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Crystal structure of 1,13,14-triazadibenz[*a*,*j*]-anthracene 1,1,2,2-tetrachloroethane monosolvate

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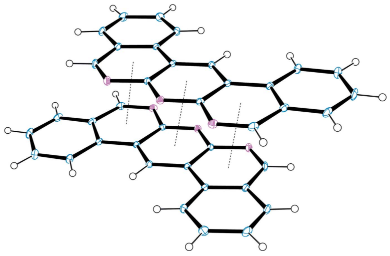
The asymmetric unit of the title compound, $C_{19}H_{11}N_3 \cdot C_2H_2Cl_4$, consists of one half-molecule of 1,13,14-triazadibenz[*a*,*j*]anthracene (dibenzo[*c*,*h*]-1.9,10-anthyridine, dbanth) and one half of 1,1,2,2-tetrachloroethane (TCE), both of which are located on a crystallographic twofold rotation axis. The dihedral angle between the planes of the terminal benzene rings in dbanth is 3.59 (7)° owing to the steric repulsion between the H atoms in the two benzo groups and the H atom in the central pyridine ring of the anthridine skeleton. In the crystal, π–π interactions between pyridine rings [centroid–centroid distances = 3.568 (2) and 3.594 (2) Å] link the dbanth molecules to form a one-dimensional columnar structure along the *c* axis. The dbanth and TCE molecules are connected through weak bifurcated C—H···(N,N) hydrogen bonds.



1. Chemical context

1,9,10-Anthyridine has an anthracene skeleton with three imine N atoms that are situated at the same edge of the molecule. Since an imine unit in an aromatic compound such as pyridine can act as a hydrogen-bond acceptor, 1,9,10-anthyridine can form a triply hydrogen-bonded structure with a corresponding H-atom donor, such as 2,6-diaminopyridinium and 2,6-bis(hydroxymethyl)phenol (Murray & Zimmerman, 1992; Xu *et al.*, 2006; Djurdjevic *et al.*, 2007; Blight *et al.*, 2009). Formation of multiple hydrogen bonds often corresponds to a large association constant (K_a = *ca* 10^4–10^{10}); therefore, 1,9,10-anthyridine derivatives are promising components for supramolecular compounds. However, there have been few reports on the crystal structures of 1,9,10-anthyridine derivatives. The crystal structure and intermolecular interactions of chlorobenzene-solvated 2,3,7,8-tetraphenyl-1,9,10-anthyridine have been reported (Madhavi *et al.*, 1997). In addition, 1,13,14-triazadibenz[*a*,*j*]anthracene (dbanth) has been synthesized and its crystal structure has been reported (Djurdjevic *et al.*, 2007; Blight *et al.*, 2009). In that case, the crystals contained no solvent molecules. In other instances, several transition-metal complexes bearing dbanth as a ligand have been reported (Wang *et al.*, 2012; Huang *et al.*, 2013; Hirakawa & Koizumi, 2014). In this paper, we report the crystal structure of dbanth 1,1,2,2-tetrachloroethane (TCE) monosolvate, (I). The H atoms in the TCE molecule form C—H···N hydrogen bonds with three dbanth N atoms (Table 1).

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H7···C11	0.98	2.53	3.372 (3)	144
N2—H7···C11	0.98	2.57	3.206 (3)	122

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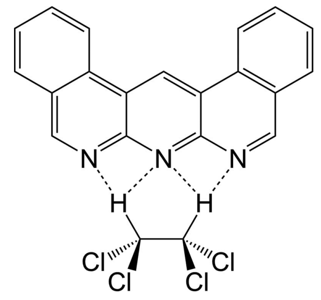

2. Structural commentary

The molecular structure of the title compound is depicted in Fig. 1. The dbanth and TCE molecules have twofold rotation symmetry. Although the structure of dbanth is almost planar, the planes of the terminal benzene rings are slightly twisted with respect to each other, with a dihedral angle of 3.59 (7)°. The distortion of the compound is considered to be due to the steric repulsion between atoms H5, H5* and H6. Atom H7 in the solvated TCE molecule forms a bifurcated hydrogen bond with the two N atoms (N1 and N2) of the dbanth molecule (Table 1). When dbanth was recrystallized from $CHCl_3$, solvation of $CHCl_3$ did not occur. This result indicates that formation of C—H⋯N hydrogen bonds stabilizes the 1:1 complex of dbanth and TCE.

