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Reaction of *m*-terphenyl with 20% oleum at 100° gives both disulfonation and double sulfonyl bridging to yield benzo[1]thieno[2,3-*b*]dibenzothiophene-3,9-disulfonic acid 5,5,7,7-tetraoxide, isolated as the disodium salt (24%) and convertible (*via* the disulfonyl chloride) to the bis-sulfonanilide (44%) and the bis-*N*-butylsulfonamide (40%). Analogously, reaction of *m*-terphenyl with chlorosulfonic acid at 100° gives disulfonation plus only single sulfonyl bridging to produce 2-(4-chlorosulfonyl)-7-chlorosulfonyldibenzothiophene 5,5-dioxide (80%), convertible to the corresponding bis-sulfonanilide (63%) and the bis-*N*-butylsulfonamide (45%).

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In 1956 VanAllan reported that 20% oleum at 90-100° converts *m*-terphenyl (**1**) into a disulfonyl disulfonic acid for which he proposed the structure **2a** [4]. The molecular formula of **2a** was crudely established by elemental analysis of its di-*o*-toluidine salt, but the results for percentages of carbon and hydrogen were not within acceptable limits. VanAllan implied that sulfonation of **1** with chlorosulfonic acid plus hydrolysis of the intermediate sulfonyl chloride also gives **2a**, but he did not provide experimental details for this conversion. We have now reexamined the sulfonation with both of these reagents and have found that compound **2a** is, indeed, formed with 20% oleum but that chlorosulfonic acid does not give the same parent system.

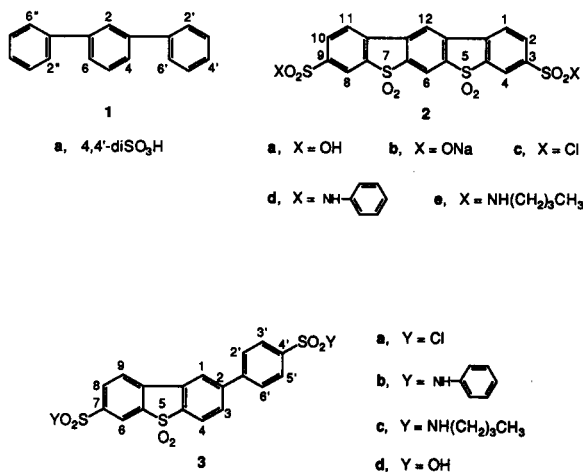
The product from treatment of **1** with 20% oleum under conditions used by VanAllan was identified from its <sup>1</sup>H nmr spectrum in deuterium oxide. This simple spectrum consists of two downfield singlets for one proton each at 8.39 and 8.36 ppm (H-6 and H-12), a singlet for 2 protons (H-4 and H-8) at 8.30, and a doublet of doublets (*J*<sub>ortho</sub> = 8.3 Hz) for two protons each (H-1 plus H-11, H-2 plus H-10) centered at 8.12. While this pattern of signals is consistent with structure **2a**, as shown, it does not eliminate a possible alternative structure (not shown) wherein the sulfonic

acid groups are located at C-2 and C-10, instead of at C-3 and C-9 as in **2a**. This alternative structure, however, is deemed exceedingly unlikely inasmuch as substitution of sulfonic acid groups at C-2 and C-10 is inconsistent with known orientation rules. Thus, the sulfonyl groups at positions 5 and 7, as well as the sulfonic acid groups at positions 3 and 9, are *meta*-directing and the *meta*-terphenyl parent molecule is *ortho*- and *para*-directing with respect to the inter-ring sigma bond [5,6]. Both orienting effects should lead to structure **2a**.

Further identification of **2a** was effected by reaction of its sodium salt **2b** with phosphorus pentachloride in refluxing 1,2-dichlorobenzene to obtain the intermediate disulfonyl chloride **2c**, convertible to the bis-sulfonanilide **2d** (mp 296°, 44% yield from **2b**) and the bis-*N*-butylsulfonamide **2e** (mp 327°, 40% from **2b**) by treatment with aniline and 1-aminobutane, respectively. Although **2c** was only obtained in crude form, the two sulfonamides were recrystallizable to analytical purity, albeit with apparent retention of solvent.

