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2,2'-Diaminodiphenylmethane and its 4,4'-dibromo-derivative both react with *N*-sulfinylmethanesulfonamide to form 2,1-benzisothiazole derivatives. Methylation or acetylation of these provides examples of the hypervalent sulfur 2,1-benzisothiazolo[2,3-*b*]-2,1-benzisothiazole system. The nmr spectra of these compounds are discussed.

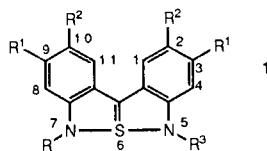
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In a previous paper [1] the synthesis of some examples of the 2,1-benzisothiazolo[2,3-*b*]-2,1-benzisothiazole system (**1**) were reported. These were the 2,10-dimethyl compound **1a**, and some of its *N*-substituted derivatives **1b,c**. Some of these compounds with free N-H atoms display tautomerism with non-fused systems **2**, similarly to certain 1,2,4-thiadiazoles [2]. These compounds **1** are of interest because of the hypervalency of the central sulfur atom, and because of their relationship to dibenzooxathiole[1,5-*e*]oxathioles and to dibenzo-1,2-dithiole[2,3-*b*]-1,2-dithioles. The former display symmetry arising from hypervalency of a central sulfur atom [3,4]. The latter system has not yet been successfully synthesised [5]. This paper describes the preparation and nmr properties of some other examples of this system.

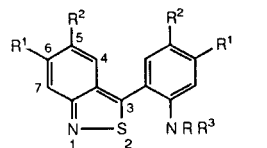
As the previous approach [1], involving *o-o'* coupling of *p*-toluidine derivatives is inappropriate for other syntheses, other approaches were based on the commercially available 4,4'-diaminodiphenylmethane (**3a**). Nitration of this by the method reported [6] to 4,4'-diamino-2,2'-dinitrodiphenylmethane (**3b**) was difficult to control, and superior results were obtained using a fuming nitric acid, sulfuric acid mixture as the nitrating agent. The resulting compound was deaminated to **3c** by the procedure reported [6], as methods based on hypophosphorous acid [7,8] gave very poor yields. The dinitro compound **3c** was satisfactorily reduced to the diamine **3d** by tin in hydrochloric acid.

Likewise the dibromo compound **3e** was made from the diamine **3b** by diazotisation and treatment with copper(I) bromide in hydrobromic acid. This was reduced to **3f** using freshly prepared Raney nickel and hydrazine. With older Raney nickel intermediate reduction products were obtained, but in contrast to other studies [9] no halogen was lost. The course of the reaction is obviously highly dependent on the quality of the Raney nickel catalyst. A standard tin in hydrochloric acid reduction also gave a good yield of **3f**.

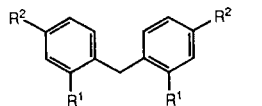
The reaction of the diamine **3d** with *N*-sulfinylmethanesulfonamide, a standard reagent for preparation of 2,1-benzisothiazoles from *o*-toluidines [10], gave a yellow



- a, R = R³ = R¹ = H, R² = CH₃
- b, R = R² = R³ = CH₃, R¹ = H
- c, R¹ = H, R³ = COCH₃, R² = H, R² = CH₃
- d, R = R¹ = R² = R³ = H
- e, R = R² = R³ = H, R¹ = Br
- f, R = R³ = CH₃, R¹ = R² = H
- g, R = R³ = CH₃, R¹ = Br, R² = H
- h, R = R¹ = R² = H, R³ = CH₃CO
- i, R = R² = H, R¹ = Br, R³ = CH₃CO



- a, R = R¹ = R² = R³ = H
- b, R = R² = R³ = H, R¹ = Br
- c, R¹ = R² = R = H, R³ = CH₃
- d, R¹ = Br, R² = R = H, R³ = CH₃
- e, R = R¹ = R³ = H, R² = CH₃
- f, R¹ = R² = H, R = R³ = CH₃CO
- g, R¹ = Br, R² = H, R = R³ = CH₃CO
- h, R¹ = H, R² = R³ = CH₃, R = H
- i, R¹ = H, R² = CH₃, R = R³ = CH₃CO



