

# Crystallographic and NMR analysis of 9-phenylthiophenanthrene and 9-*tert*-butylthiophenanthrene



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The crystal structures of 9-phenylthiophenanthrene (C<sub>20</sub>H<sub>14</sub>S) and 9-*tert*-butylthiophenanthrene (C<sub>18</sub>H<sub>18</sub>S) were determined at 193 K. The former crystallizes in orthorhombic space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (No. 19) with cell dimensions *a* = 5.602(2), *b* = 9.247(3), and *c* = 27.508(12) Å and the latter in orthorhombic space group *Pbcn* (No. 60) with cell parameters *a* = 21.335(4), *b* = 7.540(2), and *c* = 18.197(4) Å. In both compounds the substituents at sulfur are nearly perpendicular to the phenanthrene plane. NMR spectra of the compounds were recorded in CDCl<sub>3</sub>. The <sup>1</sup>H NMR spectral parameters were analyzed in detail by using an iterative spectral analysis program. The <sup>13</sup>C{<sup>1</sup>H} resonances were fully assigned with the aid of two-dimensional heteronuclear chemical shift correlation spectra. On the basis of the NOE difference spectra the orientation of the side chain was concluded to be similar to that in the solid state.

In connection with earlier studies on the preparation and reactions of new hemithiodithioacetals we developed an easy and reliable synthesis of 9-alkyl- and 9-arylthiophenanthrenes.<sup>1</sup> The present article reports X-ray and NMR structural studies on 9-phenylthiophenanthrene C<sub>20</sub>H<sub>14</sub>S (**1**) and 9-*tert*-butylthiophenanthrene C<sub>18</sub>H<sub>18</sub>S (**2**). We have earlier reported crystal structures of straight-chained 9-alkylthiophenanthrenes [alkyl = methyl, C<sub>15</sub>H<sub>12</sub>S (**3a**, **3b**), ethyl C<sub>16</sub>H<sub>14</sub>S (**4**), propyl C<sub>17</sub>H<sub>16</sub>S (**5**), and butyl C<sub>18</sub>H<sub>18</sub>S (**6**)].<sup>2</sup> Crystal structures and especially the crystal packing of **3** differed from those of compounds **4–6**: *viz.*, compound **3** crystallized in a non-centrosymmetric space group with two molecules in an asymmetric unit, while compounds **4–6** were isostructural and centrosymmetric with one molecule in an asymmetric unit. Compounds **1** and **2** were chosen for comparative study to determine the effect of the more bulky side chain on the structure.

NMR spectral data have been published for a number of phenanthrenes,<sup>3–8</sup> but for some compounds some parameters are lacking. This also applies to compounds **1** and **2** as presented by Beland and Harvey<sup>8</sup> and Dent and Halton,<sup>6</sup> respectively. In general, the aromatic *ortho*, *meta*, *para*, and long-range proton–proton couplings are well known<sup>9</sup> and give a good starting point for a computer-aided spectral analysis. With the parameters obtained from the literature and a preliminary analysis of the spectra of **1** and **2** recorded in C<sub>6</sub>D<sub>6</sub>, parameters of the <sup>1</sup>H spectra recorded in CDCl<sub>3</sub> could be analyzed in detail. After the proton spectral analysis the resonances of the <sup>13</sup>C{<sup>1</sup>H} NMR spectra were fully assigned with the aid of two-dimensional proton–carbon correlation spectra.

Liquid state conformations of **1** and **2** have been investigated by NOE difference experiments.<sup>10</sup> Analogously to the findings of Lewis *et al.*<sup>3</sup> for some *N*-(aminoalkyl)phenanthrene-9-carboximides, the liquid state conformations of **1** and **2** appear to have the side chain perpendicular to the phenanthrene plane. These results suggest comparable liquid and solid state conformations for the two compounds.

## Experimental

### Synthesis

Thiophenol or 2-methylpropane-2-thiol (3 equiv.) was slowly added to an ice-cooled solution of KOH (3 equiv.) in dry *N,N*-dimethylformamide (DMF) under argon and stirred for 15 min. A solution of 9-bromophenanthrene (1 equiv.) in DMF was added and the mixture was refluxed for 2 h. After usual work-up the product was recrystallized twice from ethanol (compound **1**) or methanol (compound **2**).