The reaction of *m*-terphenyl with chlorosulfonic acid was conducted in essentially the same manner as described by VanAllan for reaction of *p*-terphenyl, *i.e.* at about 100°. The crude disulfonyl chloride formed, **3a** (80%), was also converted into a bis-sulfonanilide, **3b** (63%, mp 283°), and a bis-*N*-butylsulfonamide, **3c** (45%, mp 206°), both analytically pure.

It is very clear that corresponding sulfonamides from the alternative synthetic routes are not identical, as based largely on comparison of melting points, <sup>1</sup>H nmr spectra, and mass spectra. Each of the products **2d** and **2e** from the oleum synthetic route shows the same symmetrical pattern of aromatic proton nmr signals as for **2a** plus only one set of signals for the two sulfonamide groups present. Contrariwise, the pattern of signals for aromatic protons in **3a** and **3c** consists of only one downfield singlet for H-6, one singlet for H-1, two double doublets for H-3 and H-4 plus H-8 and H-9, and a symmetrical 4-proton AB system (*J* ≈



8 Hz) for a *para*-disubstituted benzene ring. Additionally, there are two sets of signals for the non-equivalent *N*-butylsulfonamide groups in **3c**. The pattern for **3a** persists in the **3b** disulfonanilide spectrum, supplemented by an unresolved multiplet for 2 phenylimino groups at higher field ( $\delta$  7.0-7.3). The patterns of aromatic proton signals not only show a difference between systems **2** and **3**, but also serve to establish the parent structural features of both systems. Structure **3** is also consistent with expected orientation rules. In fact, it has been reported that sulfonation of **1** with concentrated sulfuric acid at 100° produces *m*-terphenyl-4,4'-disulfonic acid **1a** [7]. Thus, it seems plausible that **2a** may form by the reaction sequence **1**  $\rightarrow$  **1a**  $\rightarrow$  **3d**  $\rightarrow$  **2a**. Similar sequences are apparent for sulfonation of the isomeric terphenyls [4,7,8].

As expected from the high melting points, the solubilities of the sulfonamides **2d**, **2e**, **3b**, and **3c** are limited in many organic solvents. All of these compounds exhibit strong sulfonyl bands (from 2 broad ones to 4 sharp ones) in the infrared region. Their mass spectra show major differences.

#### EXPERIMENTAL [9]

##### Sulfonation of *m*-Terphenyl with Oleum.

Technical grade *m*-terphenyl (Aldrich) was recrystallized from ethanol to give white crystals, mp 87-89°; <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  7.97 (s, 1 H, H-2), 7.79 (d,  $J_{ortho}$  = 7.5 Hz, 4 H, H-2', H-6', H-2'', H-6''), 7.71 (split d,  $J_{ortho}$  = 7.0 Hz,  $J$  = 1.2 Hz, 2 H, H-4 and H-6), 7.45-7.68 (m, 7 other protons).

A quantity of 49.9 g (0.217 mole) of purified *m*-terphenyl (**1**) was added slowly with stirring to 250 ml (472 g, excess) of 20% oleum at room temperature. External heat was applied so as to maintain a reaction temperature of 90-110° for 3.3 hours. The warm mixture was poured onto 250 g of ice and the precipitate was collected by filtration with a sintered glass funnel to give crude disulfonic acid **2a**; <sup>1</sup>H nmr (deuterium oxide with sodium trimethylsilylpropanesulfonate as reference):  $\delta$  8.39 and 8.36 (2 s, 1 H each, H-6 and H-12), 8.30 (s, 2 H, H-4 and H-8), 8.12 (dd, AB system,  $J_{ortho}$  = 8.3 Hz,  $\Delta\delta$  = 31.9 Hz, 4 H, H-1, H-2, H-10, H-11). Precipitated **2a** was dissolved in 1.5 l of boiling water, basified with solid sodium hydroxide, cooled to 10°, and filtered again to remove insoluble by-products. The filtrate was treated with an equal volume of saturated aqueous sodium chloride to salt out the disodium disulfonate **2b** as a faintly tan solid which was dried in air at room temperature, yield 29.7 g (24%, if one assumes that the product is a monohydrate).

A sample of the foregoing **2b** was dried at 55° to constant weight; ir: 3700-3100 (broad, strong, water), 1310 and 1120 (sulfone), 1260-1160 (broad, strong, sulfonate anion), 1044, 581 and 563 cm<sup>-1</sup> (sulfone scissoring) [10-12].

