

Crystal structure of 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene

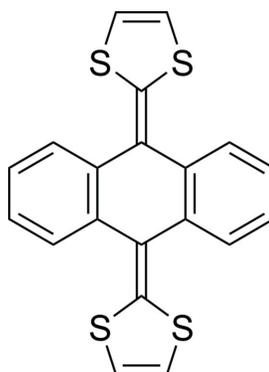
Yi Ren, Semin Lee, Jeffery A. Bertke* and Jeffrey S. Moore

Department of Chemistry, University of Illinois, Urbana, Illinois 61801, USA. *Correspondence e-mail: jbertke@illinois.edu

The crystal structure of the well-studied 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene molecule, $C_{20}H_{12}S_4$, (I), also known as exTTF, is reported. The molecular structure of (I) consists of a dihydroanthracene moiety with two 1,3-dithiol-2-ylidene substituents. This is a saddle-shaped molecule, which interacts with a close neighbor through various π – π and C–H \cdots π contacts to form a ‘dimer’. These ‘dimers’ interact through a series of C–H \cdots S and C–H \cdots π contacts to construct a complex three-dimensional extended structure.

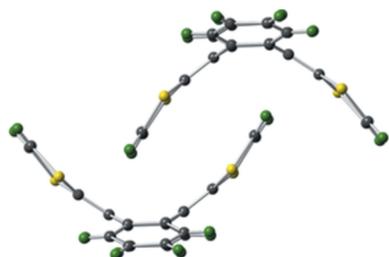
1. Chemical context

Since the first report on 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (exTTF) (I) as a highly-conjugated electron donor (Bryce & Moore, 1988), numerous studies have been conducted on the development of exTTF derivatives that are applicable toward organic electronics. (Brunetti *et al.*, 2012) To our surprise, the single crystal structure of exTTF has not been reported and most of the existing literature on exTTF focuses on theoretical calculations and modeling. (Gruhn *et al.*, 2006; Zhao & Truhlar, 2008) Herein, we report the single-crystal structure of exTTF.



2. Structural commentary

The molecular structure of (I) consists of a dihydroanthracene moiety with 1,3-dithiol-2-ylidene groups substituted at the 9 and 10 positions, Fig. 1*a*. The molecule is saddle shaped in that the 1,3-dithiol-2-ylidene groups bend significantly up out of the plane of the central ring and the two benzene rings of dihydroanthracene moiety bend down out of the plane, Fig. 1*b*. The central six-membered ring (C4–C5–C10–C11–C12–C17) is in a boat conformation in which the 1,3-dithiol-2-ylidene-substituted carbon atoms [C4 and C11] are bent out of the plane defined by C5, C10, C12, and C17. The torsion angles



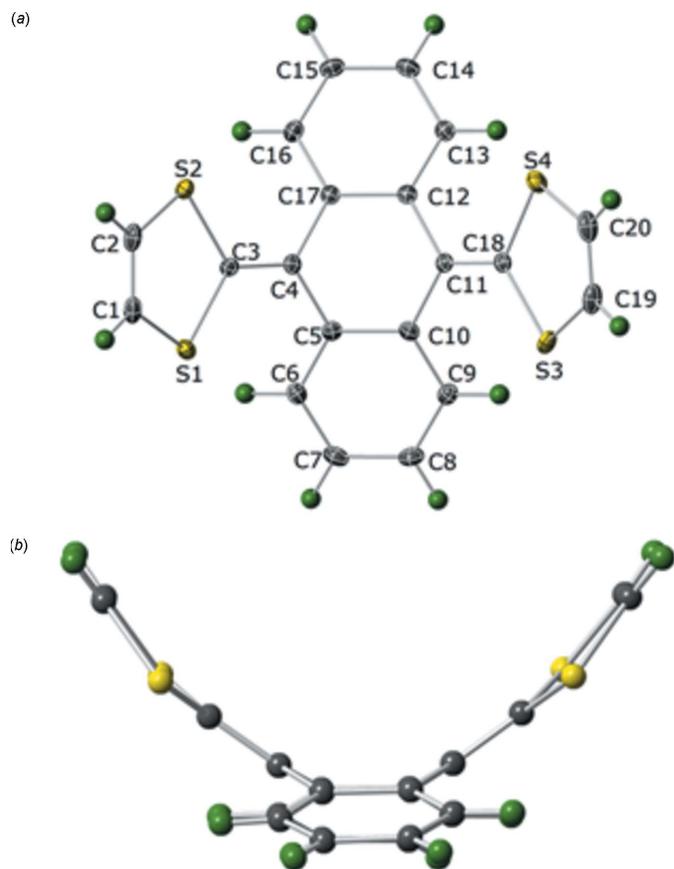


Figure 1
 (a) Plot showing 35% probability ellipsoids for non-H atoms and circles of arbitrary size for H atoms for (I). (b) A view of (I) showing the saddle shape of the molecule.

$C10-C12-C17-C4 = 17.97(12)^\circ$ and $C17-C5-C10-C11 = 17.22(16)^\circ$ for these two carbon atoms are quite similar.

