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π–π stacking in 7,8,15,16-tetraazadibenzo-[*b*,*n*]perylene monohydrate at 110 K

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Key indicators

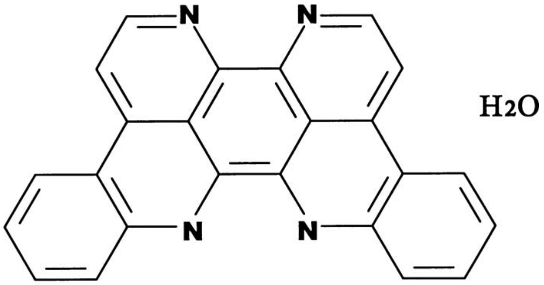
Single-crystal X-ray study
T = 110 K
Mean σ(C–C) = 0.003 Å
R factor = 0.062
wR factor = 0.166
Data-to-parameter ratio = 15.1

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

The title compound, $C_{24}H_{12}N_4\cdot H_2O$, characterized earlier with limited precision [Rudi, Benayahu, Goldberg & Kashman (1988). *Tetrahedron Lett*. **29**, 6655–6656], was redetermined at *ca* 110 K in the context of its uniquely interesting metal complexation and crystal packing features. It reveals tight stacking of the flat aromatic molecules, arranged in layered zones parallel to the *ab* plane of the crystal structure.

Comment

The title alkaloid compound, (I), was isolated from a marine tunicate Eudistoma *sp*. found in the Gulf of Eilat, hence the name 'eilatin'. It was originally identified and characterized by NMR and crystallographic techniques (Rudi *et al.*, 1988). However, the X-ray analysis of the crystal structure at room temperature suffered from low resolution, limited precision (with only 899 data above the intensity threshold of 2σ) and poor convergence of the structural refinement (R = 0.086). On the other hand, the tetrazaheptacyclic aromatic molecule along with its analogs (isoeilatin and dibenzoeilatin) were found in subsequent studies to be excellent ligands in complexation reactions, through their N-atom sites, with transition metal ions such as those of Ru and Os. Moreover, the large flat aromatic surface of these eilatin ligands provided useful means for directing intermolecular organization in crystals, as well as in solution, and effecting chiral recognition between the interacting species (Gut *et al.*, 2002, 2003; Bergman *et al.*, 2002, 2004, 2005).



(I)

In order to provide a firm structural basis for the above investigations, the crystal structure of (I) was re-determined at *ca* 110 K with a considerably higher resolution and precision [2456 intensity data above the 2$\sigma(I)$ threshold out of 3980 unique data to $\theta_{\max}$ = 27.9°]. The molecular structure of (I) is shown in Fig. 1. The perylene framework is essentially planar, with atomic deviations from its mean plane ranging from −0.052 (2) to 0.058 (2) Å and an r.m.s. deviation of 0.028 Å. The two peripheral benzene substituents C2–C7 and C22–C27

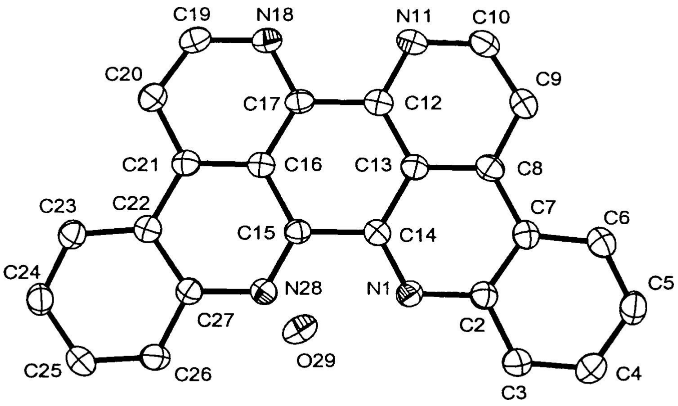


Figure 1
The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are shown at the the 50% probability level at *ca* 110 K. H atoms have been omitted.

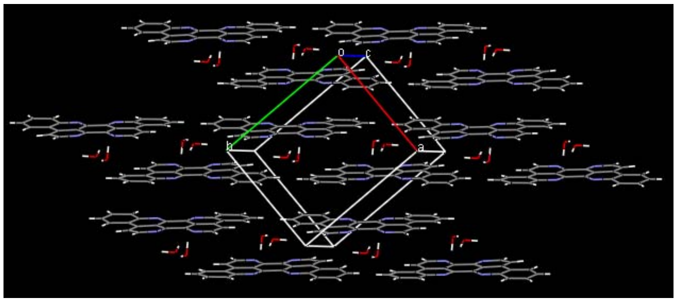
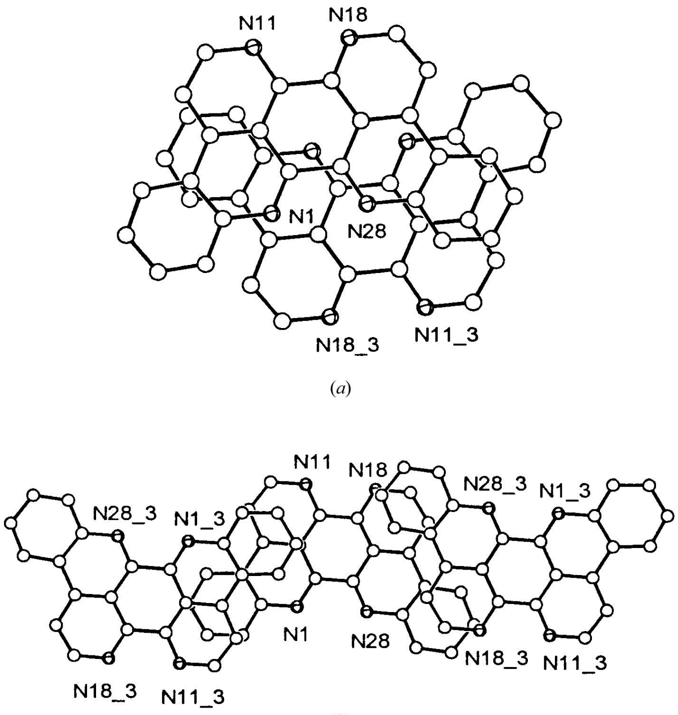


