

## Highly Twisted Substituted Arenes: X-Ray Structure and Dynamic $^1\text{H}$ NMR Spectra of 1,4-Dialkyl-2,3,5,6-tetrakis(alkylsulfonyl)benzenes

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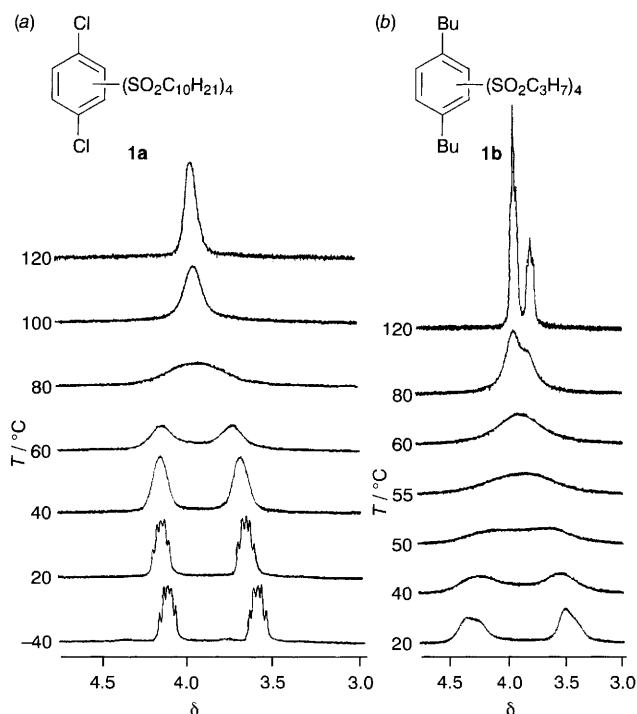
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The sulfonyl groups around 1,4-disubstituted-2,3,5,6-tetrakis(alkylsulfonyl)benzenes adopt an alternating orientation and the ring is highly twisted, with external torsion angles (S–C<sub>ar</sub>–C<sub>ar</sub>–S) of 46° and internal torsion angles (C<sub>ar</sub>–C<sub>ar</sub>–C<sub>ar</sub>–C<sub>ar</sub>) of 23°.

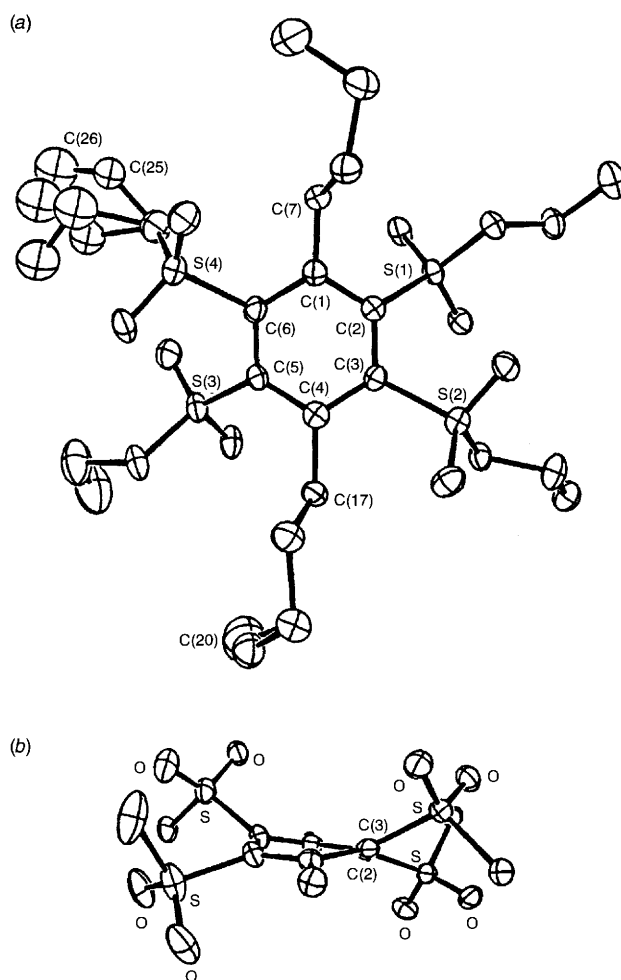
The planarity of aromatic nuclei is one of the founding principles of structural organic chemistry. Loss of planarity and the concomitant decrease in aromatic stabilization must be energetically compensated elsewhere in the molecule.<sup>1</sup> Non-planar benzene rings are most commonly observed in helicenes,<sup>2</sup> longitudinally twisted arenes<sup>3</sup> and cyclophanes in which ring strain is relieved by bending the arene.<sup>4</sup> Most hexasubstituted benzenes<sup>5</sup> and other sterically crowded derivatives (e.g. 1,2,4,5-tetra-*tert*-butylbenzene<sup>6</sup>) retain their planarity by relief of non-bonding interactions through a combination of in-plane distortions of bond angles and lengths. More sterically demanding substituents are only accommodated by bending the benzene ring. Hexakis(trimethylsilyl)benzene<sup>7</sup> and hexakis(trimethylgermyl)benzene<sup>8</sup> adopt shallow chair conformations possessing approximate  $D_{3d}$  symmetry, with small C<sub>ar</sub>–C<sub>ar</sub>–C<sub>ar</sub>–C<sub>ar</sub> internal torsion angles (Si, 8.5°; Ge, 6.8°) and larger X–C<sub>ar</sub>–C<sub>ar</sub>–X external torsion angles. 1,3,5-Tris(*N,N*-dimethylamino)-2,4,6-trinitrobenzene<sup>9</sup> and trialkyl 4,5,6-tri-*tert*-butyl-1,2,3-benzenetricarboxylates<sup>10</sup> adopt boat conformations. A study of analogues of a series of hexasulfonylbenzene-containing liquid crystals<sup>11</sup> led us to investigate the conformation and molecular geometry of 1,4-dialkyl-tetrakis(alkylsulfonyl)benzenes **1**.<sup>†</sup>