The benzene rings bend out of the $C5-C10-C12-C17$ plane; the dihedral angle between this plane and the plane of the $C5-C6-C7-C8-C9-C10$ ring is $17.72(15)^\circ$ while the dihedral angle for the $C12-C13-C14-C15-C16-C17$ ring is $20.14(13)^\circ$. The 1,3-dithiol-2-ylidene groups are bent more sharply out of the $C5-C10-C12-C17$ plane as evidenced by the torsion angles $C3-C4-C5-C10$ $\tau = 138.06(15)^\circ$ and $C18-C11-C12-C17$ $\tau = 139.23(15)^\circ$. The five-membered rings both adopt an envelope conformation with the carbon atom bonded to the dihydroanthracene [$C3$ and $C18$] being the one puckered out of the plane. The torsion angles $C3-S1-C1-C2$ $\tau = -8.09(14)^\circ$ and $C18-S4-C20-C19$ $\tau = -6.65(15)^\circ$ show that the bend in each ring is fairly similar.

The average C–C bond length within the benzene rings (excluding the edges shared with the central ring) is 1.391 \AA as is typical of phenyl rings. The length of the edges shared with the central ring are slightly longer $C5-C10 = 1.419(2) \text{ \AA}$ and $C12-C17 = 1.412(2) \text{ \AA}$. The remaining C–C distances making up the central ring are longer still with an average of 1.477 \AA . Since the distances within the central ring are in between those of typical C–C single and double bonds; this supports the idea of a highly delocalized bonding motif throughout the dihydroanthracene ring system. The bond

distances between the dihydroanthracene and the 1,3-dithiol-2-ylidene groups are on the order of typical C=C bonds, $C3=C4 = 1.360(2) \text{ \AA}$ and $C11=C18 = 1.361(2) \text{ \AA}$.

3. Supramolecular features

Through a series of C–H $\cdots\pi$ and π – π interactions, each molecule of (I) closely interacts with a neighboring molecule to form a ‘dimer’, Fig. 2. The π – π interaction is between the $C1-C2-S2-C3-S1$ ring and the $C1^i-C2^i-S2^i-C3^i-S1^i$ ring [symmetry operation: (i) $-x + 1, -y + 1, -z + 1$] and is rather long at $4.068(15) \text{ \AA}$. There are five C–H $\cdots\pi$ interactions between the two molecules in which atoms H1 and H2 of one molecule interact with various π systems of the neighbor. The shortest contact is between H1 and the $C11^i=C18^i$ double bond at $2.606(12) \text{ \AA}$ [$H1\cdots C11^i$ $2.686(19) \text{ \AA}$; $H1\cdots C18^i$ $2.700(14) \text{ \AA}$]. There is another short contact between H1 and the central ring of the dihydroanthracene, $H1\cdots$ centroid ($C4^i-C5^i-C10^i-C11^i-C12^i-C17^i$) $2.852(11) \text{ \AA}$. Two other C–H $\cdots\pi$

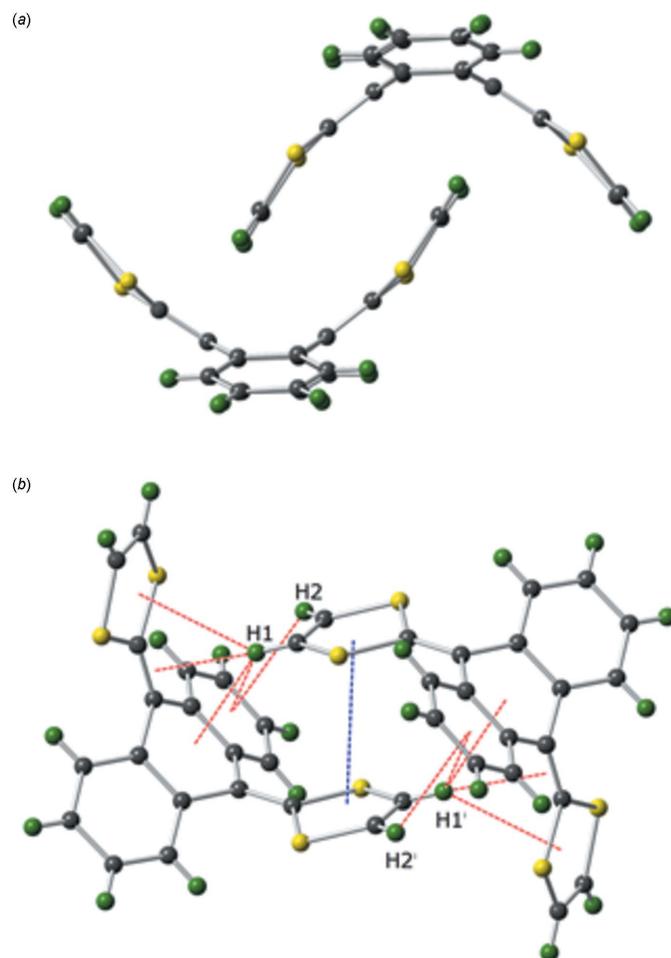


Figure 2
 A view of a ‘dimer’ of (I) showing (a) how the 1,3-dithiol-2-ylidene group of one molecule sits in the U-shape of a neighboring molecule, and (b) the interactions between the molecules that make up the ‘dimer’. Gray = Carbon, yellow = Sulfur, green = Hydrogen, blue dashed line = π – π interaction, red dashed line = C–H $\cdots\pi$ interaction. [Symmetry operation: (i) $-x + 1, -y + 1, -z + 1$.]

