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2,2′-[Anthracene-9,10-diyldi(methylenethio)]dianiline

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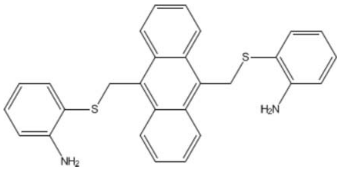
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.003 Å; R factor = 0.043; wR factor = 0.142; data-to-parameter ratio = 18.9.

The title compound, $C_{28}H_{24}N_2S_2$, is a derivative of anthracenyl compounds which are extensively used in PET sensors. The molecule of the title compound has inversion symmetry and forms two intramolecular hydrogen bonds of the type N—H···S. In the crystal structure, the molecules are linked by C—H···π hydrogen-bonding contacts with the benzenamines acting both as donor and acceptor units.

Related literature

For related literature, see: Greiner & Maier (2002); Lee *et al.* (2006); Marciniak (2007); Miller *et al.* (1955); Quici *et al.* (2000); Sclafani *et al.* (1996); Tamayo *et al.* (2005, 2006).



Experimental

Crystal data

$C_{28}H_{24}N_2S_2$
M_r = 452.63
Monoclinic, $P2_1/c$
a = 9.0670 (8) Å
b = 17.4159 (16) Å
c = 7.1200 (6) Å
β = 101.620 (1)°
V = 1101.28 (17) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.26 mm^{-1}
T = 295 (2) K
0.26 × 0.20 × 0.10 mm

Data collection

Bruker APEXII area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004) T_{min} = 0.937, T_{max} = 0.972
8318 measured reflections
2746 independent reflections
1747 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.142
S = 1.00
2746 reflections
145 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

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

*Cg*3 is the centroid of the C9–C14 ring.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*C*···S1	0.86	2.63	3.032 (2)	110
C11—H11*A*···*Cg*3^i	0.93	2.80	3.628 (2)	149

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2000).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2034).

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supplementary materials

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2,2'-[Anthracene-9,10-diyldi(methylenethio)]dianiline

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Comment

Anthracene derivatives have gained considerable interest in recent years because of its photophysical properties in PET sensors (Sclafani *et al.*, 1996; Greiner *et al.*,2002;). These important class of products was used to design macrocyclic ligands (Quici *et al.*, 2000; Tamayo *et al.*, 2005). Recently, it was shown that sulfur containing macrocyclic ligands with strong binding capability for heavy metal ions display very attractive photophysical properties (Tamayo *et al.*, 2006; Lee *et al.*, 2006;).

The molecule of the title compound (Fig. 1) has inversion symmetry and forms two intramolecular hydrogen bonds of the type N—H···S. The inversion centre of the molecule is in the middle of the anthracene skeleton. Two Csp^2===Csp^2 bonds, C1===C2 and C3===C4 clearly show local π systems with distances 1.354 (3) Å and 1.358 (3) Å, whereas the central ring of the anthracene skeleton has a delocalized π-system with distances in the range 1.400 (2) Å and 1.441 (2) Å. The Csp^2—Csp^3 bond for C7—C8, 1.514 (2) Å, represents a normal value. Atoms C9 - C14, N1 and S1 are coplanar. The bond angles of the anthracene half molecule vary between 117.54 (17)° and 121.94 (18)°, indicating that the anthracene rings exhibit distorted hexagonal configuration. In the crystal lattice the molecules are linked by C—H···π hydrogen bonding contacts with the benzenamines acting both as donor and acceptor units (Fig. 2 and Table 1).

Experimental

The title compound was prepared according to the following procedure. To 2-aminobenzenethiol(1.02 g, 4.00 mol), dissolved in 25 mL of freshly distilled THF and cooled to 0 °C, the suspended solution of sodium hydride(0.44 g, 9.00 mol, 50%) in 25 mL THF was slowly added dropwise under nitrogen. Then the solution was slowly warmed up to RT and stirred for 30 min, and 9,10-bis(chloromethyl)anthracene (Miller *et al.*, 1955) (1.10 g, 4.00 mol) in 25 ml of THF was added dropwise and stirred overnight. The solvent was removed in vacuum, the residue was taken up in water (50 ml), and the product was extracted three times with 30-ml portions of dichloromethane·The organic solvent was evaporated, and a brown oily material was obtained (1.67 g). Separation by flash chromatography (eluent, ethyl acetate: petroleum ether(60–90) =1:3), resulted in a yellow solid (1.37 g, 75.7%) m.p. 197–198°C. Single crystals suitable for X-ray diffraction were obtained by recrystallization from a mixture of dichloromethane and petroleum ether.

