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SYNTHESIS AND PROPERTIES OF 1,2-BENZODITHIINS

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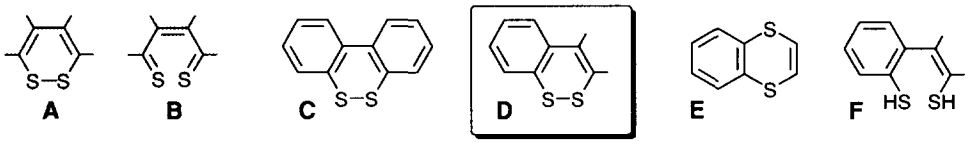
Abstract: Access to the title compounds (**12-14**) was achieved by two different syntheses starting from either phenylacetylene (**1**) or, from benzo[b]thiophene (**2**) by a reaction sequence formally equivalent to the insertion of sulfur. The key intermediates in both routes are the (*Z,Z*)-styrene-1,4-dithiol derivatives **4-6** and **9-11**, respectively. Compared with monocyclic 1,2-dithiins, the absorption maxima of compounds **12-14** occur at shorter wavelengths and they are significantly more stable towards sulfur extrusion. The oxidation of **12** and **14** to the sulfoxides **17a** and **17b**, and to the aldehyde **18**, respectively, are reported.

The 1,2-dithiin system **A** (*Scheme 1*) continues to attract considerable attention for several reasons.[1-5] Studies on this type of compound have focused on a number of areas such as (a) structure, i.e. the problem of a butadiene bridged disulfide structure **A** versus the acyclic valence tautomer **B**; (b) colour: 1,2-dithiins are red compounds with absorption maxima up to 550 nm, yet no conventional chromophoric groups are present; (c) stability: at ambient temperature and in the presence of light, solutions of 1,2-dithiins extrude sulfur with the formation of thiophenes; and (d) occurrence in plants: a number of 1,2-dithiins isolated from plants have promising biological activities (3,6-dialkynyl-1,2-dithiins, e.g. thiarubrines and dihydrothiarubrines).

Scheme 1



Anellation significantly alters the properties of 1,2-dithiins. Thus dibenzo-1,2-dithiin **C** is neither coloured nor shows any tendency to extrude sulfur.[6] These facts prompted us to investigate the properties of 1,2-benzodithiins **D** which, unlike the corresponding 1,4-benzodithiins[7] **E**, are hitherto unknown. However, from our previous successes involving the synthesis of 1,2-dithiin and 3,6-disubstituted analogues via (*Z,Z*)-buta-1,3-diene-1,4-dithiols derived from diacetylenes,[1a,b] we deduced that 1,4-dithiols **F** should be key intermediates in the synthesis of **D**. We now report a straightforward approach to the 1,2-benzodithiin series (**12-14**,**17**,**18**; *Scheme 2*) starting from either phenylacetylene (**1**) or benzo[b]thiophene (**2**). The reaction sequences are outlined below.

Treatment of **1** with *n*-butyllithium and potassium *t*-butoxide followed by the addition of dimethyl disulfide according to ref.[8] afforded *o*-methylthiophenylacetylene **3a**, which on subsequent reaction with ethanolic phenylmethanethiol in the presence of sodium ethoxide was transformed to the (*Z*)-adduct **4a**. Deblocking of the latter with sodium in liquid ammonia gave the bis-thiolate **9**. Oxidation of the latter with potassium hexacyanoferrate(III) led to the parent compound **12** of the series. In an analogous reaction metallated **1** was converted to *o*-benzylthiophenylacetylene **3b**, albeit in low isolated yield, using dibenzyl disulfide.

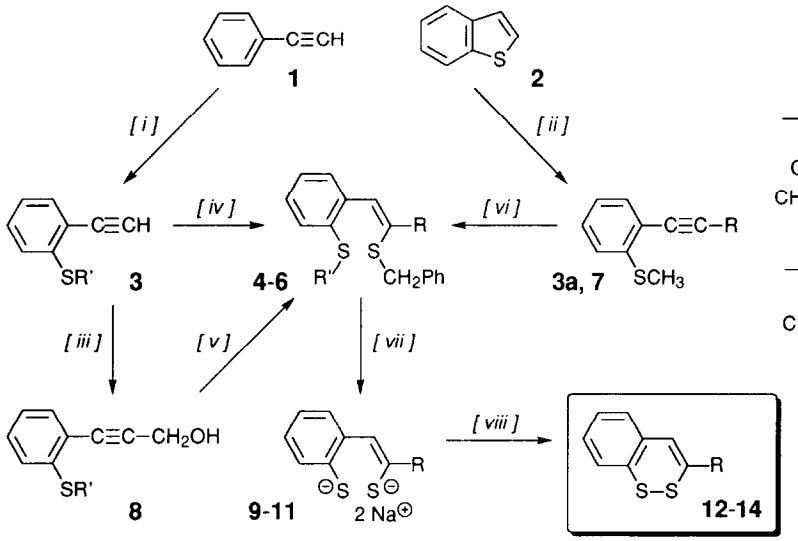
Lithiated **3a** and **3b** reacted with formaldehyde to produce the hydroxymethyl derivatives **8a** and **8b** which were then treated with phenylmethanethiolate (use of the Koreeda-Yang variant[1j] in the monocyclic series) to yield the (*Z*)-benzylthio styrenes **6a** and **6b**. Reductive deblocking and oxidation of the resulting bis-thiolate **11** (as above) gave 3-hydroxymethyl-1,2-benzodithiin **14**.