3. Supramolecular features

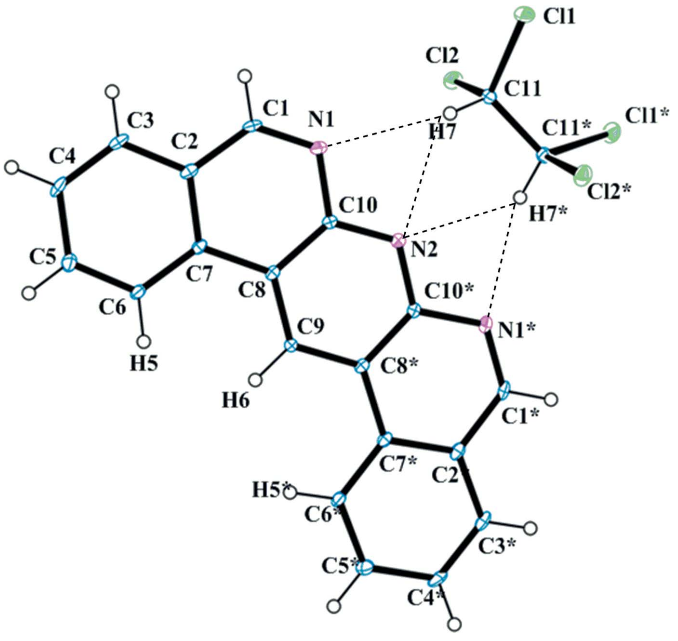

Figure 1
The two components of the title compound, (I), with displacement ellipsoids drawn at the 50% probability level. C—H⋯N hydrogen bonds are shown as dashed lines. [Symmetry code: (*) $-x + 1, y, -z + \frac{3}{2}$.]

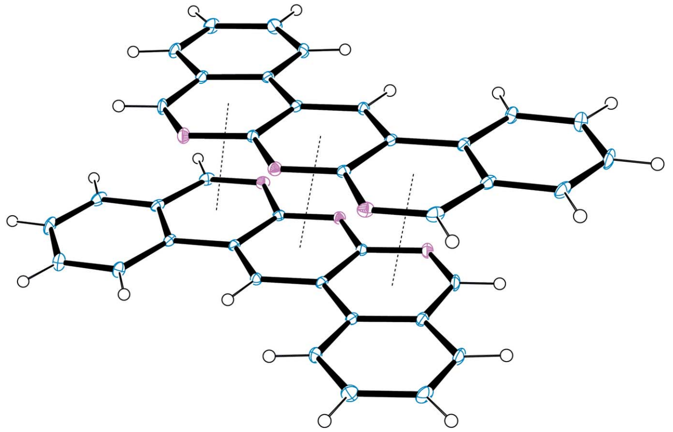

Figure 2
A partial packing diagram of the title compound, showing π–π interactions (dotted lines).

In the crystal, the dbanth molecule interacts with the neighbouring dbanth molecule through π–π stacking interactions, with an average interplanar distance of 3.36 Å; the centroid–centroid distances between pyridine rings containing atom N1 and between pyridine rings containing atom N2 are 3.568 (2) and 3.594 (2) Å, respectively (Fig. 2). The dbanth molecules form a one-dimensional columnar structure *via* successive π–π stacking interactions (Fig. 3). A twofold rotation axis passes through atoms N2, C9 and H6 of the central pyridine ring, so