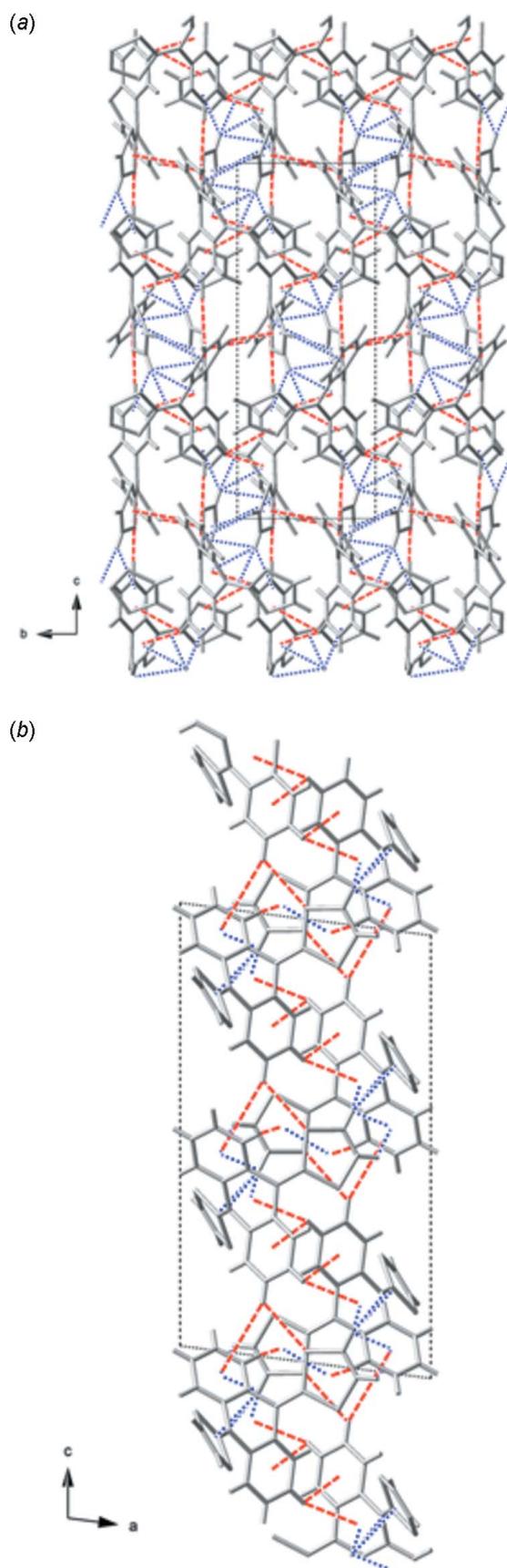
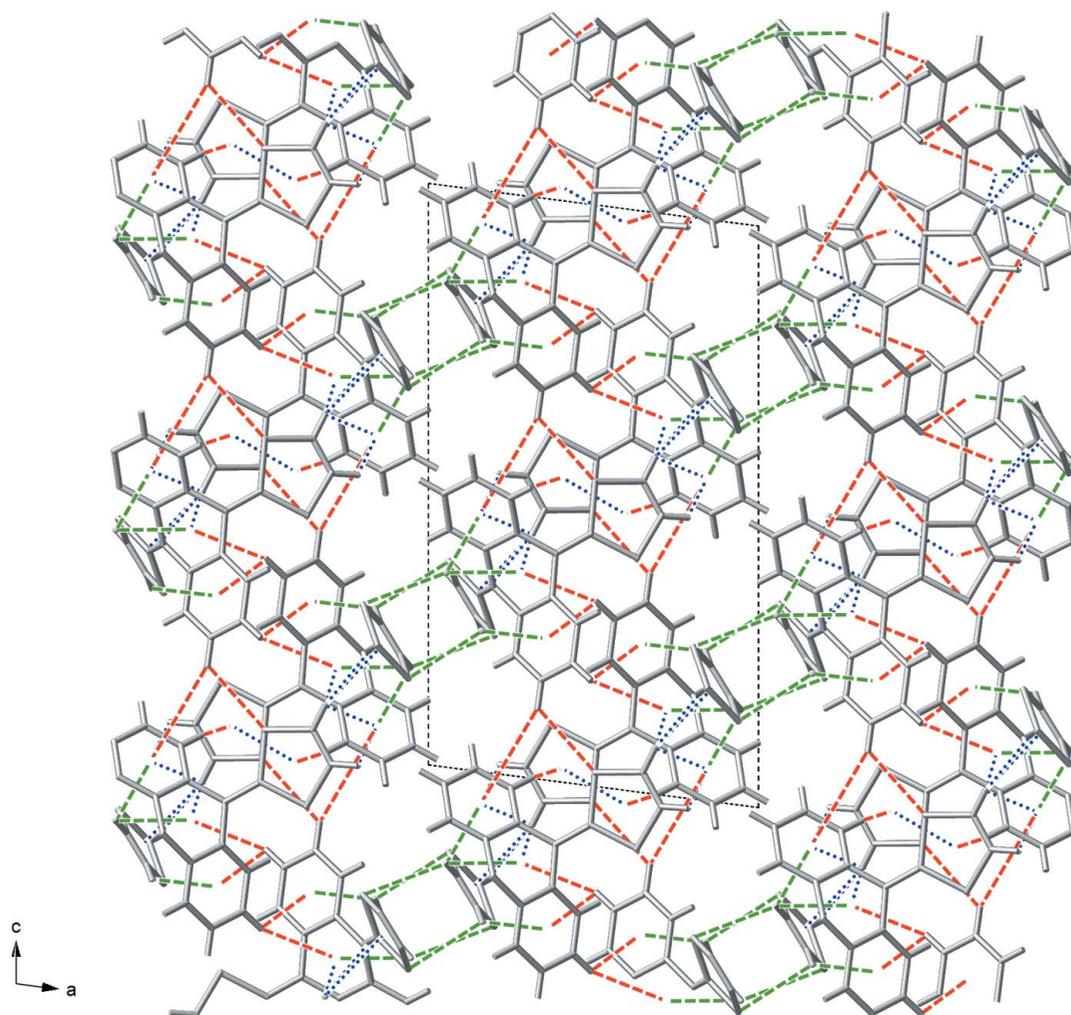