- a, R¹ = H, R² = NH₂
- b, R¹ = NO₂, R² = NH₂
- c, R¹ = NO₂, R² = H
- d, R¹ = NH₂, R² = H
- e, R¹ = NO₂, R² = Br
- f, R¹ = NH₂, R² = Br

compound whose properties were consistent with the isothiazole **2a**. There was no evidence of the formation of a symmetrical compound **1d** as found earlier for a dimethyl derivative [1]. In particular, the chemical shift of the N-H protons ($\delta = 3.78\text{--}3.84$ ppm), and the complexity of the aromatic protons signals, *i.e.* two non equivalent rings, were consistent with this formulation. This asymmetrical structure was maintained through a *ca* 60° temperature range.

Treatment of the dibromodiamine **3f** with *N*-sulfinylmethanesulfonamide gave a deep red material that was almost insoluble in all solvents tried. Its nmr spectrum in chloroform displayed a broad low field doublet at $\delta =$

8.37-8.80 ppm, which has been observed for the NH proton in fused systems, *i.e.* it is possibly compound **1e**, but attempted purification by crystallisation or chromatography gave a compound whose yellow color and nmr spectrum were consistent with an asymmetrical structure **2b**. It appears that the symmetrical compound **1e** may be tautomerising to the more soluble asymmetrical compound **2b**.

While the compound **2a** was resistant to methylation using iodomethane, treatment with dimethyl sulfate gave two materials; a yellow monomethyl compound and a red dimethyl compound, whose properties were consistent with the unfused structure **2c** and the fused structure **1f** respectively. The dibromo compound **2b** was even more resistant to methylation using either iodomethane or dimethyl sulfate, but with iodomethane in triethylamine two products, a yellow and a red material, were obtained, whose mass spectra were consistent with the non-fused monomethyl compound **2d**, and the fused dimethyl compound **1g** respectively. The latter was formed in only low yield, but further methylation of **2d** gave it in higher yield.

The ¹H chemical shift of the *N*-methyl protons in these compounds, **1f,g** and **2c,d**, as well as the earlier reported [1] **1b** and **2e** may be correlated with the presence of fused or non-fused structures (Table), *eg.*, for the former, absorption is around $\delta = 3.6$ ppm, which is in the range observed for many isothiazoles [11,12,13], including the closely related isothiazolo[5,1-*e*]isothiazoles. For the asymmetrical non-fused forms, absorptions are around $\delta = 2.8$ ppm, the range for *N*-methylanilines.

Table

Proton Chemical Shifts of *N*-Methyl or *N*-acetyl-substituents in
2,1-Benzisothiazolo[2,3-*b*]-2,1-benzisothiazoles **1** and
3-(2-Aminophenyl)-2,1-benzisothiazoles **2**

Compound	δ (R-N-R ³) in ppm	R ³	R
1b	3.64	CH ₃	H
1f	3.67	CH ₃	H
1g	3.59	CH ₃	H
1c	1.93	COCH ₃	H
1h	1.92	COCH ₃	H
1i	1.96	COCH ₃	H
2c	2.81	CH ₃	H
2h	2.80	CH ₃	H
2d	2.80	CH ₃	H
2f	2.16	CH ₃ CO	CH ₃ CO
2i	2.23	CH ₃ CO	CH ₃ CO
2g	2.18	CH ₃ CO	CH ₃ CO

As with the dimethyl compound **2e** [1], both **2a** and **b** reacted readily with acetic anhydride giving two products each whose properties were consistent with mono- and diacetylated derivatives. For the monoacetyl compound formed from **2a**, the N-H signal was in the aromatic range, consistent with the fused structure **1h**, and for the monoacetyl

compound from **2b**, the NH signal, at $\delta = 6.93$ ppm, was also consistent with its formulation as **1i**. By contrast, the two diacetylated compounds, while displaying only one type of acetyl signal each, displayed complex absorptions in the aromatic range, consistent with two types of aromatic ring each. These are thus assigned the non-fused structures **2f,g** respectively. These results are consistent with earlier studies [1]. For these acetyl compounds, the chemical shifts of the acetyl protons may also be correlated with fused or non-fused structures. For **1h** and **1i**, these are around $\delta = 1.95$ ppm, while for **2f,g** shifts are around $\delta = 2.2$ ppm. While these data are consistent (Table), suitable models are difficult to find. The *N*-acetyl group in one isothiazole absorbs at *ca* $\delta = 2.55$ ppm [14]. As this is well outside the range for normal acetyl compounds it is difficult to draw comparisons.