### Crystal structure

For both compounds a single crystal was mounted on a four-circle Rigaku AFC7S diffractometer on a glass fiber with use of the viscose oil-drop method at 193 K.<sup>11</sup> Graphite monochromated Mo-Kα ( $\lambda = 0.71073$  Å) radiation was used. Unit-cell parameters were determined by centering 25 reflections found by the search method. Data for **1** were collected using the  $\omega$ -scan method and data for **2** by the  $\omega$ - $2\theta$ -scan method. Intensities were extracted using the Lehmann–Larsen method<sup>12</sup> included in the diffractometer control software.<sup>13</sup> Three standard reflections for each compound were recorded after every 200 reflections. No decay was observed for either crystal but about 1% random intensity fluctuations were found in test reflections. Space groups were determined and intensities were corrected for Lorentz and polarization effects, but not for absorption, by using the TEXSAN program.<sup>14</sup> Absorption was checked with the empirical  $\psi$ -scan method but corrections were not applied, because variations in relative transmission were small ( $T_{\min} = 0.977$  for **1** and 0.982 for **2** when  $T_{\max} = 1.0$ ). Structures were solved with the SIR92 program<sup>15</sup> and further refinements were carried out with the SHELXL-93 software package.<sup>16</sup> The illustrations were produced with the SHELXTL-PC program.<sup>17</sup> Hydrogen atom coordinates and isotropic displacement parameters were refined in both com-

**Table 1** Structure determination summary for 9-phenylthiophenanthrene **1** and 9-*tert*-butylthiophenanthrene **2**

Compound	<b>1</b>	<b>2</b>
<i>Crystal Data</i>		
Empirical formula	C <sub>20</sub> H <sub>14</sub> S	C <sub>18</sub> H <sub>18</sub> S
Color; habit	Colorless, block	Colorless, block
Crystal size/mm	0.38 × 0.44 × 0.35	0.31 × 0.36 × 0.38
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19)	<i>Pbcn</i> (No. 60)
Unit cell dimensions/Å	<i>a</i> = 5.602(2) <i>b</i> = 9.247(3) <i>c</i> = 27.508(12)	<i>a</i> = 21.335(4) <i>b</i> = 7.540(2) <i>c</i> = 18.197(4)
Volume/Å <sup>3</sup>	1425.0(9)	2927.3(10)
<i>Z</i>	4	8
Formula weight	286.37	266.38
Density(calc.)/Mg m <sup>-3</sup>	1.335	1.209
μ(Mo-Kα)/mm <sup>-1</sup>	0.216	0.205
<i>F</i> (000)	600	1136
<i>Data Collection</i>		
Diffractometer used	Rigaku AFC7S	
Radiation	Mo-Kα (λ = 0.71069 Å)	
Temperature/K	193(2)	
Monochromator	Highly oriented graphite crystal	
2θ Range/°	3.0 to 53.0°	
Standard reflections	3 measured every 200 reflections	
Scan type	<i>ω</i>	<i>ω</i> - 2θ
Index ranges	-7 ≤ <i>h</i> ≤ 7 -11 ≤ <i>k</i> ≤ 11 -34 ≤ <i>l</i> ≤ 34	0 ≤ <i>h</i> ≤ 26 0 ≤ <i>k</i> ≤ 9 0 ≤ <i>l</i> ≤ 22
Reflections collected	3353	2724
Independent reflections	2865 ( <i>R</i> <sub>int</sub> = 0.0146)	2724
Observed reflections	2589 [ <i>I</i> > 2.0σ( <i>I</i> )]	2165 [ <i>I</i> > 2.0σ( <i>I</i> )]

pounds. Crystal data and the conditions of data collection are summarized in Table 1.

### NMR sample preparation

Samples were prepared by separately dissolving 8 mg of **1** and 33 mg of **2** in 0.8 ml of CDCl<sub>3</sub> (Aldrich, 99.8%-D). Tetramethylsilane (TMS, Sigma) served as internal chemical shift reference (δ<sub>H</sub> = δ<sub>C</sub> = 0.00 ppm). The spectra were recorded on a Bruker AMX-400 at 30 °C. The samples for NOE difference experiments were prepared by dissolving 11 mg of **1** and 25 mg of **2** in C<sub>6</sub>D<sub>6</sub>. The sample was degassed with argon flow for 15 min and the NMR tube was sealed by melting.