Figure 3

A portion of the two-dimensional network formed between 'dimers' when only the dihydroanthracene CH interactions are taken into account viewed (a) along the *a* axis, and (b) along the *b* axis. Blue dashed lines are intra-dimer interactions and red dashed lines are dihydroanthracene CH inter-dimer interactions.


Figure 4

A portion of the three-dimensional structure of (I), viewed along the *b* axis, showing the two-dimensional layers connecting along the *a* axis. Blue dashed lines are intra-dimer interactions, red dashed lines are dihydroanthracene CH inter-dimer interactions, and green dashed lines are 1,3-dithiol-2-ylidene CH inter-dimer interactions.

interactions involve H1; H1 \cdots centroid (C18ⁱ–S3ⁱ–C19ⁱ–C20ⁱ–S4ⁱ) 3.167 (11) Å, and H1 \cdots centroid (C5ⁱ–C6ⁱ–C7ⁱ–C8ⁱ–C9ⁱ–C10ⁱ) 3.553 (15) Å. The fifth interaction between the ‘dimer’ molecules is H2 \cdots centroid (C5ⁱ–C6ⁱ–C7ⁱ–C8ⁱ–C9ⁱ–C10ⁱ) 3.222 (12) Å.

The ‘dimers’ of (I) interact through C–H \cdots S and C–H \cdots π contacts with neighboring molecules to form a complex three-dimensional network. There are five C–H \cdots S and C–H \cdots π interactions in which the CH group involved resides on the dihydroanthracene portion of (I). H14 has interactions with two groups of a neighboring molecule; one C–H \cdots S contact H14 \cdots S1ⁱⁱ 2.922 (12) Å and one C–H \cdots π contact H14 \cdots centroid (C5ⁱⁱ–C6ⁱⁱ–C7ⁱⁱ–C8ⁱⁱ–C9ⁱⁱ–C10ⁱⁱ) 3.779 (17) Å [symmetry operation: (ii) $x, \frac{1}{2} - y, -\frac{1}{2} + z$]. H15 also interacts with two groups on a neighboring molecule through two C–H \cdots π contacts; H15 \cdots centroid (C12ⁱⁱⁱ–C13ⁱⁱⁱ–C14ⁱⁱⁱ–C15ⁱⁱⁱ–C16ⁱⁱⁱ–C17ⁱⁱⁱ) 3.385 (17) Å and H15 \cdots centroid (C4ⁱⁱⁱ–C5ⁱⁱⁱ–C10ⁱⁱⁱ–C11ⁱⁱⁱ–C12ⁱⁱⁱ–C17ⁱⁱⁱ) 3.543 (14) Å [symmetry operation: (iii) $-x + 1, -\frac{1}{2} + y, \frac{1}{2} - z$]. It should be noted that the molecules generated by symmetry operations (ii) and (iii) form a

‘dimer’. The final interaction involving a CH group on the dihydroanthracene is H6 \cdots centroid (S1^{iv}–C1^{iv}–C2^{iv}–S2^{iv}–C3^{iv}) 2.865 (11) Å [symmetry operation: (iv) $-x + 1, -y, -z + 1$]. Taking these interactions into account, a two-dimensional layered structure is formed (Fig. 3) in which the layers extend along the *bc* plane.

There are also five C–H \cdots S and C–H \cdots π interactions in which the CH group involved resides on the 1,3-dithiol-2-ylidene portion of (I). H19 and H20 each interact with one neighboring molecule through three C–H \cdots π contacts; H19 \cdots centroid (C5^v–C6^v–C7^v–C8^v–C9^v–C10^v) 2.829 (18) Å, H19 \cdots centroid (C4^v–C5^v–C10^v–C11^v–C12^v–C17^v) 3.301 (11) Å, and H20 \cdots centroid (C12^v–C13^v–C14^v–C15^v–C16^v–C17^v) 2.767 (11) Å [symmetry operation: (v) $x, y + 1, z$]. These hydrogen atoms also interact with another molecule *via* C–H \cdots S contacts; H19 \cdots S4^{vi} 3.367 (12) Å and H20 \cdots S3^{vi} 3.288 (14) Å [symmetry operation: (vi) $-x, y + 0.5, -z + \frac{1}{2}$]. When these interactions are taken into account, the two-dimensional layers are connected along the *a* axis to form a three-dimensional extended structure, Fig. 4.