The  $\alpha$ -methylenes of the side chains of 1,4-chloro-2,3,5,6-tetrakis(decylsulfonyl)benzene **1a** appear as an ABX<sub>2</sub>

pattern in the  $^1\text{H}$  NMR at room temperature, Fig. 1. Upon heating, the pattern broadens and the signals coalesce at approximately 75 °C with a barrier to interconversion of approximately 17 kcal mol<sup>-1</sup> (1 cal = 4.184 J). Similar dynamic behaviour is observed for analogues with other 1,4-substituents, C<sub>6</sub>X<sub>2</sub>(SO<sub>2</sub>R)<sub>4</sub> (X = H, F, Me, alkyl).<sup>‡</sup> In order to obtain diffraction quality crystals to address the origin of this effect, we prepared 1,4-dibutyltetrakis(propylsulfonyl)benzene **1b** which displays similar dynamic NMR behaviour (Fig. 1). At high temperature (120 °C), the  $\alpha$ -methylene and the benzylic methylene of **1b** appear as sharp triplets with a 2 : 1 ratio. Upon cooling, the peaks are broadened, and eventually decoalesce ( $T_c$  = 55 °C). At 20 °C, each asymmetric signal (ca.  $\delta$  3.5 and 4.3) is a composite of one of the sulfonyl  $\alpha$ -methylene protons, and one of the benzylic protons.



**Fig. 1** Variable temperature  $^1\text{H}$  NMR spectra (300 MHz, 10 mmol dm<sup>-3</sup> solution in [ $^2\text{H}_5$ ]chlorobenzene): (a) 1,4-dichloro-2,3,5,6-tetrakis(decylsulfonyl)benzene **1a**; (b) 1,4-dibutyl-2,3,5,6-tetrakis(propylsulfonyl)benzene **1b**



**Fig. 2** Structure of 1,4-dibutyl-tetrakis(propylsulfonyl)benzene **1b**: (a) view of top face; (b) side view along C(3)–C(2) bond. Determination of the crystal structure at different temperatures indicates that static disorder is present for C(2), C(25) and C(26), orthorhombic  $Pbca$  space group.

The crystal structure of **1b** is shown in Fig. 2. The sulfone oxygens are arranged around the benzene ring on alternating faces to minimize dipolar interactions.<sup>13</sup> This arrangement of sulfones and the presence of 1,4-alkyl groups around the ring imparts a pseudo-*C*<sub>2</sub> symmetry which gives rise to diastereotopic proton signals.

