10,11,12,13-Tetrahydro-4,5,9,14-tetra-azadibenz[a,c]anthracene–benzene-1,4-dicarboxylic acid (2/1)

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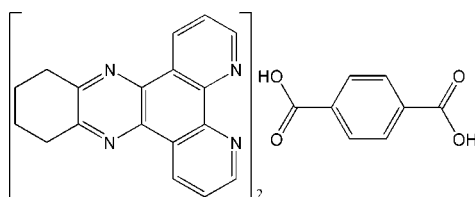Correspondence e-mail: guangbochejl@yahoo.com

In the title adduct, $2C_{18}H_{14}N_4 \cdot C_8H_6O_4$, the centrosymmetric benzene-1,4-dicarboxylic acid molecule makes two O—H⋯N hydrogen bonds to adjacent 10,11,12,13-tetrahydro-4,5,9,14-tetraazadibenzo[a,c]anthracene (TTBT) molecules. Aromatic π–π stacking interactions occur between TTBT rings [centroid–centroid distance = 3.570 (3) Å], leading to a two-dimensional supramolecular structure in the crystal.

Related literature

For related literature, see: Che *et al.* (2006, 2008); Stephenson & Hardie (2006); Xu *et al.* (2008); Yao *et al.* (2008).

Experimental

Crystal data

$2C_{18}H_{14}N_4 \cdot C_8H_6O_4$	b = 9.917 (5) Å
M_r = 738.80	c = 13.564 (9) Å
Triclinic, $P\bar{1}$	α = 101.469 (9)°
a = 7.266 (4) Å	β = 97.429 (9)°
γ = 109.697 (6)°	μ = 0.09 mm^{-1}
V = 881.2 (9) Å^3	T = 292 (2) K
Z = 1	0.32 × 0.21 × 0.08 mm
Mo $K\alpha$ radiation	

Data collection

Bruker SMART CCD diffractometer	7636 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)	3444 independent reflections
T_{min} = 0.978, T_{max} = 0.992	1394 reflections with $I > 2\sigma(I)$
	R_{int} = 0.047

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.058	253 parameters
$wR(F^2)$ = 0.180	H-atom parameters constrained
S = 0.93	$\Delta\rho_{max}$ = 0.34 e Å^{-3}
3444 reflections	$\Delta\rho_{min}$ = −0.18 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O2—H2A⋯N2	0.82	2.02	2.694 (4)	139

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

References

Bruker (2002). *SMART, SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Che, G.-B., Li, W.-L., Kong, Z.-G., Su, Z.-S., Chu, B., Li, B., Zhang, Z.-Q., Hu, Z.-Z. & Chi, H.-J. (2006). *Synth. Commun.* **36**, 2519–2524.

Che, G.-B., Liu, C.-B., Liu, B., Wang, Q.-W. & Xu, Z.-L. (2008). *CrystEngComm*, **10**, 184–191.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Stephenson, M. D. & Hardie, M. J. (2006). *Cryst. Growth Des.* **6**, 423–432.

Xu, Z.-L., Li, X.-Y., Che, G.-B., Liu, C.-B. & Wang, Q.-W. (2008). *Chin. J. Struct. Chem.* **27**, 593–597.

Yao, J.-C., Qin, J.-H., Sun, Q.-B., Qu, L. & Li, Y.-G. (2008). *Z. Kristallogr. New Cryst. Struct.* **223**, 11–12.

supplementary materials

10,11,12,13-Tetrahydro-4,5,9,14-tetraazadibenz[*a,c*]anthracene–benzene-1,4-dicarboxylic acid (2/1)

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Comment

Current crystal engineering on the basis of the supramolecular architectures assembled from various noncovalent interactions, such as hydrogen bonds and π-π stacking interactions have been extensively studied owing to their novel topologies and potential applications as functional materials (Stephenson & Hardie, 2006; Yao *et al.*,2008). 1,10-Phenanthroline (phen) and its derivatives have been widely used to build novel supramolecular architectures (Xu, Li *et al.*, 2008; Che, Liu *et al.*, 2008). As a continuation of our studies in this area, we have prepared the title compound, (I), using the phen derivative 10,11,12,13-tetrahydro-4,5,9,14-tetraazadibenz[*a,c*]anthracene (TTBA).

