

# Synthesis and Characterisation of 3,4-Dialkoxy-Substituted Benzo-1,3,2-Dithiazolyl Radicals

Antonio Alberola, Robert J. Less, Efren Navarro-Moratalla and Jeremy M. Rawson

## Supplementary Information

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### Synthesis of 2,3,8,9-bisdioxolyldibenzo[c,g]-1,2,5,6-tetrathiocine, A.

Sulphur monochloride (0.70 mL, 8.71 mmol) was added dropwise to a stirred solution of 1,3-benzodioxole (1.0 mL, 8.71 mmol) in glacial acetic acid (20 mL) under nitrogen. The initial clear solution slowly turned darker and, after stirring for 48 h at room temperature, a dense bright yellow suspension had formed under a yellow solution. The precipitate was filtered quickly in a fumescupboard, minimizing air exposure then washed with small fractions of diethyl ether and dried. The resultant yellow powder was dissolved in the minimum amount of chloroform (250 mL) to afford a clear and bright green solution which was triturated with methanolic tin(II) chloride solution (3 g of anhydrous SnCl<sub>2</sub> in 5 mL of MeOH) until the solution turned from green to bright yellow. The solution was evaporated to half its volume of chloroform and then treated with ice-cold methanol (200 mL) and stored at 0 °C for 2 h to precipitate the tetrathiocine A as a yellow solid. The product was isolated by filtration and washed ice-cold methanol (2 x 10 mL). Recrystallisation by slow evaporation of a chloroform solution afforded bright yellow plates of A. Yield: 1.38 g (86%).

Found (Calculated for C<sub>14</sub>H<sub>8</sub>S<sub>4</sub>O<sub>4</sub>): C= 43.67% (45.60); H= 2.31% (2.20). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub> solution): δ/ppm = 6.95 (4 H, s), 5.95 (4 H, s)

### Synthesis of 4,5-dioxolyl-benzo-1,3,2-dithiazolylum chloride [1]Cl

Sulphuryl chloride (2.2 mL, 27.38 mmol) was added dropwise to a bright yellow suspension of A (5.0 g, 13.59 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (45 mL) under nitrogen. A green precipitate is initially formed which dissolves upon the addition of the remaining SO<sub>2</sub>Cl<sub>2</sub> to afford a dark brown solution. The mixture was then brought to reflux (55 °C) for 2 h. Any residual gelatinous precipitate was removed by filtration to produce a dark-brown solution which was then cooled on ice. Trimethylsilyl azide (3 mL, 22.66 mmol) was added slowly to this solution with rapid stirring. Gas release was observed after each addition and only when the effervescence had ceased was further Me<sub>3</sub>SiN<sub>3</sub> added. After the complete addition of all the Me<sub>3</sub>SiN<sub>3</sub>, the yellow solid [1]Cl was isolated by filtration, washed with fresh CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and dried *in vacuo*. Dark yellow needle-shaped crystals of [1]Cl·2H<sub>2</sub>O were obtained from slow evaporation of a methanolic solution. Yield: 3.00 g (39.9%).

Found (Calc. for C<sub>7</sub>H<sub>4</sub>S<sub>2</sub>NO<sub>2</sub>Cl·<sup>1</sup>/<sub>3</sub>CH<sub>2</sub>Cl<sub>2</sub>): C= 33.68% (33.62); H= 2.03% (1.80); N= 4.93% (5.35); MS (ESI+) *m/z*: 198.0 (M<sup>+</sup>). m.p. 113 °C (dec).

### Synthesis of 4,5-dioxolyl-benzo-1,3,2-dithiazolyl, 1.

A suspension of [1]Cl (1.728 g, 7.39 mmol) and Ag powder (2.27 g, 21.04 mmol) were stirred in MeCN (20 mL) under nitrogen for 16 h to afford a fine suspension under an intense clear supernatant. The solvent was removed *in vacuo* and **1** isolated as small aubergine-coloured needles via vacuum sublimation onto a water-cooled cold finger (10<sup>-1</sup> torr, 45 - 15 °C). Yield: 0.141 g (10%).

Found (Calc. for C<sub>7</sub>H<sub>4</sub>NS<sub>2</sub>O<sub>2</sub>): C= 42.09% (42.41); H= 1.97% (2.03); N= 6.80% (7.07). EPR (THF, 298K) *g* = 2.010, *a<sub>N</sub>* = 11.15 G. M.p. 214-217 °C (dec. to a red liquid).