### NMR spectra

The 400 MHz <sup>1</sup>H NMR spectra were recorded with 16 transients, a 6.0 μs pulse duration (flip angle 45°), a 16 s repetition time, a 4425 Hz spectral width, and 128k points in the time domain. Digital resolution after zero filling in the frequency domain was 0.034 Hz point<sup>-1</sup>. Spectra that were processed using an exponential window function with a line broadening factor of 0.10 Hz did not sufficiently reveal the fine structure caused by the long-range couplings. The spectra were therefore resolution enhanced by gaussian multiplication for the iterative computer analysis.

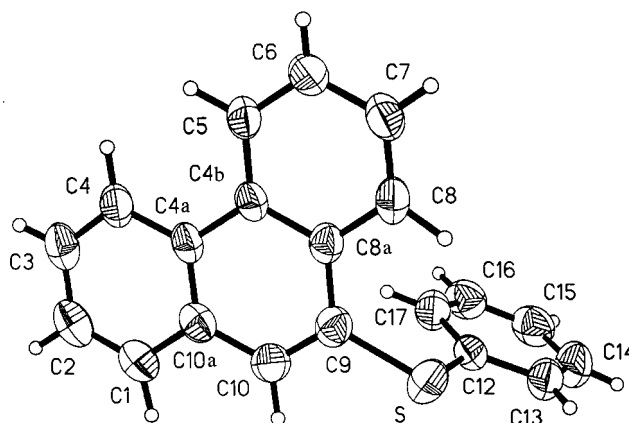
The 100 MHz <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded with 1556–4096 transients, a 3.8 μs pulse duration (flip angle 45°), a 4.6 s repetition time, a 23809.5 Hz spectral width, and 64k points in the time domain. For the frequency domain, 64k points were used to obtain a digital resolution of 0.36 Hz point<sup>-1</sup>. Exponential multiplication was applied using a 0.50 Hz line broadening factor. Owing to the interpolation of the peak top frequencies by the spectrometer software, the accuracy of the determined chemical shifts is much better than the digital resolution.

The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} resonance assignments were confirmed with the aid of two-dimensional H<sub>1</sub>H-correlation experiments,<sup>18</sup>

**Table 2** Solution and refinement for 9-phenylthiophenanthrene **1** and 9-*tert*-butylthiophenanthrene **2**

Compound	<b>1</b>	<b>2</b>
System used	TEXSAN	
Solution	Direct methods (SIR 92)	
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	
Hydrogen atoms	Refined coordinates and isotropic <i>U</i>	
Weighting scheme ( <i>w</i> <sup>-1</sup> )	σ <sup>2</sup> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) + (0.0495 <i>P</i> ) <sup>2</sup> + 0.35 <i>P</i> where <i>P</i> = max[( <i>F</i> <sub>o</sub> <sup>2</sup> , 0) + 2 <i>F</i> <sub>c</sub> <sup>2</sup> ]/3	
Goodness of fit on <i>F</i> <sup>2</sup>	1.023	0.978
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	<i>R</i> <sub>1</sub> = 0.0405, <i>wR</i> <sub>2</sub> = 0.0976	<i>R</i> <sub>1</sub> = 0.0434, <i>wR</i> <sub>2</sub> = 0.1162
<i>R</i> Indices (all data)	<i>R</i> <sub>1</sub> = 0.0467, <i>wR</i> <sub>2</sub> = 0.1026	<i>R</i> <sub>1</sub> = 0.0600, <i>wR</i> <sub>2</sub> = 0.1251
Extinction coefficient	0.0004(19)	0.0004(8)
Absolute structure parameter	-0.14(10)	
Number of parameters refined	247	245
Data-to-parameter ratio	10.5	8.8
Largest difference peak/e Å <sup>-3</sup>	0.243	0.215
Largest difference hole/e Å <sup>-3</sup>	-0.196	-0.190

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

**Fig. 1** Structure of 9-phenylthiophenanthrene **1** with atomic labeling. Anisotropic displacement ellipsoids are drawn at 50% probability level.

C,H-correlation experiments obtained with decoupling of proton-proton couplings in the F1-dimension,<sup>19</sup> and long-range <sup>1</sup>H, <sup>13</sup>C-correlation experiments.<sup>20</sup> The two latter experiments were optimized for 152 and 10 Hz coupling constants, respectively.