The asymmetric unit of (I) consists of one TTBA molecule and half of a centrosymmetric 1,4-benzenedicarboxylic acid molecule (Fig. 1). The two components of (I) interact by way of O—H···N hydrogen bonds (Table 1). Furthermore, there are π-π aromatic stacking interactions involving TTBA ligands of adjacent units [centroid-centroid distance = 3.570 (3)Å], forming an intriguing two-dimensional supramolecular motif (Fig. 2).

Experimental

The TTBA was synthesized according to the literature method (Che, Li *et al.*, 2006). TTBA (1.0 mmol) and 1,4-benzenedicarboxylic acid (0.5 mmol) were dissolved in aqueous solution and the mixture was sealed in a Teflon-lined autoclave and heated to 433 K for 4 d. Upon cooling and opening the bomb, colorless blocks of (I) were obtained.

Refinement

The hydrogen atoms were positioned geometrically (C—H = 0.93 Å, O—H = 0.82Å) and refined as riding, with $U_{iso}(H)$= $1.2U_{eq}$(carrier).
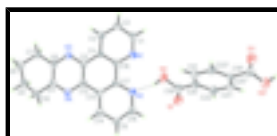
Figures

Fig. 1. View of the molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level (arbitrary spheres for the H atoms). [Symmetry code: (i) 1 - *x*, -*y*, 3 - *z*.]
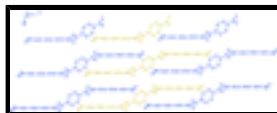

Fig. 2. Packing diagram of the two-dimensional supramolecular structure of (I) formed *via* π–π interactions and hydrogen bonds. H atoms have been omitted.

supplementary materials

10,11,12,13-Tetrahydro-4,5,9,14-tetraazadibenz[*a,c*]anthracene– benzene-1,4-dicarboxylic acid (2/1)

Crystal data

$2C_{18}H_{14}N_4 \cdot C_8H_6O_4$	$Z = 1$
$M_r = 738.80$	$F_{000} = 386$
Triclinic, $P\bar{1}$	$D_x = 1.392$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 7.266$ (4) Å	Cell parameters from 2386 reflections
$b = 9.917$ (5) Å	$\theta = 2.3$–26.0º
$c = 13.564$ (9) Å	$\mu = 0.09$ mm^{-1}
$\alpha = 101.469$ (9)º	$T = 292$ (2) K
$\beta = 97.429$ (9)º	Block, colorless
$\gamma = 109.697$ (6)º	$0.32 \times 0.21 \times 0.08$ mm
$V = 881.2$ (9) Å^3	