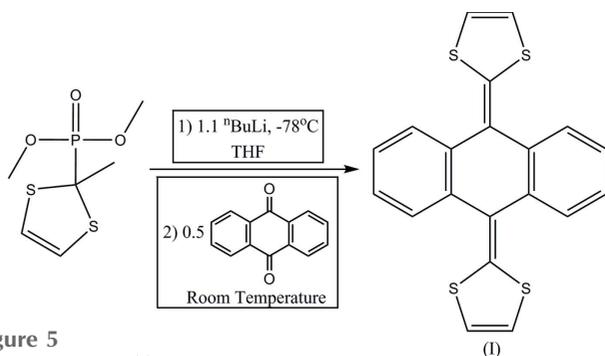


Figure 5
The synthesis of (I).

4. Database survey

Many derivatives of (I) have been crystallographically characterized with various substituents on the dihydroanthracene, the dithiol, or both moieties. A search of the Cambridge Crystal Database (CCD) (Groom & Allen, 2014) yields three derivatives of (I) with substituents on the dihydroanthracene and twelve derivatives with substituents on both the dihydroanthracene and the dithiol. There have been twenty-nine structures reported in the CCD with substituents on the dithiol ring. The complex most closely related to (I) is the tetramethyl-substituted 9,10-anthracenediylidene-2,2'-bis(4,5-dimethyl-1,3-dithiole) (Bryce *et al.*, 1990; CCD code: JIJGIS). This molecule crystallizes in the same space group as (I) (monoclinic, $P2_1/c$) and has a similar saddle shape. It also appears to form similar 'dimers' in which there are both C–H $\cdots\pi$ and π – π interactions between the two molecules.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{20}H_{12}S_4$
M_r	380.54
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a , b , c (Å)	11.2759 (3), 7.6073 (2), 19.5596 (5)
β (°)	97.313 (1)
V (Å ³)	1664.16 (8)
Z	4
Radiation type	Cu $K\alpha$
μ (mm ⁻¹)	5.21
Crystal size (mm)	0.36 × 0.10 × 0.04
Data collection	
Diffraction	Bruker APEXII CCD
Absorption correction	Integration (SADABS; Bruker, 2014)
T_{min} , T_{max}	0.999, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25822, 3056, 2757
R_{int}	0.037
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.025, 0.061, 1.08
No. of reflections	3056
No. of parameters	218
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.25, -0.25

Computer programs: APEX2, SAINT (Bruker, 2014), XPREP and XCIF (Bruker, 2014), SHELXS2014 and SHELXTL (Sheldrick, 2008), SHELXL2014 (Sheldrick, 2015), CrystalMaker (CrystalMaker, 1994), and publCIF (Westrip, 2010).

A recent computational study focused on predicting the most energetically favored 'dimers' of (I) (Denis & Iribarne, 2015). This study predicted the 'dimer' characterized in (I) as the second most favorable, being 1.7 kcal mol⁻¹ less stable than the predicted favorite. The study details π – π stacking between two of the dithiol rings, C–H $\cdots\pi$ contacts between the dithiol H atoms and the anthracene rings, π – π stacking between anthracene units, as well as an interaction between the partial positive charge of the S atoms and the anthracene rings for the preferred computational 'dimer'. The study briefly describes the C–H $\cdots\pi$ and π – π interactions found in (I), but states that the lack of π – π stacking between the anthracene moieties is the reason this orientation is slightly less favorable.

5. Synthesis and crystallization

The title complex, 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene (I), was synthesized following a literature procedure (Yamashita *et al.*, 1989), Fig. 5. X-ray quality crystals were grown from slow diffusion of chloroform into a diethyl ether solution of (I).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. A structural model consisting of the target molecule was developed. H atoms were included as riding idealized contributors with C–H = 0.95 Å $U_{iso}(H) = 1.2U_{eq}(C)$.

Acknowledgements

We acknowledge financial support from the Department of the Navy, Office of Naval Research, under grant N00014-12-1-0828.

References

- Bruker (2014). APEX2, SAINT, XCIF, XPREP and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- Brunetti, F. G., López, J. L., Atienza, C. & Martín, N. (2012). *J. Mater. Chem.* **22**, 4188–4205.
- Bryce, M. R. & Moore, A. J. (1988). *Synth. Met.* **27**, 557–561.
- Bryce, M. R., Moore, A. J., Hasan, M., Ashwell, G. J., Fraser, A. T., Clegg, W., Hursthouse, M. B. & Karaulov, A. I. (1990). *Angew. Chem. Int. Ed. Engl.* **29**, 1450–1452.
- CrystalMaker (1994). *CrystalMaker*. CrystalMaker Software Ltd, Oxford, England (www.CrystalMaker.com).
- Denis, P. A. & Iribarne, F. (2015). *Struct. Chem.* **26**, 171–176.
- Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.
- Gruhn, N. E., Macías-Ruvalcaba, N. A. & Evans, D. H. (2006). *Langmuir*, **22**, 10683–10688.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Yamashita, Y., Kobayashi, Y. & Miyashi, T. (1989). *Angew. Chem. Int. Ed. Engl.* **28**, 1052–1053.
- Zhao, Y. & Truhlar, D. G. (2008). *Phys. Chem. Chem. Phys.* **10**, 2813–2818.

supporting information

Acta Cryst. (2015). E71, 1475-1479 [https://doi.org/10.1107/S2056989015020800]

Crystal structure of 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene

Yi Ren, Semin Lee, Jeffery A. Bertke and Jeffrey S. Moore

Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINTE* (Bruker, 2014); data reduction: *SAINTE* (Bruker, 2014), *XPREP* (Bruker, 2014) and *SADABS* (Bruker, 2014); program(s) used to solve structure: *SHELXS2014* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *CrystalMaker* (*CrystalMaker*, 1994); software used to prepare material for publication: *XCIF* (Bruker, 2014) and *publCIF* (Westrip, 2010).