1H NMR (500 MHz, CDCl3): δ 4.40 (s, 4H, NH2), δ 4.94 (s, 4H, CH2), δ 6.63(t, 2H, benzene-H), δ 6.70(d, 2H, benzene-H), δ 7.12(t, 2H, benzene-H),δ 7.36(d, 2H, benzene-H), 7.47 (m, 4H, anthrance-H), 8.28 (m, 4H, anthrance-H); EI—MS: m/*z* (%) '453.17 (100) [*M*+1]'.

Refinement

The H atoms on the C atoms were located in a difference Fourier map and refined as riding on their parent atoms with U_{iso}(H)=1.2 times U_{eq}(C) and with C—H distance of 0.93 and 0.97 Å. H atoms on N atoms were included in calculated positions, constrained to an ideal geometry with N—H distance of 0.86 Å and with U_{iso}(H)=1.2 times U_{eq}(N).

Figures

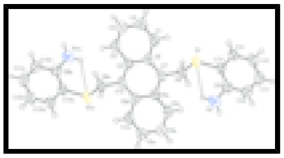

Fig. 1. View of the title compound, with labelled atoms and displacement ellipsoids drawn at the 50% probability level. Atoms labelled with "a" are related by symmetry operator (1 − *x*, −*y*, −*z*). Intramolecular in-plane N—H···S contacts are indicated as dashed lines. H atoms are shown as small spheres of arbitrary size.

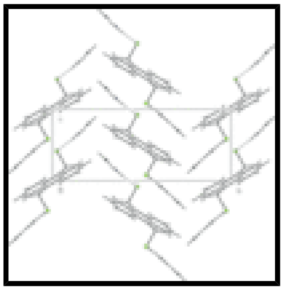

Fig. 2. View of the *b,c*-projection of the unit cell, with translational symmetry of the molecules along the *c*-axis and the C—H···π contacts between adjacent molecules in a zigzag mode along the *b* and *c* axes.

2,2'-[Anthracene-9,10-diyldi(methylenethio)]dianiline

Crystal data

$C_{28}H_{24}N_2S_2$	F_{000} = 476
M_r = 452.63	D_x = 1.365 Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: 197-198°C K
Hall symbol: -P 2ybc	Mo *K*α radiation λ = 0.71073 Å
a = 9.0670 (8) Å	Cell parameters from 1747 reflections
b = 17.4159 (16) Å	θ = 2.3–29.4°
c = 7.1200 (6) Å	μ = 0.26 mm^{-1}
β = 101.6200 (10)°	*T* = 295 (2) K
V = 1101.28 (17) Å^3	Prism, yellow
Z = 2	0.26 × 0.20 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer	2746 independent reflections
Radiation source: fine-focus sealed tube	1747 reflections with *I* > 2σ(*I*)
Monochromator: graphite	R_{int} = 0.024
T = 295(2) K	$θ_{max}$ = 29.4°
φ and ω scans	$θ_{min}$ = 2.3°

Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	$h = -12 \rightarrow 11$
$T_{\min} = 0.937$, $T_{\max} = 0.972$	$k = -24 \rightarrow 22$
8318 measured reflections	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.044$	H-atom parameters constrained
$wR(F^2) = 0.142$	$w = 1/[\sigma^2(F_o^2) + (0.0876P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{\max} < 0.001$
2746 reflections	$\Delta\rho_{\max} = 0.24$ e Å^{-3}
145 parameters	$\Delta\rho_{\min} = -0.28$ 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 $F^2 > 2\text{sigma}(F^2)$ 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}
S1	0.27792 (6)	0.02595 (3)	0.41882 (7)	0.0557 (2)
N1	0.47587 (18)	0.14579 (11)	0.6551 (3)	0.0668 (5)
H1B	0.5395	0.1774	0.7196	0.080*
H1C	0.5050	0.1130	0.5799	0.080*
C1	0.2092 (2)	−0.06449 (12)	−0.0176 (3)	0.0553 (5)
H1A	0.1404	−0.0406	0.0440	0.066*
C2	0.1701 (2)	−0.13104 (14)	−0.1130 (3)	0.0628 (6)
H2A	0.0764	−0.1528	−0.1136	0.075*
C3	0.2707 (2)	−0.16739 (13)	−0.2114 (3)	0.0681 (6)
H3A	0.2423	−0.2126	−0.2785	0.082*
C4	0.4088 (2)	−0.13685 (12)	−0.2090 (3)	0.0591 (5)
H4A	0.4731	−0.1614	−0.2763	0.071*
C5	0.45849 (19)	−0.06799 (10)	−0.1060 (2)	0.0445 (4)
C6	0.35400 (19)	−0.02986 (10)	−0.0091 (2)	0.0430 (4)