Data collection

Bruker SMART CCD diffractometer	3444 independent reflections
Radiation source: fine-focus sealed tube	1394 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.047$
$T = 292(2)$ K	$\theta_{max} = 26.1$º
ω scans	$\theta_{min} = 2.3$º
Absorption correction: multi-scan (SADABS; Bruker, 2002)	$h = -8 \rightarrow 8$
$T_{min} = 0.978$, $T_{max} = 0.992$	$k = -12 \rightarrow 12$
7636 measured reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.058$	H-atom parameters constrained
$wR(F^2) = 0.180$	$w = 1/[\sigma^2(F_o^2) + (0.0762P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.93$	$(\Delta/\sigma)_{max} < 0.001$
3444 reflections	$\Delta\rho_{max} = 0.34$ e Å^{-3}
253 parameters	$\Delta\rho_{min} = -0.18$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	y	z	$U_{iso}*/U_{eq}$
C1	0.7589 (5)	0.5815 (4)	1.2595 (3)	0.0603 (10)
H1	0.7594	0.6000	1.3295	0.072*
C2	0.7631 (5)	0.6947 (4)	1.2121 (3)	0.0593 (9)
H2	0.7692	0.7861	1.2495	0.071*
C3	0.7581 (4)	0.6668 (4)	1.1082 (3)	0.0534 (9)
H3	0.7589	0.7394	1.0739	0.064*
C4	0.7517 (4)	0.5297 (3)	1.0542 (2)	0.0411 (8)
C5	0.7492 (4)	0.4942 (3)	0.9448 (2)	0.0418 (8)
C6	0.7476 (4)	0.5624 (4)	0.7934 (3)	0.0473 (8)
C7	0.7508 (5)	0.6785 (4)	0.7365 (2)	0.0607 (10)
H7A	0.8810	0.7585	0.7590	0.073*
H7B	0.6518	0.7193	0.7543	0.073*
C8	0.7086 (6)	0.6201 (4)	0.6202 (3)	0.0773 (12)
H8A	0.5654	0.5694	0.5943	0.093*
H8B	0.7534	0.7030	0.5898	0.093*
C9	0.8103 (6)	0.5164 (4)	0.5882 (3)	0.0779 (12)
H9A	0.9537	0.5678	0.6125	0.093*
H9B	0.7826	0.4845	0.5137	0.093*
C10	0.7414 (6)	0.3822 (4)	0.6306 (2)	0.0669 (10)
H10A	0.6063	0.3186	0.5940	0.080*
H10B	0.8271	0.3265	0.6187	0.080*
C11	0.7453 (4)	0.4230 (4)	0.7430 (2)	0.0485 (8)
C12	0.7473 (4)	0.3561 (3)	0.8947 (2)	0.0433 (8)
C13	0.7493 (4)	0.2468 (3)	0.9524 (2)	0.0439 (8)
C14	0.7547 (4)	0.1100 (4)	0.9065 (3)	0.0535 (9)
H14	0.7545	0.0847	0.8367	0.064*
C15	0.7602 (5)	0.0130 (4)	0.9645 (3)	0.0578 (9)
H15	0.7664	−0.0782	0.9355	0.069*
C16	0.7563 (5)	0.0539 (4)	1.0681 (3)	0.0622 (10)
H16	0.7582	−0.0131	1.1071	0.075*
C17	0.7489 (4)	0.2799 (3)	1.0574 (2)	0.0431 (8)
C18	0.7504 (4)	0.4245 (3)	1.1102 (2)	0.0429 (8)
C19	0.7010 (6)	0.0878 (4)	1.3406 (3)	0.0611 (10)