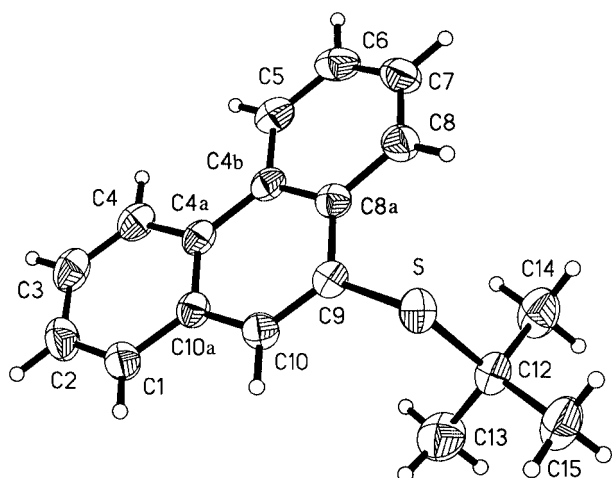
The <sup>1</sup>H NMR spectral parameters (δ<sub>H</sub>, <sup>n</sup>*J*<sub>H,H</sub>) were analyzed with PERCH NMR software.<sup>21–23</sup> The 400 MHz resolution enhanced <sup>1</sup>H spectra were imported to the program and the large spectral ranges containing only noise were removed, along with all unnecessary resonances. In the next step the spectrum line properties and noise were examined. In **2** the nine-spin system of the phenanthrene protons was analyzed separately from the phenyl protons. The analyses were carried out using digital integral transform fitting mode without peak top assignment.

### Results and discussion

A summary of the crystal structure determination is presented in Table 2. Figs. 1 and 2 show the structures and atomic labeling for **1** and **2**, respectively.† C–H distances fall in the range 0.89(4) to 1.01(3) Å for **1** and 0.92(3) to 1.01(3) Å for **2**, both with the mean value of 0.96 Å. The absolute structure parameter (Flack parameter) value of -0.14(10) indicates the correct enantiomorph.<sup>24</sup> Thus **1** crystallizes as a conglomerate

† CCDC reference number 188/174. See <http://www.rsc.org/suppdata/p2/1999/1841> for crystallographic files in .cif format.

of enantiomeric crystals in the space group  $P2_12_12_1$ , while in **2** both diastereomeric conformations crystallize together in the same crystal in a centrosymmetric space group  $Pbcn$ . Figs. 3 and 4 show the molecular packing of **1** and **2**, respectively. The

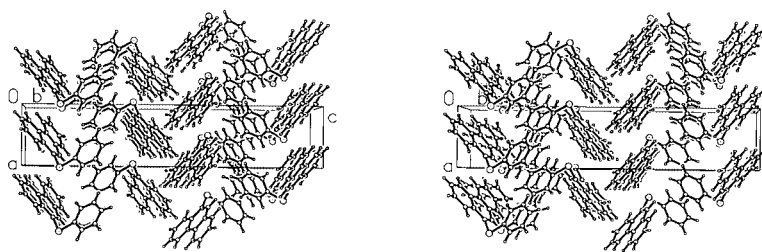


**Fig. 2** Structure of 9-*tert*-butylthiophenanthrene **2** with atomic labeling. Anisotropic displacement ellipsoids are drawn at 50% probability level.

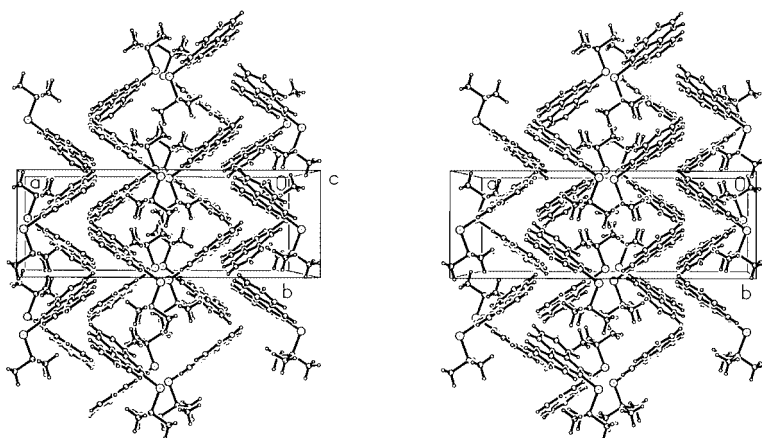
packing of **1** can be described in terms of two main features. First, viewed along the shortest axis the structure consists of tubular channels. Secondly, in the direction perpendicular to the longest axis the phenanthrene groups form a herringbone array and, alternating with the phenyl groups, appear in parallel layers through the crystal. A similar tubular structure with a herringbone pattern has been found in the structures of compounds **3–6**.<sup>2</sup>