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### Preparation of 2,3,8,9-tetramethoxydibenzo[c,g]-1,2,5,6-tetrathiocine, **B**.

Sulphur monochloride (0.62 mL, 7.78 mmol) was slowly added dropwise with vigorous stirring to a colourless solution of veratrol (1,2-dimethoxybenzene, 1 mL, 7.78 mmol) in glacial acetic acid (20 mL) under a nitrogen atmosphere. The initial bright yellow colouration gradually darkened affording to a dark blue-green colour. The reaction was left to stir for 16 h at room temperature, to afford an abundant turquoise precipitate suspended under a pale yellow solution. The precipitate was quickly isolated by filtration in a fumescupboard and washed with small fractions of diethyl ether and dried. The resultant blue solid obtained was dissolved in the minimum amount of chloroform (850 mL) to give a very dark turquoise solution which was decolourised by the dropwise addition of a concentrated methanolic solution of tin(II) chloride (3g of anhydrous SnCl<sub>2</sub> in 5 mL MeOH). The solution was then concentrated to half its volume and the tetrathiocine precipitated by treatment with ice-cold methanol (500 mL) and storage at 0°C. The product was isolated as a pale yellow solid by filtration and washed with several fractions of ice-cold methanol. Yield: 1.199g (76.3%).

Found (Calc. for C<sub>16</sub>H<sub>16</sub>S<sub>4</sub>O<sub>4</sub>): C= 47.96% (47.98); H= 4.02% (4.03); <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub> solution): δ/ppm = 7.25 (4 H, s), 3.92 (12 H, s).

### Synthesis of 4,5-dimethoxy-benzo-1,3,2-dithiazolium chloride, [2]Cl

Sulphuryl chloride (0.8 mL, 9.99mmol) was added dropwise to a suspension of tetrathiocine **B** (2.0 g, 4.99 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30mL) under a nitrogen atmosphere. The suspension cleared to afford a dark orange solution of the bis(sulfenyl chloride). The mixture was then refluxed at 55°C for a further 2h before being allowed to cool to room temperature [A small amount of blue insoluble precipitate was occasionally observed and removed by filtration]. Trimethylsilyl azide (1.1 mL, 8.30 mmol) was then added dropwise to this orange solution at 0° C with brisk stirring. Release of N<sub>2</sub> was observed after each small addition and only when the effervescence had ceased was the addition of further Me<sub>3</sub>SiN<sub>3</sub> continued. After complete addition, the yellow suspension was stirred for a few minutes, filtered under nitrogen, washed with fresh CH<sub>2</sub>Cl<sub>2</sub> (2 x 10 mL) and dried *in vacuo* to afford [2]Cl as a microcrystalline yellow solid. Yield: 2.423g (97%).

Found (Calc. for C<sub>8</sub>H<sub>8</sub>S<sub>2</sub>O<sub>2</sub>NCl·½CH<sub>2</sub>Cl<sub>2</sub>): C= 34.55% (34.94); H= 3.23% (3.10); N= 4.40% (4.79). MS (ESI+) *m/z*: 214.0 (M<sup>+</sup>).

### Synthesis of 4,5-dimethoxy-benzo-1,3,2-dithiazolyl, **2**.

A mixture of [2]Cl (1.0 g, 4.00 mmol) and an excess of Zn/Cu couple (1.0 g, 15.63 mmol) were suspended in MeCN (20 mL) and stirred under a nitrogen atmosphere for 15 min. The dark purple suspension was filtered and the filtrate evaporated *in vacuo* to afford a dark residue which was purified via sublimation onto a water-cooled cold finger (10<sup>-1</sup> Torr, 70 - 15°C) to afford **2**. Yield: 0.095 g (11%). Crystals suitable for X-ray diffraction were subsequently grown by re-sublimation under static vacuum (10<sup>-1</sup> Torr) with a small temperature gradient.

Found (Calc. for C<sub>8</sub>H<sub>8</sub>S<sub>2</sub>NO<sub>2</sub>): C= 44.36% (44.84); H= 3.45% (3.76); N= 6.18% (6.54); MS (ESI+-TOF) *m/z* (%) = 214.0 (M<sup>+</sup>, 100), 215.0 (20), 216.0 (20); mp 212 - 217 °C (dec. to a red liquid); EPR (THF, 298 K): *g*= 2.010, *a<sub>N</sub>* = 11.15 G.