Before further reaction the main part of **2b** was dried at 144° (0.1 mm) for 24 hours. A mixture of 7.81 g (0.014 mole) of this **2b**, 4.2 g (0.02 mole) of phosphorus pentachloride, and 50 ml of 1,2-dichlorobenzene was refluxed and stirred for 22 hours. The two-phased, cooled reaction mixture was filtered by means of a sintered glass funnel and the solid residue added to an ice-water

mixture [13]. The resultant precipitate was collected by suction filtration and dried in a vacuum desiccator, yield 3.91 g (51%) of crude disulfonyl chloride **2c**, violet fluorescence, used without further characterization, for forming sulfonamides (*vide infra*).

3,9-Bis-(*N*-phenylsulfamoyl)benzo[1]thieno[2,3-*b*]dibenzothiophene 5,5,7,7-Tetraoxide (**2d**).

A mixture of 1.03 g (1.86 mmoles) of preceding **2c** and 2 ml of aniline (22 mmoles) was refluxed for ten minutes and then allowed to stand overnight. The dark red reaction mixture was poured into ice-water. The suspension of gummy precipitate in aqueous solution was stirred vigorously for several hours until the precipitate became granular. Filtration yielded 1.08 g (86%) [14] of tan, crude **2d**. This solid was extracted with two 50-ml portions of boiling 95% ethanol (extract discarded) [15] and then recrystallized first from ethyl acetate and then from 2-butanone to give light yellow, fine, electrostatic needles, mp 295-297°,  $R_f$  0.55 (silica gel/ethyl acetate), violet fluorescence; ir: 3635 (water?), 3287 (NH), 1320, 1174, and 1158 (sulfonyl groups), 817 cm<sup>-1</sup>; <sup>1</sup>H nmr (hexadeuteriodimethyl sulfoxide):  $\delta$  9.15 and 9.07 (2 s, 1 H each, H-6 and H-12), 8.33 (dd, AB system,  $J_{ortho}$  = 8.2 Hz,  $\Delta\delta$  = 67.3 Hz, 4 H, H-1, H-2, H-10, H-11), 8.32 (s, 2 H, H-4 and H-8), 7.26 (t,  $J$  = 7.8 Hz) plus 7.04-7.16 (m, 12 H total, 2 phenyl plus 2 NH groups); ms:  $m/e$  664 ( $M^+$ , 5), 139 (Ph-N=S=O<sup>+</sup>, 2), 93 (PhNH<sub>2</sub><sup>+</sup>, 100), 65 (34).

*Anal.* Calcd. for C<sub>30</sub>H<sub>20</sub>N<sub>2</sub>S<sub>4</sub>O<sub>8</sub>·½ H<sub>2</sub>O: C, 53.48; H, 3.14; N, 4.15. Found: C, 53.67; H, 2.90; N, 3.95.

3,9-Bis-(*N*-butylsulfamoyl)benzo[1]thieno[2,3-*b*]dibenzothiophene 5,5,7,7-Tetraoxide (**2e**).

A mixture of 1.03 g (1.86 mmoles) of preceding **2c** and 3.5 ml (35 mmoles) of 1-aminobutane was refluxed for ten minutes and then allowed to stand overnight. The yellow solid which precipitated from the reaction mixture was collected by filtration (filtrate discarded) and added to ice-water. This suspension was stirred vigorously for 30 minutes and the precipitate was collected by filtration to give 0.92 g (79%) of crude **2e**, mp 325° dec, soluble in DMSO and 2-butanone, insoluble in 95% ethanol, acetone, acetonitrile, and ethyl acetate. For infrared and nmr spectra this solid was triturated with 95% ethanol and dried in air; ir: 3309 (NH), 3090, 2957, 2931, 2871 (all sharp, medium), 1326, 1308, 1174, 1159 (two pairs of strong sulfonyl bands), 816 cm<sup>-1</sup>; <sup>1</sup>H nmr (hexadeuteriodimethyl sulfoxide):  $\delta$  9.34 and 9.14 (2 s, 1 H each, H-6 and H-12), 8.46 (dd, AB system,  $J_{ortho}$  = 8.2 Hz,  $\Delta\delta$  = 64.0 Hz, 4 H, H-1, H-2, H-10, H-11), 8.38 (s, 2 H, H-4 and H-8), 7.92 (t,  $J$  = 5.7 Hz, 2 H, 2 NH), 2.84 (m, 4 H, 2 CH<sub>2</sub>NH), 1.1-1.5 (dm, 4 H, 2 CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.79 (t,  $J$  = 7.2 Hz, 6 H, 2 methyl groups).