The aromatic ring proton absorptions for the compounds designated **1e-h** were consistent with fused structures. *Eg.*, compounds **1e** and **g** were completely symmetrical and displayed pure ABX type spectra, compound **1f** exhibited two doublets and two triplets, and compound **1i** exhibited two ABX patterns with AB subspectra in the range 7.22-7.44 ppm. While it has a fused structure the two aromatic rings are non-equivalent. The nmr of **1i** exhibited two low-field signals at $\delta = 8.08$ and 8.57 ppm due to the protons H(8) and H(4) respectively. These were distinguished by double resonance experiments whereby H(8) exhibited a slight nOe, when the NH signal was irradiated. The aromatic absorptions of **1h** were more complicated, as there are two different disubstituted aromatic rings and the amino proton also absorbs in that range.

These aromatic proton absorptions for the non-fused compounds **2a-d,f,g** were in the range $\delta = 6.8$ -7.9 ppm for **2a,c** and **f** and for **2b,d**, and **g** in the range 6.90-8.06. The former were very complex while the latter displayed two separate ABX type patterns each.

EXPERIMENTAL

Unless otherwise stated ¹H nmr spectra were obtained in deuteriochloroform solution using tetramethylsilane as an internal standard, on a Varian model AM 300 spectrometer. Mass spectra were obtained on a VG707E spectrometer. Thick layer chromatography was carried out on Merck type silica gel 60 PF 254. Where necessary solutions were dried over anhydrous magnesium sulfate. *N*-Sulfinyl methanesulfonamide (**10**) was freshly prepared or used within a few days of preparation.

Preparation of 2,2'-Dinitro-4,4'-diaminodiphenylmethane (**3b**).

Commercially available 4,4'-diaminodiphenylmethane (Aldrich) was nitrated in concentrated sulfuric acid as reported [6] except that the reaction was done at -40° (acetone/dry ice bath), and a mixture of concentrated sulfuric acid and the calculated quantity of fuming nitric acid used as the nitrating agent. Work up as reported gave the dinitrodiamine **3b** as the dihydrogen sulfate (93%).

Preparation of 2,2'-Dinitrodiphenylmethane (**3c**).

The procedure of Partridge and Vipond [6] was modified as follows. To sodium nitrite (7.1 g, 0.103 mole) in concentrated sulfuric acid (80 ml),

maintained below 10°, was added portionwise the dinitrodiamine **3b**, as its dihydrogen sulfate, (20.0 g, 0.041 mole). To this mixture was added glacial acetic acid (110 ml) over 1 hour, keeping the temperature below 18°. After 30 minutes the solution was added to a vigorously stirred suspension of copper(I) oxide (31.3 g, 0.219 mole) in ethanol (200 ml) over 50 minutes. The temperature rose to 60° during the addition and was maintained at 65° for a further 30 minutes. The mixture was filtered, the residue washed with hot ethanol (50 ml) and combined filtrate and washings added to cold water. After 1 hour a pale brown precipitate was collected and purified by chromatography or alumina in benzene. The product was recrystallised from methanol as pale yellow needles mp 80-82° lit [7] 83.5° (64%).

Preparation of 4,4'-Dibromo-2,2'-dinitrodiphenylmethane (**3e**).

The diazonium salt from **3b**, made as above, was added in portions to a solution of copper(I) bromide (14.8 g, 1.03 moles) in 48% hydrobromic acid (80 ml) and water (100 ml) at 50°. After the addition was complete the solution was kept at 65-70° for a further 30 minutes and then at room temperature for 24 hours. Dilution with water gave a pale yellow precipitate which was collected and purified by chromatography on alumina in benzene. The product was recrystallised from carbon tetrachloride as pale yellow prisms mp 132-134°, lit [7,9] 130° (75%).

Preparation of 2,2-Diaminodiphenylmethane (**3d**).