9,10-Bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene

Crystal data

$C_{20}H_{12}S_4$

$M_r = 380.54$

Monoclinic, $P2_1/c$

$a = 11.2759$ (3) Å

$b = 7.6073$ (2) Å

$c = 19.5596$ (5) Å

$\beta = 97.313$ (1)°

$V = 1664.16$ (8) Å³

$Z = 4$

$F(000) = 784$

$D_x = 1.519$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å

Cell parameters from 9948 reflections

$\theta = 4.0$ – 68.3 °

$\mu = 5.21$ mm⁻¹

$T = 100$ K

Needle, yellow

$0.36 \times 0.10 \times 0.04$ mm

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: microfocus sealed tube

Multilayer mirrors monochromator

profile data from φ and ω scans

Absorption correction: integration
(*SADABS*; Bruker, 2014)

$T_{\min} = 0.999$, $T_{\max} = 1.000$

25822 measured reflections

3056 independent reflections

2757 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$

$\theta_{\max} = 68.4$ °, $\theta_{\min} = 4.0$ °

$h = -13 \rightarrow 13$

$k = -9 \rightarrow 9$

$l = -23 \rightarrow 23$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.025$

$wR(F^2) = 0.061$

$S = 1.08$

3056 reflections

218 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0242P)^2 + 1.0937P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.25$ e Å⁻³

$\Delta\rho_{\min} = -0.25$ e Å⁻³

Extinction correction: *SHELXL2014*

(Sheldrick, 2015),

$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.00303 (14)

Special details

Experimental. One distinct cell was identified using *APEX2* (Bruker, 2014). Fourteen frame series were integrated and filtered for statistical outliers using *SAINTE* (Bruker, 2014) then corrected for absorption by integration using *SAINTE/SADABS* v2014/2 (Bruker, 2014) to sort, merge, and scale the combined data. No decay correction was applied.

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. Structure was phased by direct methods (Sheldrick, 2015). Systematic conditions suggested the unambiguous space group. The space group choice was confirmed by successful convergence of the full-matrix least-squares refinement on F^2 . The final map had no significant features. A final analysis of variance between observed and calculated structure factors showed little dependence on amplitude and resolution.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.50450 (3)	0.25084 (5)	0.52454 (2)	0.01521 (11)
S2	0.63047 (3)	0.26765 (5)	0.40288 (2)	0.01627 (11)
S3	0.06123 (3)	0.70767 (5)	0.35517 (2)	0.01672 (11)
S4	0.19863 (4)	0.71272 (5)	0.23764 (2)	0.01788 (11)
C1	0.64924 (14)	0.3346 (2)	0.53580 (9)	0.0183 (3)
H1	0.6861	0.3720	0.5798	0.022*
C2	0.70600 (14)	0.3442 (2)	0.48073 (9)	0.0195 (4)
H2	0.7846	0.3908	0.4834	0.023*
C3	0.49073 (14)	0.24302 (19)	0.43367 (8)	0.0124 (3)
C4	0.38454 (13)	0.23077 (18)	0.39233 (8)	0.0117 (3)
C5	0.26881 (13)	0.22783 (19)	0.41988 (8)	0.0118 (3)
C6	0.24960 (14)	0.1319 (2)	0.47833 (8)	0.0150 (3)
H6	0.3121	0.0610	0.5009	0.018*
C7	0.14057 (14)	0.1385 (2)	0.50395 (8)	0.0183 (3)
H7	0.1295	0.0746	0.5444	0.022*
C8	0.04781 (15)	0.2381 (2)	0.47066 (8)	0.0189 (3)
H8	-0.0266	0.2435	0.4885	0.023*
C9	0.06369 (14)	0.3300 (2)	0.41104 (8)	0.0152 (3)
H9	-0.0010	0.3955	0.3877	0.018*
C10	0.17326 (13)	0.32754 (19)	0.38499 (7)	0.0119 (3)
C11	0.19641 (13)	0.42281 (19)	0.32222 (7)	0.0112 (3)
C12	0.27915 (13)	0.33216 (19)	0.28095 (7)	0.0114 (3)
C13	0.26370 (13)	0.3330 (2)	0.20902 (8)	0.0135 (3)
H13	0.1987	0.3962	0.1849	0.016*
C14	0.34196 (14)	0.2427 (2)	0.17217 (8)	0.0163 (3)
H14	0.3304	0.2443	0.1232	0.020*
C15	0.43704 (14)	0.1501 (2)	0.20707 (8)	0.0176 (3)
H15	0.4917	0.0904	0.1820	0.021*
C16	0.45236 (14)	0.1447 (2)	0.27850 (8)	0.0154 (3)
H16	0.5165	0.0786	0.3020	0.018*
C17	0.37462 (13)	0.23512 (19)	0.31631 (8)	0.0118 (3)
C18	0.15426 (13)	0.5873 (2)	0.30614 (7)	0.0127 (3)
C19	0.08465 (15)	0.9113 (2)	0.31802 (9)	0.0217 (4)