The mass spectrum and elemental analysis were obtained on the preceding sample after it was recrystallized from 2-butanone/petroleum ether (30-60°) and dried at 78° (0.1 mm) for 24 hours to give faintly cream-colored granules, electrostatic, and with green fluorescence, mp 326-328° dec; ms:  $m/e$  581 ( $M^+$ -Pr, 84), 552 ( $M^+$ -NHBu, 100), 445 (581<sup>+</sup>-SO<sub>2</sub>NHBu, 49), 416 (552<sup>+</sup>-SO<sub>2</sub>NHBu, 32), 352 ( $M^+$ -2 SO<sub>2</sub>NHBu, 37), 64 (SO<sub>2</sub><sup>+</sup>, 67), 48 (SO<sup>+</sup>, 58), 42 (15), 41 (26) [16].

*Anal.* Calcd. for C<sub>26</sub>H<sub>22</sub>N<sub>2</sub>S<sub>4</sub>O<sub>8</sub>·½ C<sub>4</sub>H<sub>8</sub>O: C, 50.89; H, 4.88; N, 4.24. Found: C, 50.53; H, 5.04; N, 4.49.

##### Direct Chlorosulfonation of *m*-Terphenyl (**1**).

Ten g (43.5 mmoles) of recrystallized *m*-terphenyl was shaken

in an oven-dried reflux apparatus, protected from atmospheric moisture, while 50 ml (760 mmoles) of chlorosulfonic acid was added dropwise. The resultant solution was stirred magnetically, heated at 90-105° for one hour, and allowed to stand at room temperature overnight. The mixture was poured onto ice to give a cream-colored gummy and finely divided precipitate which was hard to filter. Some of the water separated by decantation and the remainder was removed by rotoevaporation, aided by the addition of toluene in the final stages. The residue was dried in an evacuated desiccator, yield 17 g (80%) of crude **3a**, used directly in reaction to form sulfonamides (*vide infra*).

For characterization only, a sample of crude **3a** was recrystallized from 2-butanone to yield tan 2-(4-chlorosulfonylphenyl)-7-chlorosulfonyldibenzothiophene 5,5-dioxide (**3a**), mp 258-265°; <sup>1</sup>H nmr (hexadeuteriodimethyl sulfoxide): δ 8.55 (s, 1 H, H-6), 8.37 (d, J<sub>3,4</sub> = 8.1 Hz, 1 H, H-4), 8.02 (dd, AB system, J<sub>8,9</sub> = 8.1 Hz, Δδ = 18.7 Hz, 2 H, H-8 and H-9), 7.94 (d, H-3) which overlaps 7.93 (s, 2 H total, H-1), 7.79 (dd, AB system, J<sub>ortho</sub> = 8.1 Hz, Δδ = 32.6 Hz, 4 H, H-2', H-3', H-5', H-6').

2-(4-*N*-Phenylsulfamoyl)phenyl-7-(*N*-phenylsulfamoyl)dibenzothiophene 5,5-Dioxide (**3b**).

A mixture of 5 g (10.2 mmoles) of preceding crude chlorosulfonation product and 8 ml (92 mmoles) of aniline was refluxed for 10 minutes. The warm mixture was poured onto ice to give a gummy precipitate, which became granular on stirring. This precipitate was collected by suction filtration, washed repeatedly with water, and dried in air, yield 3.85 g (63%) of **3b** as slightly tan crystals, mp 238-260°, changed to colorless needles, mp 282-284°, on repetitive recrystallizations from 95% ethanol, ir: 3332 and 3242 (NH), 1349, 1298, and 1168 (broad, very strong-sulfonyl groups), 760 and 743 (doublet), 581, 575 cm<sup>-1</sup> [12]; <sup>1</sup>H nmr (hexadeuteriodimethyl sulfoxide): δ 8.63 (s, 1 H, H-6), 8.49 (d, J<sub>3,4</sub> = 8.1 Hz, 1 H, H-4), 8.22 (s, 1 H, H-1), 8.15 (d, 1 H, H-3) which overlaps 8.11 (dd, AB system, Δδ = 37.5 Hz, J<sub>8,9</sub> = 8.1 Hz, 2 H, H-8 and H-9), which overlaps 7.95 (dd, AB system, Δδ = 32.8 Hz, J<sub>ortho</sub> = 8.4 Hz, 4 H, H-2', H-3', H-5', H-6'), 7.0-7.3 (m, 12 H, 2 phenyl and 2 NH groups); ms: m/e 602 (M<sup>+</sup>, 100), 479 (M<sup>+</sup>-C<sub>6</sub>H<sub>5</sub>NS, 20), 448 (22), 447 (M<sup>+</sup>-C<sub>6</sub>H<sub>5</sub>NSO<sub>2</sub>, 85), 383 (447-SO<sub>2</sub>, 38), 382 (35).