C20	0.5949 (5)	0.0433 (3)	1.4226 (2)	0.0527 (9)
C21	0.4077 (6)	0.0460 (4)	1.4252 (3)	0.0597 (10)
H21	0.3439	0.0761	1.3747	0.072*
C22	0.6860 (5)	−0.0042 (4)	1.4971 (3)	0.0611 (10)
H22	0.8116	−0.0082	1.4950	0.073*
N1	0.7543 (4)	0.4499 (3)	1.2122 (2)	0.0533 (7)
N2	0.7502 (4)	0.1824 (3)	1.1147 (2)	0.0513 (7)
N3	0.7496 (4)	0.5981 (3)	0.89318 (19)	0.0472 (7)
N4	0.7442 (4)	0.3203 (3)	0.79299 (19)	0.0491 (7)
O1	0.8422 (4)	0.0570 (3)	1.3217 (2)	0.0853 (9)
O2	0.6271 (4)	0.1674 (3)	1.29255 (18)	0.0766 (8)
H2A	0.6112	0.1355	1.2302	0.115*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.067 (2)	0.068 (3)	0.049 (2)	0.028 (2)	0.0207 (18)	0.014 (2)
C2	0.070 (2)	0.053 (2)	0.057 (3)	0.0253 (19)	0.0208 (19)	0.0101 (19)
C3	0.054 (2)	0.053 (2)	0.058 (2)	0.0230 (18)	0.0178 (18)	0.0190 (19)
C4	0.0385 (18)	0.0422 (19)	0.043 (2)	0.0169 (15)	0.0081 (15)	0.0082 (16)
C5	0.0338 (18)	0.046 (2)	0.045 (2)	0.0133 (15)	0.0059 (15)	0.0148 (17)
C6	0.0439 (19)	0.050 (2)	0.049 (2)	0.0188 (17)	0.0066 (16)	0.0151 (18)
C7	0.069 (2)	0.065 (2)	0.051 (2)	0.0243 (19)	0.0119 (19)	0.0243 (19)
C8	0.106 (3)	0.082 (3)	0.053 (3)	0.043 (3)	0.015 (2)	0.026 (2)
C9	0.100 (3)	0.093 (3)	0.057 (2)	0.047 (3)	0.025 (2)	0.029 (2)
C10	0.084 (3)	0.070 (3)	0.043 (2)	0.027 (2)	0.0104 (19)	0.0135 (19)
C11	0.049 (2)	0.052 (2)	0.041 (2)	0.0161 (17)	0.0074 (16)	0.0106 (18)
C12	0.0388 (18)	0.047 (2)	0.042 (2)	0.0156 (15)	0.0067 (15)	0.0103 (17)
C13	0.0391 (18)	0.044 (2)	0.048 (2)	0.0137 (15)	0.0108 (15)	0.0134 (17)
C14	0.058 (2)	0.050 (2)	0.052 (2)	0.0230 (18)	0.0093 (17)	0.0091 (19)
C15	0.070 (2)	0.043 (2)	0.064 (2)	0.0256 (19)	0.0160 (19)	0.0128 (19)
C16	0.072 (2)	0.049 (2)	0.067 (3)	0.0211 (19)	0.015 (2)	0.023 (2)
C17	0.0412 (18)	0.0398 (19)	0.049 (2)	0.0132 (15)	0.0120 (15)	0.0146 (17)
C18	0.0401 (18)	0.048 (2)	0.043 (2)	0.0173 (16)	0.0116 (15)	0.0135 (17)
C19	0.079 (3)	0.053 (2)	0.057 (2)	0.025 (2)	0.024 (2)	0.0211 (19)
C20	0.067 (2)	0.043 (2)	0.050 (2)	0.0207 (18)	0.0185 (18)	0.0124 (17)
C21	0.074 (3)	0.059 (2)	0.054 (2)	0.030 (2)	0.0161 (19)	0.0227 (19)
C22	0.069 (2)	0.060 (2)	0.066 (2)	0.0287 (19)	0.023 (2)	0.025 (2)
N1	0.0634 (18)	0.0523 (19)	0.0464 (18)	0.0224 (15)	0.0166 (14)	0.0131 (15)
N2	0.0600 (18)	0.0427 (17)	0.0547 (18)	0.0202 (14)	0.0139 (14)	0.0171 (15)
N3	0.0502 (16)	0.0494 (17)	0.0433 (17)	0.0193 (13)	0.0087 (13)	0.0143 (14)
N4	0.0541 (17)	0.0485 (17)	0.0435 (18)	0.0194 (14)	0.0095 (13)	0.0098 (14)
O1	0.099 (2)	0.097 (2)	0.101 (2)	0.0578 (18)	0.0578 (18)	0.0550 (17)
O2	0.101 (2)	0.0836 (19)	0.0687 (17)	0.0465 (16)	0.0330 (15)	0.0399 (15)

Geometric parameters (Å, °)

C1—N1	1.323 (4)	C10—H10B	0.9700
C1—C2	1.393 (4)	C11—N4	1.329 (4)