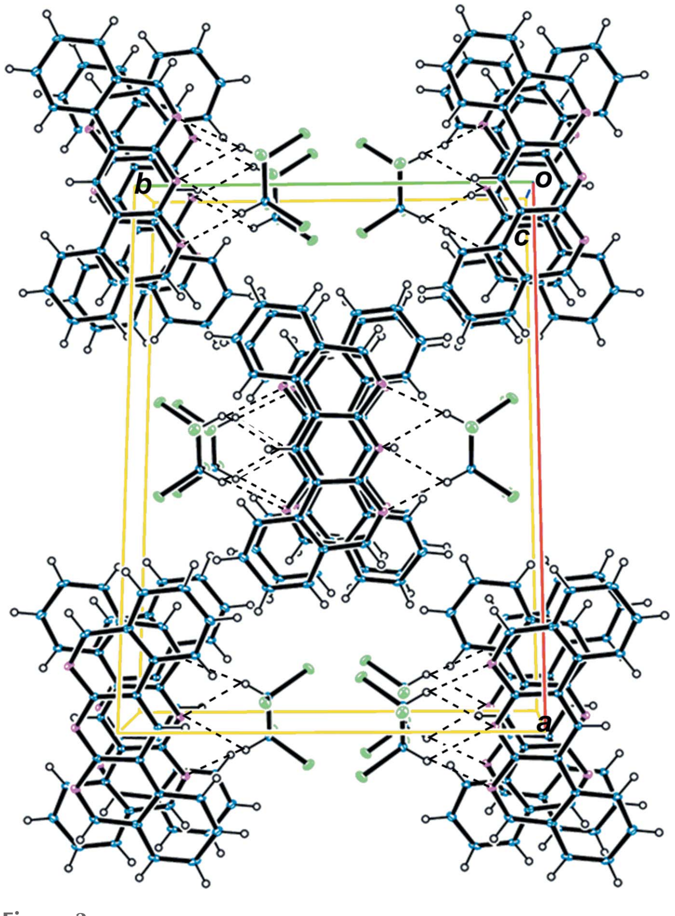

Figure 3
A crystal packing of the title compound, viewed down the *c* axis. Dashed lines indicate C—H⋯N hydrogen bonds.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{19}H_{11}N_3 \cdot C_2H_2Cl_4$
M_r	449.14
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	90
a, *b*, *c* (Å)	20.072 (7), 14.190 (5), 7.079 (3)
β (°)	110.255 (4)
V (Å^3)	1891.5 (11)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.64
Crystal size (mm)	0.79 × 0.40 × 0.10
Data collection	
Diffractometer	Bruker APEXII CCD area detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 1996)
$T_{\min}$, $T_{\max}$	0.511, 0.938
No. of measured, independent and observed [$F^2 > 2\sigma(F^2)$] reflections	4336, 1670, 1606
R_{int}	0.038
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.081, 1.06
No. of reflections	1670
No. of parameters	128
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.50, −0.27

Computer programs: *APEX2* (Bruker, 2006), *SAINT* (Bruker, 2004), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) and *CrystalStructure* (Rigaku, 2010).

that all of the dbanth molecules are arranged parallel to one another in the space group *C*2/*c*. In the crystal of nonsolvated dbanth (space group $P2_1/c$; Djurdjevic *et al.*, 2007), dbanth molecules are also stacked in a column, but the molecules in the neighbouring columns are inclined to each other by 41.8 (2)°.

4. Synthesis and crystallization

1,13,14-Triazadibenz[*a*,*j*]anthracene (dbanth) was synthesized *via* the reaction of 2,6-diamino-3,5-diiodopyridine with two equivalents of 2-formylbenzeneboronic acid using $Pd(PPh_3)_4$ as a catalyst according to a literature method (Djurdjevic *et al.*, 2007). Single crystals suitable for X-ray diffraction were obtained from a TCE solution by slow evaporation.

5. Refinement

Crystal data, data collection, and refinement details are summarized in Table 2. All H atoms were fixed geometry (C—H = 0.93 or 0.98 Å) and refined using a riding model, with U_{iso}(H) values set at $1.2U_{\text{eq}}$ of the parent atom.

Acknowledgements

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Crystal structure of 1,13,14-triazadibenz[*a*,*j*]anthracene 1,1,2,2-tetrachloroethane monosolvate

Take-aki Koizumi, Tomohiro Hariu and Yoshihisa Sei

Computing details

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT* (Bruker, 2004); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015*b*); molecular graphics: *CrystalStructure* (Rigaku, 2010); software used to prepare material for publication: *CrystalStructure* (Rigaku, 2010).