To the dinitro compound **3c**, (2.58 g, 0.01 moles) and granulated tin (2.7 g, 0.023 mole), was added concentrated hydrochloric acid (45 ml) in three portions, each time swirling and cooling if necessary after the initial reaction had subsided. Ethanol (15 ml) was added and the mixture refluxed 1 hour. The mixture was made strongly alkaline, cooled, and extracted with chloroform. The extract was washed with water, dried, and evaporated to a yellow solid which was recrystallised from 80% aqueous methanol as pale yellow needles mp 132-133°, lit [7], 132-134° (52%).

Preparation of 2,2'-Diamino-4,4'-dibromodiphenylmethane (**3f**).

Method a.

This was performed as above except that the reflux was maintained for 5 hours. Work up gave the diamine **3f** as pale yellow needles mp 153-154° lit [9] 153-154° (67%).

Method b.

To the dinitro compound **3e** (0.5 g, 1.20 mmoles), and 97% hydrazine (1 ml) in ethanol (20 ml) was added freshly prepared Raney nickel catalyst (0.1 g). The mixture was refluxed 15 minutes, cooled, and filtered. The filtrate was diluted with water and extracted with chloroform. The dried extract on evaporation gave a pale yellow crystalline solid that was virtually pure diamine **3f**. It was recrystallised from 80% aqueous methanol as pale yellow needles identical to the material prepared above (92%).

Reaction of 2,2'-Diaminodiphenylmethane with *N*-Sulfinylmethanesulfonamide.

2,2'-Diaminodiphenylmethane (2.4 g, 12 mmoles) in dry benzene (30 ml) was cooled in an ice bath and a solution of *N*-sulfinylmethanesulfonamide (**10**) (3.7 g, 26.2 mmoles) in dry benzene (15 ml) added. To the mixture of 0° was added dry pyridine (2.0 ml, 25.3 mmoles) and the mixture refluxed 48 hours. Solvents were removed *in vacuo*, the residue cooled to 0° and water added. The mixture was extracted with chloroform which was separated, dried and evaporated to an orange pasty solid. This was purified by chromatography using a dichloromethane/ethyl acetate 6:1 mixture as an eluent and the yellow oil obtained on work up crystallised by trituration with hexane. Recrystallisation from a 1:1 mixture of hexane and carbon tetrachloride gave **2a** as deep yellow prisms mp 74-75° (21%).

Compound **2a** had nmr: δ = 3.78-3.84 (2H, broad S, the amino pro-

tons), 6.84-7.85 ppm (8H m, the aromatic protons). This was virtually unchanged between 0° and 57°; ms: M^+ = 226; M Calcd. = 226.

Anal. Calcd. for $C_{13}H_{10}N_2S$: C, 69.00; H, 4.45; N, 12.38; S, 14.17. Found: C, 69.13; H, 4.44; N, 12.42; S, 14.01.

Reaction of 2,2'-Diamino-4,4'-dibromodiphenylmethane with *N*-Sulfinylmethanesulfonamide.

This was done as above but with refluxing only 24 hours. Work-up gave a dark red material which was only partially soluble in any solvent tried. Chromatography of a chloroform extract in a dichloromethane/ethyl acetate 5:1 mixture gave a dark yellow material which recrystallised from cyclohexane giving **2b** as yellow plates mp 128-129° (43%).

Compound **2b** had nmr: δ = 3.82-3.89 ppm (2H, broad s, the amino protons), 6.99-7.09 ppm (3H, m, the aromatic protons), 7.28-7.32 ppm (1H, m, H(5)), 7.82-7.45 ppm (1H, m, H(4)), 8.05-8.06 ppm (1H, m, H(7)); ms: M^+ = 386, 384, 382; M Calcd. = 386, 384, 382.

Anal. Calcd. for $C_{13}H_8Br_2N_2S$: C, 40.65; H, 2.10; Br, 41.67; N, 7.29; S, 8.35. Found: C, 40.48; H, 2.19; Br, 41.92; N, 7.40; S, 8.38.

The solid residue could not be recrystallised, but it dissolved slightly in boiling toluene giving a dark red solution. It was too insoluble for a satisfactory nmr spectrum; ms: M^+ = 386, 384, 382; M Calcd. = 386, 384, 382.