Figure 2
A section of the crystal structure of (I) parallel to the *ab* plane. It shows the nearly coplanar and partly overlapping arrangement of the flat molecules, indicating strong π–π interaction between them.

twist slightly up and down with respect to this plane, the dihedral angle between them being 5.73 (12)°.

In the crystal structure, the polycyclic aromatic species are arranged in layers, which are parallel to the *ab* plane of the unit cell. Adjacent layers displaced along the *c* axis are related to one another by the screw/glide symmetry in a herring-bone fashion. Every layer consists of parallel molecules as shown in Fig. 2. Molecular units displaced along $[1\bar{1}0]$ form a row of coplanar species. Adjacent molecular rows displaced along the [110] axis reveal an offset stacked arrangement. A more detailed inspection of the intermolecular organization reveals two different modes of overlap and π–π interaction (Fig. 3). Neighboring molecules in the crystal structure related by inversion at (0, 0, 0) and $(0, \frac{1}{2}, \frac{1}{2})$ exhibit a significant overlap and an intermolecular spacing of 3.370 (1) Å (Fig. 3*a*). Each molecule of such an interacting pair interacts simultaneously with two other species on its opposite surface, side-overlapping with them at both ends (Fig. 3*b*). The latter relate to the parent unit by inversion at at $(\frac{1}{2}, 0, 0)$ and $(0, \frac{1}{2}, 0)$ in one layer or by $(0, 0, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ in another layer. The spacing between the mean planes of the partly overlapping species is 3.352 (1) Å. The relatively short distances between the offset stacked molecules are indicative of a strong attraction between them. The tight intermolecular organization of molecules displaced along *a* is depicted in Fig. 4. The co-operative nature of these interactions and their extent throughout the *ab* plane of the structure impart a significant stability to the supramolecular organization. The observed topologies and the associated energetics of these interactions should be confirmed and evaluated by theoretical calculations. The molecules of water hydrogen bond weakly to the N-atom sites of molecules located in neighboring screw/glide-related layers, interfacing and bridging between them (Table 1).



(*a*)

(*b*)

Figure 3
Detail of (I), showing the stacking and overlapping modes between π–π interacting molecules. H atoms have been omitted. (*a*) Bimolecular overlap between units related by inversion at 1,0,0. (*b*) Trimolecular interactions between the parent species at *x,y,z* (center) and two additional units related by inversion to it at $\frac{1}{2}$,0,0 and $\frac{3}{2}$,1,0. Atoms with the suffix _3 refer to species related by the corresponding inversion center to the parent molecules at (*x, y, z*).

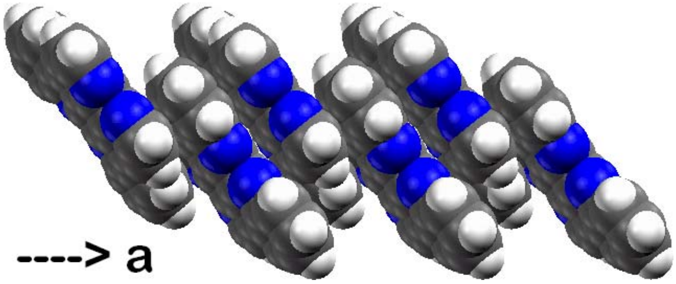


Figure 4
Space-filling diagram of molecules of (I) arranged along the *a* axis.

Experimental

The analysed crystals were obtained by dissolving the originally isolated eilatin compound (Rudi *et al.*, 1988) in a chloroform–methanol–water mixture, followed by very slow evaporation.

Crystal data

$C_{24}H_{12}N_4 \cdot H_2O$
$M_r = 374.39$
Monoclinic, $P2_1/c$
$a = 9.3302$ (3) Å
$b = 10.9224$ (4) Å
$c = 16.5491$ (7) Å
$\beta = 93.641$ (2)°
$V = 1683.08$ (11) Å^3
$Z = 4$

$D_x = 1.478$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3619 reflections
$\theta = 2.2$–27.9°
$\mu = 0.09$ mm^{-1}
$T = 110$ (2) K
Prism, yellow
0.25 × 0.20 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: none
12 446 measured reflections
3980 independent reflections
2456 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.047$
$\theta_{\rm max} = 27.9°$
$h = -12 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.166$
$S = 1.03$
3980 reflections
264 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0864P)^2 + 0.2186P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.38$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.26$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O29—H29B···N28	1.03	2.20	3.162 (2)	155
O29—H29A···N18$^{\rm i}$	0.95	2.07	2.996 (2)	163

Symmetry code: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$.

H atoms bound to carbon were located at idealized positions and refined as riding on their carrier atoms, with C—H distances of 0.95 Å and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). O-bound H atoms were located in difference Fourier maps and their displacement parameters were allowed to refine freely.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97*.

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