1,13,14-Triazadibenz[*a*,*j*]anthracene 1,1,2,2-tetrachloroethane monosolvate

Crystal data

$C_{19}H_{11}N_3{\cdot}C_2H_2Cl_4$
$M_r = 449.14$
Monoclinic, $C2/c$
Hall symbol: -C 2yc
$a = 20.072\ (7)$ Å
$b = 14.190\ (5)$ Å
$c = 7.079\ (3)$ Å
$\beta = 110.255\ (4)°$
$V = 1891.5\ (11)$ Å^3
$Z = 4$
$F(000) = 912.00$
$D_x = 1.577$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 94 reflections
$\theta = 5.4–26.8°$
$\mu = 0.64$ mm^{-1}
$T = 90$ K
Needle, colorless
0.79 × 0.40 × 0.10 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1996)
$T_{\min} = 0.511$, $T_{\max} = 0.938$
4336 measured reflections
1670 independent reflections
1606 reflections with $F^2 > 2\sigma(F^2)$
$R_{\rm int} = 0.038$
$\theta_{\max} = 25.0°$
$h = -23 \rightarrow 19$
$k = -13 \rightarrow 16$
$l = -7 \rightarrow 8$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.081$
$S = 1.06$
1670 reflections
128 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0378P)^2 + 2.3451P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.50$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement was performed using all reflections. The weighted *R*-factor (*wR*) and goodness of fit (*S*) are based on F^2. *R*-factor (gt) are based on *F*. The threshold expression of $F^2 > 2.0\ \sigma(F^2)$ is used only for calculating *R*-factor (gt).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
Cl1	0.41196 (2)	0.93210 (3)	0.70600 (6)	0.02318 (16)
Cl2	0.46383 (2)	0.83298 (3)	0.42650 (6)	0.02069 (15)
N1	0.38456 (7)	0.62220 (9)	0.53448 (19)	0.0148 (3)
N2	0.5000	0.61449 (12)	0.7500	0.0129 (4)
C1	0.32689 (8)	0.57917 (11)	0.4258 (2)	0.0158 (3)
H1	0.2883	0.6168	0.3558	0.019*
C2	0.31719 (8)	0.47862 (11)	0.4035 (2)	0.0144 (3)
C3	0.25243 (8)	0.43881 (12)	0.2803 (2)	0.0179 (3)
H2	0.2145	0.4778	0.2120	0.022*
C4	0.24495 (8)	0.34260 (12)	0.2603 (3)	0.0205 (4)
H3	0.2021	0.3164	0.1793	0.025*
C5	0.30269 (8)	0.28419 (12)	0.3637 (2)	0.0193 (4)
H4	0.2978	0.2191	0.3497	0.023*
C6	0.36626 (8)	0.32177 (11)	0.4851 (2)	0.0152 (3)
H5	0.4039	0.2820	0.5522	0.018*
C7	0.37471 (8)	0.42004 (11)	0.5082 (2)	0.0122 (3)
C8	0.43950 (7)	0.46557 (10)	0.6339 (2)	0.0112 (3)
C9	0.5000	0.41722 (14)	0.7500	0.0110 (4)
H6	0.5000	0.3517	0.7500	0.013*
C10	0.44225 (8)	0.56624 (10)	0.6410 (2)	0.0115 (3)
C11	0.46206 (8)	0.83406 (10)	0.6758 (2)	0.0150 (3)
H7	0.4386	0.7764	0.6963	0.018*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0185 (2)	0.0215 (2)	0.0267 (3)	0.00797 (15)	0.00433 (19)	−0.00421 (15)
Cl2	0.0227 (2)	0.0234 (3)	0.0136 (2)	0.00366 (15)	0.00322 (19)	−0.00042 (14)
N1	0.0132 (7)	0.0162 (7)	0.0140 (7)	0.0038 (5)	0.0035 (5)	0.0018 (5)
N2	0.0126 (9)	0.0133 (9)	0.0129 (9)	0.000	0.0043 (7)	0.000
C1	0.0119 (8)	0.0202 (8)	0.0135 (8)	0.0070 (6)	0.0023 (6)	0.0039 (6)
C2	0.0102 (7)	0.0211 (8)	0.0118 (7)	0.0020 (6)	0.0039 (6)	0.0016 (6)
C3	0.0079 (7)	0.0284 (9)	0.0154 (8)	0.0033 (6)	0.0014 (6)	0.0029 (6)
C4	0.0089 (7)	0.0298 (9)	0.0186 (9)	−0.0055 (6)	−0.0005 (7)	−0.0003 (7)
C5	0.0157 (8)	0.0187 (8)	0.0204 (8)	−0.0042 (6)	0.0026 (7)	0.0004 (6)
C6	0.0103 (7)	0.0176 (8)	0.0146 (8)	−0.0002 (6)	0.0006 (6)	0.0020 (6)

C7	0.0091 (7)	0.0174 (8)	0.0103 (7)	−0.0004 (6)	0.0036 (6)	0.0009 (5)
C8	0.0092 (7)	0.0152 (8)	0.0097 (7)	−0.0001 (6)	0.0039 (6)	−0.0002 (5)
C9	0.0108 (10)	0.0104 (10)	0.0114 (10)	0.000	0.0036 (9)	0.000
C10	0.0111 (7)	0.0136 (7)	0.0104 (8)	0.0011 (5)	0.0045 (6)	0.0010 (5)
C11	0.0158 (8)	0.0130 (8)	0.0154 (8)	0.0017 (6)	0.0046 (7)	−0.0008 (6)