Ring opening of benzo[b]thiophene (**2**) using sodamide in liquid ammonia[9] followed by quenching with iodomethane gave **3a** and **7** (ratio depending on the ratio of **2** and iodomethane).[9b,10] Transformation of **7** via **5a** and **10** using the above reaction sequence gave 3-methyl-1,2-benzodithiin **13** (overall ring expansion of a thiophene to a 1,2-dithiin by the formal insertion of sulfur).

When **6a** was treated with sodium in liquid ammonia, preferential reduction of the alkenyl system occurred.[11] Oxidation of the intermediate using potassium hexacyanoferrate(III) gave, after chromatography, two crystalline products. These are tentatively assigned the structures **15** and **16** (*Scheme 3*), presumably arising by an intramolecular mechanism as illustrated in **G**.

In common with other heterocyclic compounds possessing a structure similar to naphthalene such as 2H-thiochromene[12] and 1,2-dihydroquinoline[13], the 1,2-benzodithiins **12** and **13** have naphthalene like odors. Compounds **12-14** are characterized by absorption maxima in the visible region, but these occur at shorter wavelengths compared with compounds of general structure **A** (see table 1). In addition, their electronic spectra are significantly different from the isomeric 1,4-benzodithiins **E** (see table 1, footnote [b]). The 1,2-benzodithiins **12-14** show less tendency for sulfur extrusion compared with their monocyclic counterparts, e.g. **13** is unaltered in boiling toluene solution for 6 hours in the absence of light.[14]

Scheme 2

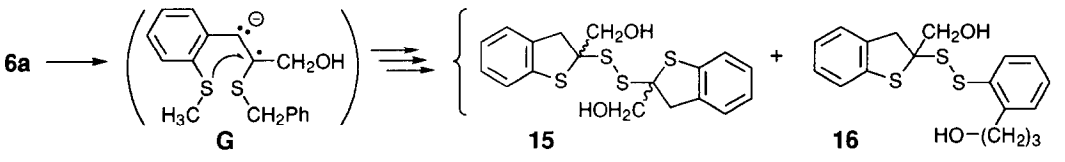


R	
H	4 9 12
CH_3	5 7 10 13
CH_2OH	6 11 14

R'	
CH_3	a
CH_2Ph	b

[i] *n*BuLi/*t*BuOK, THF, -70°C; R'SSR', -60°C; → **3a**: 65%; **3b**: 10% (Kugelrohr distill.). — *[ii]* $NaNH_2$/ NH_3/Et_2O, 4 -5 h, -35°C, MeI: → **3a**: 56%; **7**: 70%. — *[iii]* *n*BuLi, Et_2O/THF, $(CH_2O)_n$, 35°C; → **8a**: 73%; **8b**: 78%. — *[iv]* $PhCH_2SH$, EtONa/ EtOH, reflux, 9 h; → **4a**: 65%. — *[v]* $PhCH_2SH$, DMF/KOH (catal.), 3 h, 20°C; → **6a**: 71%; **6b**: 72%. — *[vi]* $PhCH_2SH$, 18-crown-6/benzene/H_2O/KOH, reflux, 24 h; → **5a**: 20%. — *[vii]*/*[viii]* Na/NH_3, -70°C; $K_3[Fe(CN_6)]/H_2O$ → **12**: 35%; **13**: 45%; **14**: 48%.

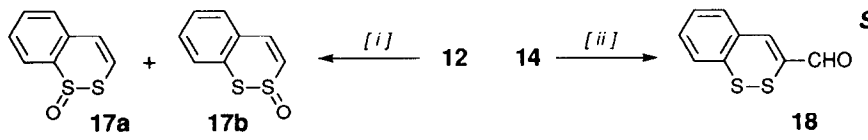
Scheme 3



Na/NH_3, -70°C; $K_3[Fe(CN_6)]/ H_2O$; → **15**: 27%; **16**: 38% (isolated yields).