Comparison of the present structures with the straight-chained 9-alkylthiophenanthrenes **3–6** shows the main differences to be the C10–C9–S–C12 torsion angles of 92.1(2) and 91.7(2)° in **1** and **2** compared with values of 3.3(3), 3.6(3), 5.9(2), 4.0(3), and 3.1(2)° for **3a**, **3b**, **4**, **5**, and **6**, respectively (Table 3). All C–C distances are close to those found in compounds **3** to **6**. Large deviations can be seen in the S–C9 and S–C12 distances (Table 3). Non-bonded hydrogen atom distances H4···H5 are 2.03(3) and 2.05(3) Å for **1** and **2**, respectively. The distances are almost equal to the values of 2.02(2) in phenanthrene-9-carboxylic acid given by Fitzgerald and Gerkin from refined X-ray data<sup>25</sup> and 2.04(2) in phenanthrene by Kay *et al.* from neutron data.<sup>26</sup> The corresponding value for **5** is 2.13(3) Å, which is close to the value 2.11 Å found in 9-(trimethylsilyl)phenanthrene.<sup>27</sup>

In **1** the distances H8···H13 and H10···H17 are 4.14(3) and 3.20(3) Å, respectively. In **2** H8 is located at distances of



**Fig. 3** A stereoscopic view of 9-phenylthiophenanthrene **1** seen in the *a*-axis direction.



**Fig. 4** A stereoscopic view of 9-*tert*-butylthiophenanthrene **2** seen in the *c*-axis direction.

**Table 3** Selected bond lengths (Å) and bond and torsion angles (°) for 9-R-thiophenanthrenes; R = Ph (**1**), *t*-Bu (**2**), Me (**3**), Et (**4**), *n*-Pr (**5**), *n*-Bu (**6**)<sup>a</sup>

	Bond lengths				Angles	
	S–C9	S–C12	C4a–C4b	C9–C10	C9–S–C12	C10–C9–S–C12
<b>1</b>	1.782(2)	1.769(2)	1.463(3)	1.353(3)	102.10(11)	92.1
<b>2</b>	1.777(2)	1.861(2)	1.454(3)	1.353(3)	104.55(9)	91.7
<b>3a</b>	1.765(7)	1.797(9)	1.465(9)	1.363(9)	103.1(4)	3.3
<b>3b</b>	1.797(7)	1.741(9)	1.470(9)	1.372(10)	104.7(4)	3.6
<b>4</b>	1.769(4)	1.794(4)	1.462(5)	1.360(6)	104.1(2)	5.9
<b>5</b>	1.764(2)	1.806(2)	1.462(2)	1.363(3)	104.06(9)	4.0
<b>6</b>	1.766(3)	1.803(3)	1.449(4)	1.357(4)	104.51(13)	3.1

<sup>a</sup> Data of **3a–6** are from ref. 2.

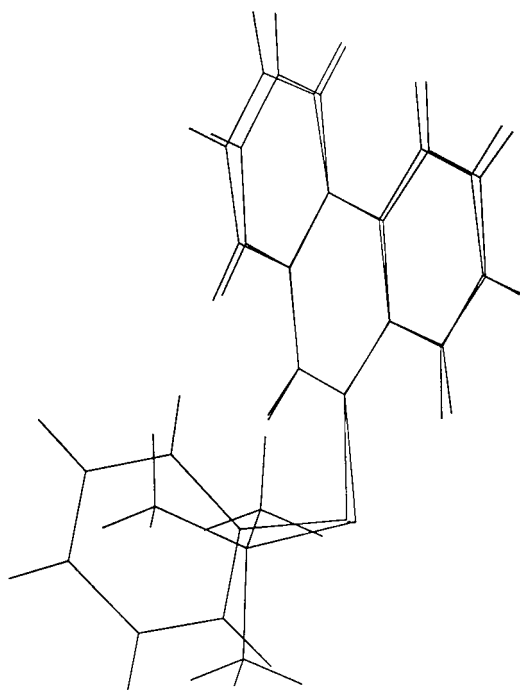


Fig. 5 Superposition of 9-phenylthiophenanthrene **1** and 9-*tert*-butylthiophenanthrene **2**.