Geometric parameters (Å, º)

Cl1—C11	1.7722 (15)	C4—H3	0.9300
Cl2—C11	1.7778 (17)	C5—C6	1.376 (2)
N1—C1	1.299 (2)	C5—H4	0.9300
N1—C10	1.3913 (19)	C6—C7	1.407 (2)
N2—C10	1.3373 (18)	C6—H5	0.9300
N2—C10^{i}	1.3373 (18)	C7—C8	1.449 (2)
C1—C2	1.441 (2)	C8—C9	1.3891 (18)
C1—H1	0.9300	C8—C10	1.430 (2)
C2—C7	1.407 (2)	C9—C8^{i}	1.3891 (18)
C2—C3	1.409 (2)	C9—H6	0.9300
C3—C4	1.375 (2)	C11—C11^{i}	1.522 (3)
C3—H2	0.9300	C11—H7	0.9800
C4—C5	1.406 (2)		

C1—N1—C10	117.16 (13)	C7—C6—H5	119.8
C10—N2—C10^{i}	118.40 (18)	C6—C7—C2	118.69 (14)
N1—C1—C2	126.09 (14)	C6—C7—C8	124.04 (14)
N1—C1—H1	117.0	C2—C7—C8	117.28 (14)
C2—C1—H1	117.0	C9—C8—C10	117.23 (13)
C7—C2—C3	120.14 (15)	C9—C8—C7	123.92 (14)
C7—C2—C1	118.16 (14)	C10—C8—C7	118.86 (13)
C3—C2—C1	121.70 (14)	C8^{i}—C9—C8	120.80 (19)
C4—C3—C2	120.41 (15)	C8^{i}—C9—H6	119.6
C4—C3—H2	119.8	C8—C9—H6	119.6
C2—C3—H2	119.8	N2—C10—N1	114.40 (14)
C3—C4—C5	119.38 (15)	N2—C10—C8	123.16 (14)
C3—C4—H3	120.3	N1—C10—C8	122.44 (13)
C5—C4—H3	120.3	C11^{i}—C11—Cl1	113.02 (9)
C6—C5—C4	121.04 (15)	C11^{i}—C11—Cl2	109.00 (14)
C6—C5—H4	119.5	Cl1—C11—Cl2	109.48 (8)
C4—C5—H4	119.5	C11^{i}—C11—H7	108.4
C5—C6—C7	120.35 (14)	Cl1—C11—H7	108.4
C5—C6—H5	119.8	Cl2—C11—H7	108.4

C10—N1—C1—C2	−0.6 (2)	C6—C7—C8—C9	−1.8 (2)
N1—C1—C2—C7	0.2 (2)	C2—C7—C8—C9	178.34 (11)
N1—C1—C2—C3	−179.50 (14)	C6—C7—C8—C10	178.32 (13)
C7—C2—C3—C4	−0.3 (2)	C2—C7—C8—C10	−1.6 (2)
C1—C2—C3—C4	179.35 (15)	C10—C8—C9—C8^{i}	−0.54 (9)
C2—C3—C4—C5	−0.2 (2)	C7—C8—C9—C8^{i}	179.54 (15)

C3—C4—C5—C6	0.4 (3)	C10^{i}—N2—C10—N1	179.30 (14)
C4—C5—C6—C7	0.0 (2)	C10^{i}—N2—C10—C8	−0.61 (10)
C5—C6—C7—C2	−0.6 (2)	C1—N1—C10—N2	180.00 (12)
C5—C6—C7—C8	179.54 (14)	C1—N1—C10—C8	−0.1 (2)
C3—C2—C7—C6	0.7 (2)	C9—C8—C10—N2	1.18 (19)
C1—C2—C7—C6	−178.97 (14)	C7—C8—C10—N2	−178.90 (11)
C3—C2—C7—C8	−179.37 (13)	C9—C8—C10—N1	−178.71 (11)
C1—C2—C7—C8	0.9 (2)	C7—C8—C10—N1	1.2 (2)

Symmetry code: (i) −*x*+1, *y*, −*z*+3/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H7···C11	0.98	2.53	3.372 (3)	144
N2—H7···C11	0.98	2.57	3.206 (3)	122