H19	0.0541	1.0166	0.3352	0.026*
C20	0.14664 (15)	0.9132 (2)	0.26496 (9)	0.0226 (4)
H20	0.1622	1.0200	0.2426	0.027*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0144 (2)	0.0198 (2)	0.01084 (19)	0.00031 (14)	-0.00078 (15)	-0.00062 (14)
S2	0.01037 (19)	0.0225 (2)	0.0160 (2)	0.00129 (14)	0.00170 (15)	0.00215 (15)
S3	0.0145 (2)	0.0149 (2)	0.0206 (2)	0.00404 (14)	0.00183 (15)	-0.00264 (15)
S4	0.0217 (2)	0.0146 (2)	0.0173 (2)	0.00085 (15)	0.00232 (16)	0.00485 (15)
C1	0.0149 (8)	0.0181 (8)	0.0203 (8)	0.0026 (6)	-0.0042 (6)	-0.0033 (7)
C2	0.0129 (8)	0.0186 (8)	0.0252 (9)	0.0005 (6)	-0.0043 (7)	-0.0007 (7)
C3	0.0132 (7)	0.0113 (7)	0.0129 (7)	0.0022 (6)	0.0034 (6)	0.0008 (6)
C4	0.0132 (7)	0.0088 (7)	0.0133 (7)	0.0017 (6)	0.0015 (6)	0.0011 (6)
C5	0.0126 (7)	0.0101 (7)	0.0127 (7)	-0.0020 (6)	0.0015 (6)	-0.0031 (6)
C6	0.0163 (8)	0.0141 (7)	0.0142 (8)	-0.0006 (6)	0.0005 (6)	0.0004 (6)
C7	0.0206 (8)	0.0210 (8)	0.0137 (8)	-0.0052 (7)	0.0038 (6)	0.0032 (6)
C8	0.0160 (8)	0.0234 (8)	0.0188 (8)	-0.0024 (7)	0.0079 (6)	-0.0009 (7)
C9	0.0131 (7)	0.0158 (8)	0.0168 (8)	0.0000 (6)	0.0016 (6)	-0.0017 (6)
C10	0.0138 (7)	0.0112 (7)	0.0103 (7)	-0.0023 (6)	0.0004 (6)	-0.0023 (6)
C11	0.0086 (7)	0.0134 (7)	0.0112 (7)	-0.0010 (6)	-0.0005 (6)	-0.0013 (6)
C12	0.0112 (7)	0.0103 (7)	0.0128 (7)	-0.0030 (6)	0.0018 (6)	-0.0003 (6)
C13	0.0124 (7)	0.0143 (7)	0.0137 (8)	-0.0020 (6)	0.0004 (6)	0.0006 (6)
C14	0.0189 (8)	0.0193 (8)	0.0108 (7)	-0.0031 (6)	0.0024 (6)	-0.0016 (6)
C15	0.0187 (8)	0.0186 (8)	0.0166 (8)	0.0012 (6)	0.0066 (6)	-0.0053 (6)
C16	0.0137 (7)	0.0149 (8)	0.0176 (8)	0.0020 (6)	0.0019 (6)	-0.0011 (6)
C17	0.0117 (7)	0.0110 (7)	0.0125 (7)	-0.0021 (6)	0.0013 (6)	-0.0004 (6)
C18	0.0102 (7)	0.0159 (7)	0.0113 (7)	-0.0007 (6)	-0.0014 (6)	-0.0008 (6)
C19	0.0195 (8)	0.0126 (8)	0.0311 (10)	0.0023 (6)	-0.0046 (7)	-0.0020 (7)
C20	0.0239 (9)	0.0114 (7)	0.0299 (10)	-0.0005 (7)	-0.0064 (7)	0.0026 (7)

Geometric parameters (Å, °)

S1—C1	1.7398 (16)	C8—C9	1.391 (2)
S1—C3	1.7654 (16)	C8—H8	0.9500
S2—C2	1.7471 (16)	C9—C10	1.395 (2)
S2—C3	1.7670 (16)	C9—H9	0.9500
S3—C19	1.7454 (17)	C10—C11	1.477 (2)
S3—C18	1.7647 (16)	C11—C18	1.361 (2)
S4—C20	1.7421 (17)	C11—C12	1.480 (2)
S4—C18	1.7680 (16)	C12—C13	1.396 (2)
C1—C2	1.323 (2)	C12—C17	1.412 (2)
C1—H1	0.9500	C13—C14	1.390 (2)
C2—H2	0.9500	C13—H13	0.9500
C3—C4	1.360 (2)	C14—C15	1.387 (2)
C4—C5	1.474 (2)	C14—H14	0.9500
C4—C17	1.477 (2)	C15—C16	1.386 (2)