As a result of their enhanced stability, the 1,2-benzodithiins are capable of oxidation without disruption of the dithiin ring (*Scheme 4*). Thus oxidation of **12** with 3-chloroperoxybenzoic acid leads to the formation of the isomeric sulfoxides **17a** and **17b** (ratio 2.4:1), whilst *Swern*-oxidation of **14** produces the aldehyde **18**. Compound **18** was also obtained as a by-product during the oxidation of **11** to **14** (see *Scheme 2*). The pronounced bathochromic shift (> 40 nm) in the UV/Vis spectrum of **18** should be noted (cf. also ref.[1j]).

Scheme 4



[i] MCPBA, CH_2Cl_2, 0°C, 1 h; → **17a,b**: 65% (2.45:1). — *[ii]* $(COCl)_2$, DMSO, CH_2Cl_2, NEt_3, -50/-60°C, 10 min; → **18**: 100%.

Table 1. Physical and spectroscopic data for selected compounds [a]

12: Yellow needles (*n*-hexane)/orange-coloured oil; m.p. 15-16°C. – UV (EtOH): λ_{max} (lg ε) = 242 (3.56), 263 (3.79; sh), 267 (3.83; sh), 271 (3.92), 314 (2.94), 407 (2.48) nm. [b] – ^{1}H NMR ($CDCl_3$): δ = 6.55 (d, J = 9.4 Hz; 1 H, =CH-S-), 6.85 (d, J = 9.4 Hz; 1 H, =CH-arene), 7.00-7.08 (m; 1 H, arene H), 7.15-7.27 (m; 3 H, arene H). – ^{13}C NMR ($CDCl_3$): δ = 125.3, 128.1, 128.4(0), 128.4(3), 128.4(4), 129.4, 132.1, 134.8 (8 C, arene and alkene C). – MS (70 eV): m/z (%) = 166 (100) $[M]^+$, 134 (49) $[M - S]^+$, 90 (21) $[M - S - CS]^+$.

13: Yellow needles (*n*-hexane); m.p. 39-40°C. – UV (EtOH): λ_{max} (lg ε) = 236 (4.01), 266 (4.07; sh), 269 (4.15), 308 (3.56), 405 (2.22) nm. – ^{1}H NMR ($CDCl_3$): δ = 2.17 (d, J = 1.5 Hz; 3 H, $-CH_3$), 6.66 (q, J = 1.5 Hz; 1 H, =CH-arene), 6.93-7.28 (m, 4 H, arene H). – ^{13}C NMR ($CDCl_3$): δ = 23.7 ($-CH_3$), 127.1, 127.6(2), 127.6(4), 128.0, 128.2, 128.5, 136.3, 138.0 (8 C, arene and alkene C). – MS (70 eV): m/z (%) = 180 (100) $[M]^+$, 147 (85) $[M - SH]^+$, 135 (24) $[M - CHS]^+$.

14: Yellow prisms (*n*-hexane/$CHCl_3$); m.p. 47-48°C. – UV (EtOH): λ_{max} (lg ε) = 265 (3.75), 267 (3.73; sh), 297 (3.43; sh), 404 (2.37) nm. – ^{1}H NMR ($CDCl_3$): δ = 1.56 (s, 1 H, unassociat. OH), 1.87 (t, J = 6.2 Hz; 1 H, associat. OH), 4.34 (pseudo-s, 2 H, $-CH_2OH$), 6.90 (s, 1 H, alkene H), 7.07-7.30 (m, 4 H, arene H). – ^{13}C NMR ($CDCl_3$): δ = 65.0 ($-CH_2OH$), 127.3, 128.1, 128.3, 128.4, 128.6, 129.3, 135.4, 141.1 (8 C, arene and alkene C). – MS (70 eV): m/z (%) = 196 (100) $[M]^+$, 178 (33) $[M - H_2O]^+$, 166 (88) $[M - CH_2O]$, 164 (31) $[M - S]^+$, 147 (26) $[M - S - OH]^+$, 134 (75) $[M - CH_2O - S]^+$, 121 (55) $[M - CH_2O - CHS]^+$. – IR: $\tilde{\nu}$ (KBr) = 3000-3400 (m, broad, associat. OH) cm^{-1}; $\tilde{\nu}$ (CCl_4; dilute solution) = 3150-3565 (intermolecul. associat. OH), 3612 (sharp, intramolecul. OH/S bond), 3630 (sharp, unassociat. OH) cm^{-1}.