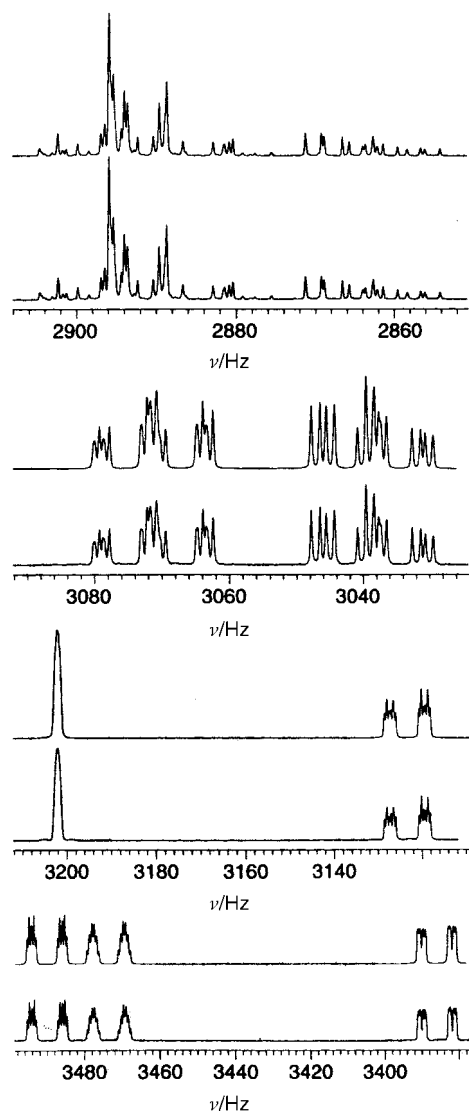


Fig. 6 Comparison of experimental (bottom) and simulated (top)  $^1\text{H}$  NMR spectra of **1** in  $\text{CDCl}_3$ .

Table 4 NMR spectral parameters ( $\delta$  in ppm;  $J$  in Hz)<sup>a</sup> of 9-phenylthiophenanthrene **1** and 9-*tert*-butylthiophenanthrene **2**

	Compound	
	1	2
$\delta(\text{H1})$	7.805	7.877
$\delta(\text{H2})$	7.593	7.596
$\delta(\text{H3})$	7.674	7.666
$\delta(\text{H4})$	8.681	8.666
$\delta(\text{H5})$	8.722	8.685
$\delta(\text{H6})$	7.676	7.653
$\delta(\text{H7})$	7.598	7.647
$\delta(\text{H8})$	8.462	8.879
$\delta(\text{H10})$	8.003	8.141
$\delta(\text{CH}_3)_3$	—	1.336
$\delta(\text{H13,H17})$	7.241	—
$\delta(\text{H14,H16})$	7.221	—
$\delta(\text{H15})$	7.157	—
$^3J(\text{H1,H2})$	7.96	7.96
$^4J(\text{H1,H3})$	1.39	1.39
$^5J(\text{H1,H4})$	0.64	0.65
$^4J(\text{H1,H10})$	-0.46	-0.46
$^3J(\text{H2,H3})$	7.03	7.02
$^4J(\text{H2,H4})$	1.13	1.13
$^3J(\text{H3,H4})$	8.38	8.38
$^5J(\text{H4,H5})$	0.50	0.51
$^5J(\text{H4,H10})$	0.80	0.81
$^3J(\text{H5,H6})$	8.34	8.32
$^4J(\text{H5,H7})$	1.22	1.23
$^5J(\text{H5,H8})$	0.60	0.62
$^3J(\text{H6,H7})$	6.98	6.94
$^4J(\text{H6,H8})$	1.33	1.36
$^7J(\text{H6,H10})$	0.26	0.29
$^3J(\text{H7,H8})$	8.30	8.36
$^5J(\text{H8,H10})$	0.26	0.29
$^3J(\text{H13,H14})$	7.95	—
$^4J(\text{H13,H15})$	1.14	—
$^5J(\text{H13,H16})$	0.54	—
$^4J(\text{H13,H17})$	2.04	—
$^3J(\text{H14,H15})$	7.48	—
$^4J(\text{H14,H16})$	1.56	—
$\delta(\text{C1})$	128.54	128.71
$\delta(\text{C2})$	127.02	126.80
$\delta(\text{C3})$	127.45	127.51
$\delta(\text{C4})$	122.68	122.59
$\delta(\text{C4a})$	130.72	131.00
$\delta(\text{C4b})$	131.12	130.82
$\delta(\text{C5})$	123.02	122.69
$\delta(\text{C6})$	127.10	126.68
$\delta(\text{C7})$	127.23	126.64
$\delta(\text{C8})$	126.57	128.24
$\delta(\text{C8a})$	131.66	134.57
$\delta(\text{C9})$	129.74	129.48
$\delta(\text{C10})$	134.00	138.75
$\delta(\text{C10a})$	131.74	131.39
$\delta(\text{C12})$	—	47.73
$\delta(\text{CH}_3)_3$	—	31.41
$\delta(\text{C12})$	136.71	—
$\delta(\text{C13/C17})$	128.95	—
$\delta(\text{C14/C16})$	129.13	—
$\delta(\text{C15})$	126.20	—