C5—C6	1.396 (2)	C15—H15	0.9500
C5—C10	1.419 (2)	C16—C17	1.398 (2)
C6—C7	1.386 (2)	C16—H16	0.9500
C6—H6	0.9500	C19—C20	1.323 (3)
C7—C8	1.385 (2)	C19—H19	0.9500
C7—H7	0.9500	C20—H20	0.9500
C1—S1—C3	95.78 (8)	C9—C10—C11	123.73 (13)
C2—S2—C3	95.46 (8)	C5—C10—C11	117.26 (13)
C19—S3—C18	95.87 (8)	C18—C11—C10	123.34 (14)
C20—S4—C18	95.80 (8)	C18—C11—C12	121.89 (14)
C2—C1—S1	117.40 (12)	C10—C11—C12	114.52 (13)
C2—C1—H1	121.3	C13—C12—C17	119.07 (14)
S1—C1—H1	121.3	C13—C12—C11	122.78 (13)
C1—C2—S2	117.29 (13)	C17—C12—C11	118.10 (13)
C1—C2—H2	121.4	C14—C13—C12	120.97 (14)
S2—C2—H2	121.4	C14—C13—H13	119.5
C4—C3—S1	123.98 (12)	C12—C13—H13	119.5
C4—C3—S2	124.09 (12)	C15—C14—C13	119.83 (14)
S1—C3—S2	111.82 (8)	C15—C14—H14	120.1
C3—C4—C5	122.49 (14)	C13—C14—H14	120.1
C3—C4—C17	123.03 (14)	C16—C15—C14	120.03 (15)
C5—C4—C17	114.27 (13)	C16—C15—H15	120.0
C6—C5—C10	119.05 (14)	C14—C15—H15	120.0
C6—C5—C4	122.96 (13)	C15—C16—C17	120.83 (14)
C10—C5—C4	118.00 (13)	C15—C16—H16	119.6
C7—C6—C5	120.94 (14)	C17—C16—H16	119.6
C7—C6—H6	119.5	C16—C17—C12	119.25 (14)
C5—C6—H6	119.5	C16—C17—C4	123.32 (14)
C8—C7—C6	120.09 (15)	C12—C17—C4	117.40 (13)
C8—C7—H7	120.0	C11—C18—S3	124.44 (12)
C6—C7—H7	120.0	C11—C18—S4	123.16 (12)
C7—C8—C9	119.94 (15)	S3—C18—S4	112.16 (8)
C7—C8—H8	120.0	C20—C19—S3	117.33 (13)
C9—C8—H8	120.0	C20—C19—H19	121.3
C8—C9—C10	120.92 (14)	S3—C19—H19	121.3
C8—C9—H9	119.5	C19—C20—S4	117.59 (13)
C10—C9—H9	119.5	C19—C20—H20	121.2
C9—C10—C5	119.01 (14)	S4—C20—H20	121.2
C3—S1—C1—C2	-8.09 (14)	C18—C11—C12—C13	-43.5 (2)
S1—C1—C2—S2	-1.21 (19)	C10—C11—C12—C13	142.00 (14)
C3—S2—C2—C1	9.82 (14)	C18—C11—C12—C17	139.23 (15)
C1—S1—C3—C4	-162.04 (13)	C10—C11—C12—C17	-35.31 (18)
C1—S1—C3—S2	14.06 (9)	C17—C12—C13—C14	-1.2 (2)
C2—S2—C3—C4	161.58 (14)	C11—C12—C13—C14	-178.48 (14)
C2—S2—C3—S1	-14.51 (9)	C12—C13—C14—C15	0.0 (2)
S1—C3—C4—C5	1.8 (2)	C13—C14—C15—C16	1.4 (2)

S2—C3—C4—C5	-173.83 (11)	C14—C15—C16—C17	-1.6 (2)
S1—C3—C4—C17	176.22 (11)	C15—C16—C17—C12	0.3 (2)
S2—C3—C4—C17	0.6 (2)	C15—C16—C17—C4	178.43 (15)
C3—C4—C5—C6	-41.9 (2)	C13—C12—C17—C16	1.0 (2)
C17—C4—C5—C6	143.19 (14)	C11—C12—C17—C16	178.43 (13)
C3—C4—C5—C10	138.06 (15)	C13—C12—C17—C4	-177.19 (13)
C17—C4—C5—C10	-36.82 (18)	C11—C12—C17—C4	0.2 (2)
C10—C5—C6—C7	-2.6 (2)	C3—C4—C17—C16	42.7 (2)
C4—C5—C6—C7	177.45 (14)	C5—C4—C17—C16	-142.47 (14)
C5—C6—C7—C8	1.5 (2)	C3—C4—C17—C12	-139.19 (15)
C6—C7—C8—C9	0.7 (2)	C5—C4—C17—C12	35.66 (18)
C7—C8—C9—C10	-1.7 (2)	C10—C11—C18—S3	-2.8 (2)
C8—C9—C10—C5	0.6 (2)	C12—C11—C18—S3	-176.84 (11)
C8—C9—C10—C11	-179.69 (14)	C10—C11—C18—S4	171.04 (11)
C6—C5—C10—C9	1.5 (2)	C12—C11—C18—S4	-3.0 (2)
C4—C5—C10—C9	-178.52 (13)	C19—S3—C18—C11	163.72 (13)
C6—C5—C10—C11	-178.22 (13)	C19—S3—C18—S4	-10.70 (9)
C4—C5—C10—C11	1.8 (2)	C20—S4—C18—C11	-163.82 (13)
C9—C10—C11—C18	40.0 (2)	C20—S4—C18—S3	10.68 (9)
C5—C10—C11—C18	-140.37 (15)	C18—S3—C19—C20	6.74 (14)
C9—C10—C11—C12	-145.59 (14)	S3—C19—C20—S4	-0.06 (19)
C5—C10—C11—C12	34.08 (18)	C18—S4—C20—C19	-6.65 (15)