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### Intra-dimer S...S contacts in published neutral dithiazolyl radical dimer structures

CCDC code	$d_{S...S}$	Ref
BEZQAZ	3.2119(9) – 3.2574(9)	[1]
BEZQAZ01	3.2717(8) – 3.3222(9)	[1]
BEZQAZ03	3.295(2) – 3.342(2)	[1]
ECOBUU01	3.263(1) – 3.347(1)	[2]
FAGRIO	3.1752(9)	[3]
FAGRIO10	3.1752(8)	[3]
NEWYET	3.458(5) – 3.511(5)	[4]
SAXPOW01	3.2356(8) – 3.3207(8)	[5]
SAXPOW06	3.2841(8) – 3.3653(8)	[5]
SETTIU	3.142(2) – 3.146(2)	[6]
TIVXUS	3.321(2) – 3.374(2)	[7]
TIVXUS01	3.253(2) – 3.260(2)	[7]
XAJDAN	3.097(2) – 3.239(2)	[8]

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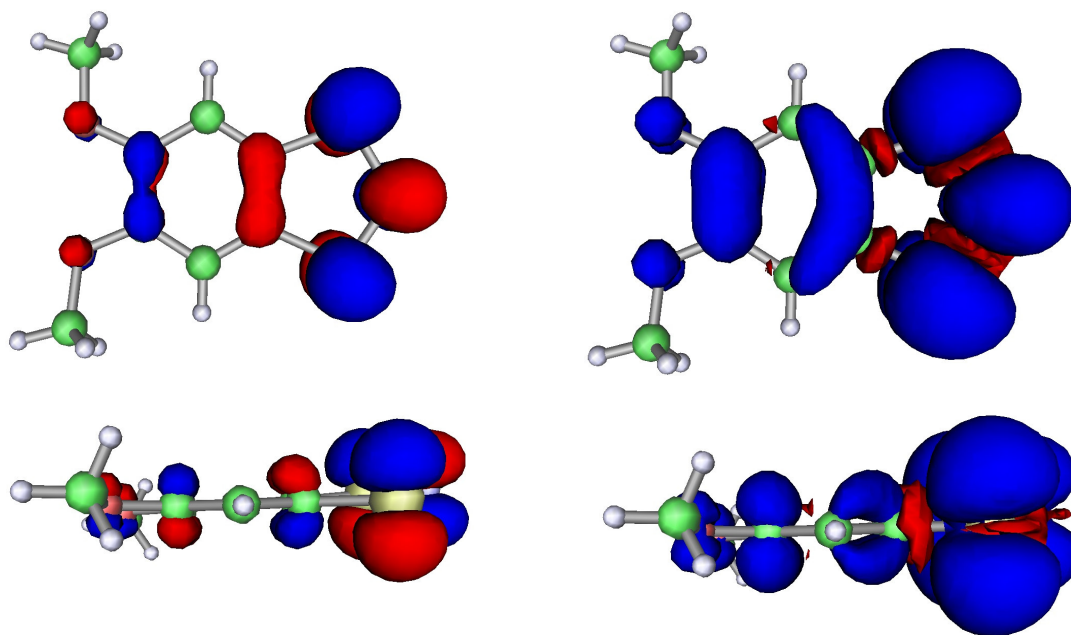
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### DFT Studies on 2

Single point DFT studies were undertaken at the UB3LYP/6-31G\* level within GAMESS-UK<sup>1</sup> in order to determine the spin density distribution in **2**. The singly occupied molecular orbital is shown (below left), alongside the total molecular spin density distribution (positive spin density is in blue and negative spin density in red).



Singly Occupied Molecular Orbital

Spin Density isosurface  $\pm 0.0005 e\text{\AA}^{-3}$

<sup>1</sup> GAMESS-UK is a package of *ab initio* programs. See: "<http://www.cfs.dl.ac.uk/gamess-uk/index.shtml>", M.F. Guest, I. J. Bush, H.J.J. van Dam, P. Sherwood, J.M.H. Thomas, J.H. van Lenthe, R.W.A Havenith, J. Kendrick, "The GAMESS-UK electronic structure package: algorithms, developments and applications", *Molecular Physics*, Vol. 103, No. 6-8, 20 March-20 April 2005, 719-747.