<sup>a</sup> Chemical shifts are given relative to internal TMS ( $\delta_{\text{H}} = \delta_{\text{C}} = 0.0$  ppm). The estimated error in a chemical shift is  $\pm 1$  in the last digit, and in a coupling constant  $\pm 0.02$  Hz.

2.65(3) and 2.63(3) Å from the *tert*-butyl hydrogens H14a and H14b, respectively, while the distances to H10 from the two nearest hydrogens H13a and H13b are 2.71(3) and 3.01(3) Å, respectively. In compound **5**, by comparison, the distances from H10 to the nearest hydrogens of the propyl group H12a and H12b are 2.24(3) and 2.31(3) Å, respectively.<sup>2</sup>

The phenanthrene group is nearly planar. The angles between the three planes formed by rings I (C1, C2, C3, C4, C4a, C10a),

II (C4a, C4b, C8a, C9, C10, C10a), and III (C4b, C5, C6, C7, C8, C8a) are 2.7(2) and 3.8(2)° for I–II, 4.5(2) and 6.0(2)° for I–III, and 2.3(2) and 2.3(2)° for II–III in **1** and **2**, respectively. Fig. 5 shows a superposition of **1** and **2** drawn by fitting atoms C4a, C8a, C9, and C10 using crystallographic coordinates and MacroModel software.<sup>28</sup>

The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectral parameters of **1** and **2** are given in Table 4. <sup>1</sup>H–<sup>1</sup>H coupling constants in C<sub>6</sub>D<sub>6</sub> (not presented here) were within 0.02 Hz of the values in CDCl<sub>3</sub>. The <sup>1</sup>H–<sup>1</sup>H coupling constants are comparable to those presented in the literature.<sup>4,7,9</sup> The signs of couplings were adopted from work of Laatikainen on the spin–spin couplings of naphthalene.<sup>9</sup> The sign of <sup>5</sup>J<sub>H<sub>4</sub>H<sub>5</sub> (assumed positive) was evaluated with PERCH by changing it to negative, but no effect on the spectrum was seen. The couplings between the phenanthrene protons are almost the same in **1** and **2**. The largest difference is 0.06 Hz. The substituent does not affect the coupling constants.</sub>

For nuclei that are far from the point of substitution, the <sup>1</sup>H chemical shifts are comparable in **1** and **2**. When the *tert*-butyl group is replaced by a phenyl group the resonance of H8 exhibits a 0.41 ppm shift to lower frequency, while the resonance of H10 shifts by only 0.14 ppm. The resonance of carbon C8 is shifted by 1.67 ppm and that of C10 by 4.75 ppm. The aromatic ring current has an opposite effect on the carbons and the protons. The rotation around the axis C9–S causes simultaneous reorientation of the phenyl group, which is especially pronounced as the coplanar conformation is approached. The stronger shielding of H8 than of H10 could be explained if the phenyl group, in general, is facing toward H8, as in the solid state. Why the carbons show reversed sensitivity to the ring current remains unexplained.

In the NOE difference experiment, irradiation of the *tert*-butyl protons of **2** yielded an 8% increase in the area of H8 and a 7% increase in H10. This would suggest that, on average, the *tert*-butyl protons lie at equal distances from H8 and H10. This also indicates an approximately 90° torsion angle C10–C9–S–C12. In the case of compound **1**, H8 and H10 were irradiated separately. The area of protons H13/H15 increased in both experiments, but the magnitude could not be established. This would suggest a perpendicular orientation of the substituent at sulfur relative to the phenanthrene plane.

## Acknowledgements

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