C7	0.39599 (19)	0.03772 (10)	0.0944 (2)	0.0436 (4)
C8	0.2844 (2)	0.07694 (11)	0.1947 (3)	0.0482 (4)
H8A	0.1853	0.0769	0.1120	0.058*
H8B	0.3144	0.1299	0.2225	0.058*
C9	0.3273 (2)	0.14774 (11)	0.6723 (2)	0.0493 (4)
C10	0.2771 (3)	0.20063 (11)	0.7940 (3)	0.0571 (5)
H10A	0.3462	0.2332	0.8690	0.069*
C11	0.1291 (3)	0.20522 (12)	0.8044 (3)	0.0603 (5)
H11A	0.0989	0.2407	0.8867	0.072*
C12	0.0233 (2)	0.15810 (12)	0.6950 (3)	0.0596 (5)
H12A	−0.0778	0.1622	0.7016	0.072*
C13	0.0696 (2)	0.10473 (11)	0.5755 (3)	0.0507 (5)
H13A	−0.0011	0.0723	0.5029	0.061*
C14	0.2195 (2)	0.09871 (10)	0.5618 (2)	0.0448 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0736 (4)	0.0450 (3)	0.0583 (3)	0.0108 (2)	0.0366 (3)	0.0037 (2)
N1	0.0562 (11)	0.0756 (13)	0.0704 (12)	−0.0031 (8)	0.0171 (8)	0.0058 (10)
C1	0.0462 (10)	0.0667 (14)	0.0577 (12)	0.0027 (9)	0.0216 (9)	−0.0040 (10)
C2	0.0533 (11)	0.0732 (15)	0.0656 (13)	−0.0122 (10)	0.0206 (9)	−0.0097 (11)
C3	0.0717 (14)	0.0650 (14)	0.0721 (14)	−0.0140 (11)	0.0254 (11)	−0.0182 (11)
C4	0.0668 (13)	0.0552 (12)	0.0622 (12)	0.0013 (9)	0.0297 (10)	−0.0117 (10)
C5	0.0513 (10)	0.0458 (11)	0.0405 (9)	0.0058 (8)	0.0189 (8)	0.0035 (8)
C6	0.0453 (10)	0.0473 (11)	0.0398 (9)	0.0071 (7)	0.0170 (7)	0.0034 (8)
C7	0.0478 (10)	0.0457 (11)	0.0421 (9)	0.0096 (7)	0.0204 (7)	0.0047 (8)
C8	0.0527 (10)	0.0451 (11)	0.0531 (10)	0.0100 (8)	0.0254 (8)	0.0022 (8)
C9	0.0571 (11)	0.0498 (11)	0.0429 (9)	0.0026 (8)	0.0149 (8)	0.0098 (8)
C10	0.0822 (14)	0.0465 (11)	0.0427 (10)	−0.0026 (10)	0.0128 (9)	0.0014 (9)
C11	0.0913 (15)	0.0471 (12)	0.0500 (11)	0.0095 (10)	0.0320 (11)	−0.0004 (9)
C12	0.0661 (12)	0.0560 (13)	0.0673 (13)	0.0121 (10)	0.0386 (10)	0.0072 (10)
C13	0.0552 (11)	0.0489 (11)	0.0531 (11)	−0.0019 (8)	0.0227 (9)	−0.0002 (8)
C14	0.0562 (11)	0.0390 (10)	0.0448 (9)	0.0048 (7)	0.0233 (8)	0.0041 (7)

Geometric parameters (Å, °)

S1—C14	1.7720 (17)	C6—C7	1.400 (2)
S1—C8	1.8375 (18)	C7—C5^{i}	1.408 (2)
N1—C9	1.377 (2)	C7—C8	1.514 (2)
N1—H1B	0.86	C8—H8A	0.97
N1—H1C	0.86	C8—H8B	0.97
C1—C2	1.354 (3)	C9—C10	1.402 (3)
C1—C6	1.435 (3)	C9—C14	1.412 (3)
C1—H1A	0.93	C10—C11	1.361 (3)
C2—C3	1.407 (3)	C10—H10A	0.93
C2—H2A	0.93	C11—C12	1.378 (3)
C3—C4	1.358 (3)	C11—H11A	0.93

C3—H3A	0.93	C12—C13	1.381 (3)
C4—C5	1.430 (3)	C12—H12A	0.93
C4—H4A	0.93	C13—C14	1.386 (2)
C5—C7$^{\mathrm{i}}$	1.408 (2)	C13—H13A	0.93
C5—C6	1.441 (2)		