Methylation of 3-(2-Aminophenyl)-2,1-benzisothiazole (**2a**).

The isothiazole (0.12 g, 0.54 mmole), anhydrous potassium carbonate (0.166 g, 1.2 mmoles) and dimethyl sulfate (0.150 g, 1.2 mmoles) in anhydrous acetone (10 ml) were refluxed 24 hours. The mixture was diluted with water and the dried chloroform extract evaporated to give an orange semi-crystalline solid. This separated by chromatography in chloroform into a deep yellow and a red compound, corresponding to compounds **2c** and **1f** respectively. Compound **2c** crystallised from cyclohexane as yellow prisms mp 96-97° (86%).

Compound **2c** had nmr: δ = 2.81 ppm (3H, d, the *N*-methyl protons), 3.90 ppm (1H, broad, s, the amino proton), 6.80-7.91 ppm (3H, bands, the aromatic protons); ms: M^+ = 240; M Calcd. = 240.

Anal. Calcd. for $C_{14}H_{12}N_2S$: C, 69.97; H, 5.03; N, 11.66; S, 13.34. Found: C, 69.83; H, 5.08; N, 11.54; S, 13.26.

Compound **1f** crystallised from ethanol as deep red needles mp 163-165° (11%).

Compound **1f** had nmr: δ = 3.67 ppm (6H, s, the *N*-methyl protons), 7.10-7.15 ppm (2H, txd), 7.23-7.27 ppm (2H, d), 7.49-7.54 ppm (2H, txd), and 8.75-8.78 ppm (2H, d); ms: M^+ = 254; M Calcd. = 254.

Anal. Calcd. for $C_{15}H_{14}N_2S$: C, 70.87; H, 5.51; N, 11.02; S, 12.60. Found: C, 71.10; H, 5.49; N, 11.08; S, 12.53.

Methylation of 3-(2-Amino-4-bromophenyl)-6-bromo-2,1-benzisothiazole (**2b**).

The isothiazole (300 mg, 0.8 mmole) in dichloromethane (20 ml), methyl iodide (4 ml) and triethylamine (121 mg, 1.2 mmoles), was refluxed 3 days. Solvents were removed *in vacuo* and the residue examined by chromatography using dichloromethane as an eluent. The main product was a yellow solid corresponding to **2d**. Small amounts of a red material corresponding to **1g** were also obtained.

Compound **2d** crystallised from hexanes as metallic yellow prisms mp 141-145° (67%).

Compound **2d** had nmr: δ = 2.80 ppm (3H, s, the *N*-methyl protons), 3.68-4.12 ppm (1H, broad s, the amino proton), 6.90-8.00 ppm (6H, bands, the aromatic protons); ms: M^+ = 400, 398, 396; M Calcd. = 400, 398, 396.

Anal. Calcd. for $C_{14}H_{10}Br_2N_2S$: C, 42.24; H, 2.53; Br, 40.20; N, 7.04; S, 8.05. Found: C, 42.37; H, 2.64; Br, 39.92; N, 6.89; S, 8.32.

Compound **1g** crystallised from ethanol as deep red needles mp 258-260° (6%).

The nmr spectrum of **1g**, δ = 3.59 (6H, s, the *N*-methyl protons), 7.16-7.20 (2H, dxd, H(2), H(10)), 7.38-7.39 ppm (2H, d, H(4), H(8)), 8.43-8.46 ppm (2H, d, H(1), H(11)); ms: M^+ = 414, 412, 410; M Calcd. = 414, 412, 410.

Anal. Calcd. for $C_{15}H_{12}Br_2N_2S$: C, 43.71; H, 2.93; Br, 38.83; N, 6.80; S,

7.78. Found: C, 43.82; H, 3.07; Br, 38.56; N, 6.72; S, 39.02.

Conversion of 3-(4-Bromo-2-methylaminophenyl)-6-bromo-2,1-benzisothiazole (**2d**) into 3,9-Dibromo-5,7-dimethyl-2,1-benzisothiazolo[2,3-*b*]-2,1-benzisothiazole (**1g**).