*Anal.* Calcd. for C<sub>30</sub>H<sub>22</sub>N<sub>2</sub>O<sub>6</sub>S<sub>3</sub>: C, 59.78; H, 3.68; N, 4.65. Found: C, 60.04; H, 3.81; N, 4.53.

2-(4-*N*-Butylsulfamoyl)phenyl-7-(*N*-butylsulfamoyl)dibenzothiophene 5,5-Dioxide (**3c**).

To a flask containing 12.1 g (24.7 mmoles) of crude **3a**, cooled in an ice bath, was added, in small portions, 10 ml (101 millimoles) of dried (over potassium hydroxide pellets) 1-aminobutane (exothermic reaction). The mixture was then refluxed for ten minutes and allowed to cool somewhat. The gel which formed was scraped into ice-water and the mixture was stirred vigorously to give a granular solid. The precipitate was collected, washed, and recrystallized from 95% ethanol (as with **3b**) to give 6.2 g (45%) of **3c** as a faintly pinkish solid, mp 192-200°, changed to a white

powder on further recrystallizations from the same solvent, mp 205-207°, purple fluorescence, ir: 3292 (NH), 2975, 2935, 2890 (all sharp, medium), 1334-1300 and 1177-1141 (strong sulfonyl bands), 818 cm<sup>-1</sup>; <sup>1</sup>H nmr (hexadeuteriodimethyl sulfoxide): δ 8.736 (s, 1 H, H-6), 8.599 (d, J<sub>3,4</sub> = 8.1 Hz, 1 H, H-4), 8.292 (s, 1 H, H-1), 8.233 and 8.196 (2 overlapping d, J ≈ 8.2 Hz, 2 H total, H-3 and H-8), 8.093 (2 overlapping d, 3 H, H-3', H-5', H-9), 7.940 (d, J<sub>ortho</sub> = 8.1 Hz, 2 H, H-2' and H-6'), 7.873 and 7.709 (2 t, J<sub>CH<sub>2</sub>NH</sub> = 6 Hz, 1 H each, 2 NH), 2.7-2.9 (2 overlapping t, 4 H total, 2 CH<sub>2</sub>NH), 1.1-1.5 (2 overlapping m, J = 6-7 Hz, 8 H, 2 CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>NH), 0.787 (t, J = 6-7 Hz, 6 H, 2 methyl groups); ms: m/e 562 (M<sup>+</sup>, 41), 520 (27), 519 (M<sup>+</sup>-Pr, 90), 491 (28), 490 (M<sup>+</sup>-NHBu, 100), 426 (M<sup>+</sup>-SO<sub>2</sub>NHBu, 23).

*Anal.* Calcd. for C<sub>26</sub>H<sub>30</sub>N<sub>2</sub>O<sub>6</sub>S<sub>3</sub>: C, 55.49; H, 5.37; N, 4.98. Found: C, 55.74; H, 5.26; N, 4.87.

## REFERENCES AND NOTES

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- [13] The filtrate was discarded.
- [14] Percentage yield corresponds to the isolation of a hemihydrate.
- [15] Tlc of the extract showed the presence of three components, including **2d**.
- [16] Except for signals at m/e 553 and 554 all of the peaks of relative abundance > 1% are reported here. Conceivably the appreciable size of fragment ions at m/e 42 and 41 results either from loss of propene from **2e** and/or ketene from solvent of crystallization. See F. W. McLafferty and R. Venkataraghavan, *Mass Spectral Correlations*, 2nd Ed, American Chemical Society, Washington, DC, 1982, pp 19-20.