C1—H1	0.9300	C12—N4	1.349 (4)
C2—C3	1.375 (4)	C12—C13	1.461 (4)
C2—H2	0.9300	C13—C14	1.392 (4)
C3—C4	1.393 (4)	C13—C17	1.397 (4)
C3—H3	0.9300	C14—C15	1.366 (4)
C4—C18	1.405 (4)	C14—H14	0.9300
C4—C5	1.452 (4)	C15—C16	1.389 (4)
C5—N3	1.355 (3)	C15—H15	0.9300
C5—C12	1.398 (4)	C16—N2	1.322 (4)
C6—N3	1.327 (4)	C16—H16	0.9300
C6—C11	1.408 (4)	C17—N2	1.357 (4)
C6—C7	1.504 (4)	C17—C18	1.466 (4)
C7—C8	1.520 (4)	C18—N1	1.351 (4)
C7—H7A	0.9700	C19—O1	1.208 (4)
C7—H7B	0.9700	C19—O2	1.317 (4)
C8—C9	1.486 (5)	C19—C20	1.488 (5)
C8—H8A	0.9700	C20—C21	1.375 (4)
C8—H8B	0.9700	C20—C22	1.381 (4)
C9—C10	1.511 (4)	C21—C22[i]	1.384 (4)
C9—H9A	0.9700	C21—H21	0.9300
C9—H9B	0.9700	C22—C21[i]	1.384 (4)
C10—C11	1.491 (4)	C22—H22	0.9300
C10—H10A	0.9700	O2—H2A	0.8200
N1—C1—C2	124.8 (3)	N4—C11—C6	121.7 (3)
N1—C1—H1	117.6	N4—C11—C10	116.5 (3)
C2—C1—H1	117.6	C6—C11—C10	121.8 (3)
C3—C2—C1	117.8 (3)	N4—C12—C5	121.5 (3)
C3—C2—H2	121.1	N4—C12—C13	118.5 (3)
C1—C2—H2	121.1	C5—C12—C13	120.1 (3)
C2—C3—C4	119.9 (3)	C14—C13—C17	118.3 (3)
C2—C3—H3	120.1	C14—C13—C12	122.0 (3)
C4—C3—H3	120.1	C17—C13—C12	119.7 (3)
C3—C4—C18	117.4 (3)	C15—C14—C13	119.6 (3)
C3—C4—C5	122.5 (3)	C15—C14—H14	120.2
C18—C4—C5	120.1 (3)	C13—C14—H14	120.2
N3—C5—C12	121.2 (3)	C14—C15—C16	118.3 (3)
N3—C5—C4	118.5 (3)	C14—C15—H15	120.8
C12—C5—C4	120.3 (3)	C16—C15—H15	120.8
N3—C6—C11	121.7 (3)	N2—C16—C15	124.0 (3)
N3—C6—C7	116.9 (3)	N2—C16—H16	118.0
C11—C6—C7	121.4 (3)	C15—C16—H16	118.0
C6—C7—C8	113.5 (3)	N2—C17—C13	122.2 (3)
C6—C7—H7A	108.9	N2—C17—C18	117.4 (3)
C8—C7—H7A	108.9	C13—C17—C18	120.4 (3)
C6—C7—H7B	108.9	N1—C18—C4	123.4 (3)
C8—C7—H7B	108.9	N1—C18—C17	117.1 (3)
H7A—C7—H7B	107.7	C4—C18—C17	119.4 (3)
C9—C8—C7	112.1 (3)	O1—C19—O2	123.7 (4)

C9—C8—H8A	109.2	O1—C19—C20	123.6 (4)
C7—C8—H8A	109.2	O2—C19—C20	112.6 (4)
C9—C8—H8B	109.2	C21—C20—C22	119.2 (3)
C7—C8—H8B	109.2	C21—C20—C19	121.8 (3)
H8A—C8—H8B	107.9	C22—C20—C19	119.0 (4)
C8—C9—C10	111.6 (3)	C20—C21—C22ⁱ	120.1 (3)
C8—C9—H9A	109.3	C20—C21—H21	119.9
C10—C9—H9A	109.3	C22ⁱ—C21—H21	119.9
C8—C9—H9B	109.3	C20—C22—C21ⁱ	120.6 (3)
C10—C9—H9B	109.3	C20—C22—H22	119.7
H9A—C9—H9B	108.0	C21ⁱ—C22—H22	119.7
C11—C10—C9	112.4 (3)	C1—N1—C18	116.7 (3)
C11—C10—H10A	109.1	C16—N2—C17	117.6 (3)
C9—C10—H10A	109.1	C6—N3—C5	117.0 (3)
C11—C10—H10B	109.1	C11—N4—C12	116.9 (3)
C9—C10—H10B	109.1	C19—O2—H2A	109.5
H10A—C10—H10B	107.9		

Symmetry codes: (i) $-x+1$, $-y$, $-z+3$.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2A···N2	0.82	2.02	2.694 (4)	139

Fig. 1

Fig. 2