dashed lines; 50% displacement ellipsoids; all H atoms except H5 omitted for clarity). See Table 1 for symmetry code.

planar, consisting of two six-membered rings and one five-membered ring fused on to the bipyridine system. Based on their geometries, atoms N1, N2 and N3 are sp^2 -hybridized, while N4 and N5 are sp^3 -hybridized. The two pyridine (N1 and N2) rings retain aromatic structural features with C—N distances in the range 1.3321 (19)–1.3425 (18) Å. The N3=C11 double bond length is typical at 1.2710 (18) Å. The non-aromatic C—C and C—N bond lengths fall into the ranges 1.503 (2)–1.5298 (19) and 1.454 (2)–1.4824 (18) Å, respectively. The twist angle between the two pyridine rings is 12.81 (7)°.

There are intermolecular π – π interactions between adjacent bipyridine systems, the distance between the bipyridine least-square planes being 3.135 Å. Atom C12 is chiral: in the arbitrarily chosen asymmetric unit it has an *R* configuration, but crystal symmetry generates a racemic mix of enantiomers.

A bifurcated intermolecular N—H...N(N) hydrogen bond (Table 1) leads to inversion-symmetry-generated dimeric associations of molecules (Fig. 2) but the bonds are evidently

quite weak as the N—N distances are over 3.0 Å. *PLATON* (Spek, 2003) indicated a possible intramolecular C8—H8...N4 bond, although its bond angle is quite acute.

Experimental

A mixture of 1,10-phenanthroline-5,6-dione (1 mmol) and diethylenetriamine (1 mmol) in ethanol (10 ml) was stirred at room temperature for 1.5 h. Yellow single crystals of (I) were obtained from the filtered solution in 2 d in 67% yield.

Crystal data

$C_{16}H_{15}N_5$	$Z = 4$
$M_r = 277.33$	$D_x = 1.385 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 10.7254$ (2) Å	$\mu = 0.09 \text{ mm}^{-1}$
$b = 13.0587$ (3) Å	$T = 273$ (2) K
$c = 10.2122$ (2) Å	Block, yellow
$\beta = 111.609$ (1)°	$0.3 \times 0.3 \times 0.2 \text{ mm}$
$V = 1329.79$ (5) Å ³	

Data collection

Bruker SMART CCD diffractometer	2402 independent reflections
ω scans	1963 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{\text{int}} = 0.021$
11156 measured reflections	$\theta_{\text{max}} = 25.2^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0692P)^2 + 0.1716P]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.117$	$(\Delta\sigma)_{\text{max}} < 0.001$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.17 \text{ e \AA}^{-3}$
2402 reflections	$\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$
190 parameters	
H-atom parameters constrained	

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N5—H5...N1 ⁱ	0.91	2.60	3.3497 (18)	140
N5—H5...N2 ⁱ	0.91	2.33	3.1689 (18)	153
C8—H8...N4	0.93	2.50	2.836 (2)	102

Symmetry code: (i) $-x + 1, -y, -z + 2$.

The N-bound H atom (H5) was located in a difference map and refined as riding in its as-found relative position, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. The C-bound H atoms were placed in calculated positions ($C-H = 0.93\text{--}0.97$ Å) and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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References

- Bruker (1998). *SMART* (Version 5.0) and *SHELXTL* (Version 5.1). Bruker AXS Inc, Madison, Wisconsin, USA.
- Bruker (1999). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Coyle, B., McCann, M., McKee, V. & Devereux, M. (2003). *ARKIVOC*, **7**, 59–66.
- Elemans, J. A. A. W., de Gelder, R., Rowan, A. E. & Nolte, R. J. M. (1998). *Chem. Commun.* pp. 1553–1554.
- Elemans, J. A. A. W., Rowan, A. E. & Nolte, R. J. M. (2002). *J. Am. Chem. Soc.* **124**, 1532–1540.
- Hiort, C., Lincoln, P. & Norden, B. (1993). *J. Am. Chem. Soc.* **115**, 3448–3454.
- Ji, L.-N., Zou, X.-H. & Liu, J.-G. (2001). *Coord. Chem. Rev.* **216–217**, 513–536.
- Kurth, D. G., Fromm, K. M. & Lehn, J.-M. (2001). *Eur. J. Inorg. Chem.* 1523–1526.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Wu, J.-Z., Wang, L., Yang, G., Ji, L.-N., Katsaros, N. & Koutsodimou, A. (1996). *Cryst. Res. Technol.* **31**, 857–861.
- Wu, J.-Z., Ye, B.-H., Wang, L., Ji, L.-N., Zhou, J.-Y., Li, R.-H. & Zhou, Z.-Y. (1997). *J. Chem. Soc. Dalton Trans.* pp. 1395–1401.
- Wu, J.-Z., Yuan, L. & Wu, J.-F. (2005). *J. Inorg. Biochem.* **99**, 2211–2216.
- Yamada, M., Tanaka, Y., Yoshimoto, Y., Kuroda, S. & Shimao, I. (1992). *Bull. Chem. Soc. Jpn.* **65**, 1006–1011.
- Yam, V. W.-W., Lo, K. K.-W., Cheung, K.-K. & Kong, R. Y.-C. (1995). *J. Chem. Soc. Chem Commun.* pp. 1191–1193.