C14—S1—C8	102.65 (8)	C7—C8—S1	109.45 (12)
C9—N1—H1B	120.0	C7—C8—H8A	109.8
C9—N1—H1C	120.0	S1—C8—H8A	109.8
H1B—N1—H1C	120.0	C7—C8—H8B	109.8
C2—C1—C6	121.73 (17)	S1—C8—H8B	109.8
C2—C1—H1A	119.1	H8A—C8—H8B	108.2
C6—C1—H1A	119.1	N1—C9—C10	121.08 (18)
C1—C2—C3	120.28 (19)	N1—C9—C14	121.02 (17)
C1—C2—H2A	119.9	C10—C9—C14	117.85 (17)
C3—C2—H2A	119.9	C11—C10—C9	121.26 (19)
C4—C3—C2	120.4 (2)	C11—C10—H10A	119.4
C4—C3—H3A	119.8	C9—C10—H10A	119.4
C2—C3—H3A	119.8	C10—C11—C12	121.04 (18)
C3—C4—C5	121.94 (18)	C10—C11—H11A	119.5
C3—C4—H4A	119.0	C12—C11—H11A	119.5
C5—C4—H4A	119.0	C11—C12—C13	119.04 (18)
C7$^{\mathrm{i}}$—C5—C4	122.58 (16)	C11—C12—H12A	120.5
C7$^{\mathrm{i}}$—C5—C6	119.87 (16)	C13—C12—H12A	120.5
C4—C5—C6	117.54 (17)	C12—C13—C14	121.22 (19)
C7—C6—C1	121.67 (16)	C12—C13—H13A	119.4
C7—C6—C5	120.26 (16)	C14—C13—H13A	119.4
C1—C6—C5	118.04 (17)	C13—C14—C9	119.58 (16)
C6—C7—C5$^{\mathrm{i}}$	119.86 (15)	C13—C14—S1	120.35 (14)
C6—C7—C8	119.41 (16)	C9—C14—S1	119.94 (13)
C5$^{\mathrm{i}}$—C7—C8	120.73 (17)		

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1C···S1	0.86	2.63	3.032 (2)	110
C11—H11A···Cg3$^{\mathrm{ii}}$	0.93	2.80	3.628 (2)	149

Symmetry codes: (ii) $x, -y-1/2, z-1/2$.

Fig. 1

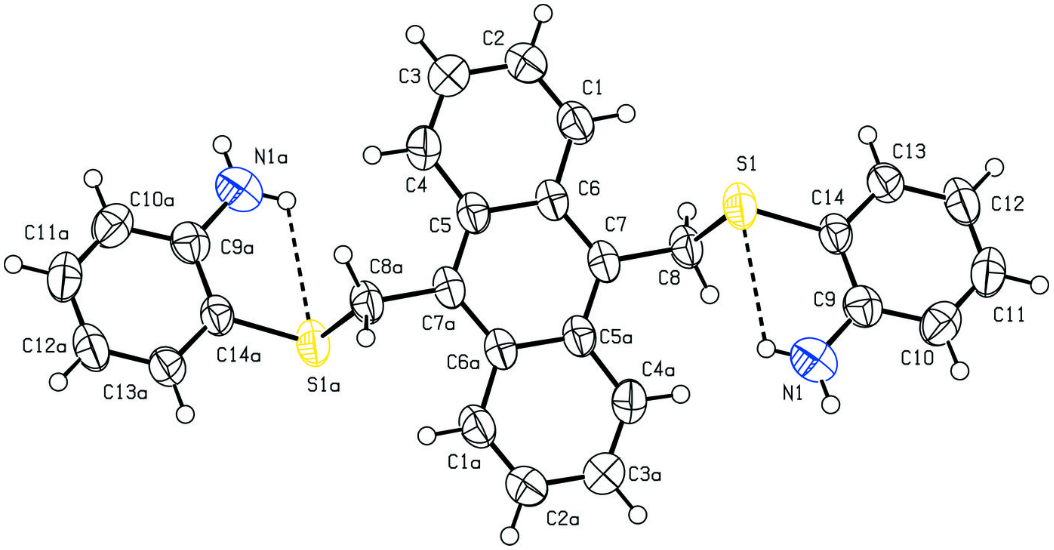
C2
C3
C1
N1a
C4
S1
C13
C10a
C6
C14
C12
C11a
C5
C7
C9a
C8a
C8
C9
C11
C7a
C5a
C12a
C14a
C6a
C10
C4a
S1a
N1
C13a
C1a
C3a
C2a

Fig. 2