The C<sub>6</sub>X<sub>2</sub>S<sub>4</sub> core of the molecule is severely distorted from planarity, with formation of a twisted chair conformation. This core is shown in projection along a C<sub>ar</sub>-C<sub>ar</sub> bond in Fig. 2(b).§ There are large external torsion angles between substituents (average S-C<sub>ar</sub>-C<sub>ar</sub>-S, 45.6°; C<sub>Bu</sub>-C<sub>ar</sub>-C<sub>ar</sub>-S, 33.8° and 11.4°) and smaller internal torsion angles in the arene [average C(1)-C-C-C(4), 22.7°; C(2)-C-C-C(5), 2.9°; C(3)-C-C-C(6), 19.2°]. The average torsion angle in the ring is 14.9°, and the average external torsion angle is 30.8°. This discrepancy between internal and external torsion angle is the result of pyramidalization<sup>14</sup> of the nominally sp<sup>2</sup> aromatic carbons; S(1) and S(3) are bent 13° out of the plane containing the *ipso* and *ortho* carbons.

The C<sub>ar</sub>-S bond length of **1b** (average: 1.83 ± 0.01 Å) is longer than that of methyl phenyl sulfone<sup>15</sup> (1.773 Å) whereas the S-C<sub>Bu</sub> bond of **1b** (average: 1.78 ± 0.02 Å) is unexceptional (S-C<sub>Me</sub>, 1.785 Å in PhSO<sub>2</sub>Me). The C<sub>ar</sub>-C<sub>ar</sub> bond lengths are unexceptional (1.40 Å), and do not display a strong alternation around the ring. As a result of these distortions of bond length and torsion angle, C(3) and C(6) lie approximately 0.5 Å out of the best-fit plane of the aromatic carbons, and S(1) and S(3) lie over 1 Å from this plane.

Steric and electronic interactions between bulky and dipolar substituents of **1** are relieved by orientation of neighbouring sulfone oxygens on opposite faces of the molecule, and the long C<sub>ar</sub>-S bond. Although the alternating orientation of substituents around the ring relieves alignment of dipoles, it does not alleviate the electrostatic repulsion between positive ends of neighbouring sulfonyl groups. Since the 1,4-substituents hinder in-plane bending, these interactions can only be relieved by out-of-plane distortions. These distortions result in large external torsion angles and a puckered ring with slightly pyramidalized sp<sup>2</sup> arene carbons. The out-of-plane distortion of the benzene ring of **1b** (*i.e.* 22.7° internal torsion angles), owing to both strong steric and electronic interactions, is substantially larger than that experienced by arenes bearing bulky non-polar substituents.<sup>7,8</sup> The influence of other structural features on the geometry of arenes substituted with polar groups is under investigation.

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## Footnotes

† Tetrasulfones **1** were prepared by the reaction of excess sodium alkylthiolate and 1,4-dialkyltetrahalobenzenes<sup>12</sup> and subsequent oxidation with MCPBA. X-Ray quality crystals of **1b** were obtained by slow solvent exchange of methanol into a THF solution. Selected data for **1a**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) diastereotopic protons: δ 3.44, 4.17 (ABX<sub>2</sub>; *J* 13, 7 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>) aromatic signals: δ 143, 152; IR (KBr) ν/cm<sup>-1</sup> SO<sub>2</sub> asym and sym. str. 1287, 1140. **1b**: <sup>1</sup>H NMR, diastereotopic protons: δ 3.45, 4.20 (br. m); IR ν/cm<sup>-1</sup> SO<sub>2</sub> asym and sym. str.: 1307, 1146.

‡ Coalescence temperatures (°C) for R = decyl: X = H, < -40; X = F, -35; X = Cl, 75; X = Me, 70.

§ Selected crystal data for **1b**: *a* = 19.324(4), *b* = 9.7140(2), *c* = 33.462(7) Å; *T* = -100 °C. Average bond lengths: C<sub>ar</sub>-S 1.83 ± 0.01, C<sub>ar</sub>-C<sub>ar</sub> 1.40 ± 0.01 Å. Torsion angles: C(7)-C(1)-C(2)-S(1) 33.3°, S(1)-C(2)-C(3)-S(2) 45.0°, S(2)-C(3)-C(4)-C(17) 13.0°, C<sub>ar</sub>-C<sub>ar</sub>-S-C 82.8°. Out-of-plane (best fit C<sub>6</sub> plane) displacements: C(2) 0.53, S(1) 1.12, C(5) 0.51, S(3) 1.05 Å. Pyramidalization (out-of-plane bend angle of substituent from C<sub>ortho</sub>-C<sub>ipso</sub>-C<sub>ortho</sub> plane): C(7) 0.8, S(1) 13.4, S(2) 6.4, C(11) 0.8, S(3) 11.8, S(4) 8.1°. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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