The compound **2d** (50 mg, 0.13 mmole) in anhydrous acetone (5 ml), with dimethyl sulfate (19.0 mg, 0.15 mmole) and potassium carbonate (20.7 mg, 0.15 mmole) was refluxed 48 hours. The mixture was diluted with water and extracted with chloroform. Evaporation gave an orange oil that was separated by chromatography in dichloromethane. The compound **1g** was crystallised from ethanol as red needles, identical to that prepared above (16%). Starting material (80%) was recovered.

Acetylation of 3-(2-Aminophenyl)-2,1-benzisothiazole (**2a**).

The isothiazole (50 mg, 0.22 mmole) in acetic anhydride (5 ml) was refluxed 20 minutes, then water (5 ml) was added and the mixture stirred a further 20 minutes to decompose unreacted acetic anhydride. A chloroform extract was washed with sodium bicarbonate solution, dried and evaporated to an oily solid. This separated by chromatography using a dichloromethane/ethyl acetate 2:1 mixture as an eluent into two pale yellow bands with a blue fluorescence in uv light.

Evaporation of eluents gave **1h** and **2f** as a pale yellow solid and a pale yellow oil respectively.

Compound **1h** crystallised from methanol as colorless plates mp 183-184° (78%).

Compound **1h** had nmr: δ = 1.92 ppm (3H, s, the acetyl protons), 7.20-7.53 ppm (7H, m, the aromatic and amino protons), 7.76-7.79 ppm (1H, d, H(6)), 8.19-8.27 ppm (1H, d, H(8)); ms: M^+ = 268; M Calcd. = 268.

Anal. Calcd. for $C_{15}H_{12}N_2OS$: C, 67.14; H, 4.50; N, 10.44; S, 11.95. Found: C, 66.90; H, 4.56; N, 10.38; S, 11.70.

Compound **2f**, obtained as a pale yellow oil, could not be crystallised (21%).

Compound **2f** had nmr: δ = 2.16 ppm (6H, s, the acetyl protons), 7.21-7.84 ppm (8H, bands, the aromatic protons); ms: M^+ = 310; M Calcd. = 310.

This compound appears to decompose readily and satisfactory analyses were not obtained.

Acetylation of 3-(2-Amino-4-bromophenyl)-6-bromo-2,1-benzisothiazole (**2b**).

This was performed as above except that the mixture was heated 1 hour. Work-up gave a mixture of mono- and di-acetylated products which were separated by chromatography using a 3:1 mixture of dichloromethane and ethyl acetate as an eluent.

The monoacetyl compound **1i** recrystallised from ethyl acetate as long colorless needles mp 199-200.5° (43%).

Compound **1i** had nmr: δ = 1.96 ppm (3H, s, the acetyl protons), 6.93

ppm (1H, broad, the amino proton) 7.22-7.25 (1H, d, H(11)), 7.30-7.34 (1H, dxd, H(1)), 7.35-7.39 (1H, dxd, H(2)), 7.41-7.45 (1H, dxd, H(10)), 8.08-8.09 (1H, dxd, H(4)), 8.57 (1H, m, H(8)), H(8) and H(4) were assigned on the basis that the peak at δ = 8.57 ppm showed a slight nOe when the amino proton was irradiated; ms: M^+ = 428, 426, 424; M Calcd. = 428, 426, 424.

Anal. Calcd. for $C_{15}H_{10}Br_2N_2OS$: C, 42.28; H, 2.36; Br, 37.56; N, 6.57; S, 7.52. Found: C, 41.96; H, 2.37; Br, 37.22; N, 6.69; S, 7.89.

The diacetyl compound **2g** was obtained as a yellowish oil that crystallised on trituration with ice cold ethanol. It was recrystallised from acetone as yellow needles mp 135°-137° (48%).

Compound **2g** had nmr: δ = 2.18 ppm (6H, s, the acetyl protons), 7.32-8.06 ppm (6H, bands, the aromatic protons); ms: M^+ = 470, 468, 466; M Calcd. = 470, 468, 466.

Anal. Calcd. for $C_{17}H_{12}Br_2N_2O_2S$: C, 43.61; H, 2.58; Br, 34.19; N, 5.98; S, 6.85. Found: C, 43.43; H, 2.61; Br, 34.06; N, 5.86; S, 6.99.

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