15: Colourless prisms; 1:1-diastereom. mixture; m.p. 145-165°C [after recrystall. (AcOEt): Colourless rod-like crystals; 85:15-diastereom. mixture; m.p. 175-178°C]. – ^{1}H NMR (DMSO-d_6): δ (double set of signals) = 3.26-3.54 (m, 4 H, arene-CH_2-), 3.68-3.83 (m, 4 H, $-CH_2OH$), {5.66 (t, J = 5.4 Hz, 2 H, -OH), 5.75 (t, J = 4.8 Hz, 2 H, -OH)}, 7.01-7.33 (m, 8 H, arene H). – ^{13}C NMR (DMSO-d_6): δ (double set of signals) = {42.1, 42.2 (2 C, arene-CH_2-)}, {65.1, 65.2 (2 C, $-CH_2OH$)}, {77.8, 78.0 [2 C, -C(S-)(S-)CH_2OH]}, {122.1, 122.2}, {125.0, 125.1}, {125.1, 125.4}, {127.4, 127.5}, {137.8, 138.0}, {138.9, 139.0} (12 C, arene C). – MS (20 eV): m/z (%) = 394 (0.02) $[M]^+$, 376 (0.08) $[M - H_2O]^+$, 358 (0.3) $[M - 2\,H_2O]^+$, 179 (3) $[M/2 - H_2O]^+$, 165 (98) $[M/2 - S]^+$, 135 (100) $[M/2 - S - CH_2OH]^+$. – IR (nujol): $\tilde{\nu}$ = 3200-3600 (m, broad, assoc. OH) cm^{-1}.

16: Colourless prisms (*n*-hexane/AcOEt); m.p. 102-103°C. – ^{1}H NMR ($CDCl_3$): δ = 1.58 [s, broad, 2 H, -C(S-)(S-)CH_2OH, $-(CH_2)_3$-OH; disappears on addition of D_2O], 1.88 (m, 2 H, $-CH_2-CH_2-CH_2OH$), 2.88 (t, J = 7.7 Hz; 2 H, $-CH_2-CH_2-CH_2OH$), 3.34 [s, 2 H, arene-CH_2-C(S-)(S-)-], 3.68 (t, J = 6.3 Hz; 2 H, $-CH_2-CH_2CH_2OH$), 3.83 [d, J = 12.0 Hz; 1 H, -C(S-)(S-)CH_2OH], 4.01 [d, J = 12.0 Hz; 1 H, -C(S-)(S-)CH_2OH], 6.94 (d, J = 7.6 Hz; 1 H, arene H), 7.02-7.21 (m, 6 H, arene H), 7.62 (d, J = 6.8 Hz; 1 H, arene H). – ^{13}C NMR ($CDCl_3$): δ = 29.8, 33.3 (2 C, arene-CH_2-CH_2), 42.4 [arene-CH_2-C(S-)(S-)CH_2OH), 62.1 ($-CH_2-CH_2-CH_2OH$), 65.9 [-C(S-)(S-)CH_2OH], 78.6 [-C(S-)(S-)CH_2OH], 122.6, 125.3, 125.7, 127.0, 127.3, 127.7, 128.3, 129.7, 135.7, 137.5, 138.7, 140.2 (12 C, arene C). – MS (20 eV): m/z (%) = 346 (14) $[M - H_2O]^+$, 334 (2) $[M - CH_2O]^+$, 200 (2) $[C_6H_4(C_3H_6OH)(SSH)]^+$, 167 (7) $[C_6H_4(C_3H_6OH)(S)]^+$, 165 (63) $[C_6H_4CH_2C(CH_2OH)(S-)]^+$, 147 (61) $[C_6H_4CH_2C(CH_2OH)(S-) - H_2O]^+$, 135 (100) $[C_6H_4CH_2C(CH_2OH)(S-) - CH_2O]^+$. – IR (nujol): $\tilde{\nu}$ = 3100-3500 (m, broad, assoc. OH) cm^{-1}.

17a,b: Pale yellow oil (**a**/**b** = 2.45:1). – ^{1}H NMR (DMSO-d_6): δ = 6.80 (d, J = 9.6 Hz; 1 H, C^3-H [**a**]), 7.33 (d, J = 10.0 Hz; 1 H, C^4-H [**b**]), 7.41 (d, J = 10 Hz; 1 H, C^3-H [**b**]), 7.45 (t, d, 7.5 and 1.2 Hz; 1 H, C^6-H, [**b**]), 7.49 (d, J = 9.6 Hz; 1 H, C^4-H [**a**]), 7.51 (t, d, J = 7.6 and 1.6 Hz; 1 H, C^7-H [**b**]), 7.56 (t, d, J = 7.5 and 1.4 Hz; 1 H, C^6-H [**a**]), 7.58-7.62 (m, 3 H, C^5-H [**a**], C^5-H [**b**], C^8-H [**b**]), 7.65 (t, d, J = 7.5 and 1.1 Hz; 1 H, C^7-H [**a**]), 7.77 (d, J = 7.7 Hz, 1 H, C^8-H [**a**]). – ^{13}C NMR ($CDCl_3$): δ = 112.5, 124.1, 124.4, 126.3, 126.8, 127.3, 127.9, 128.1, 129.4, 130.0, 130.8, 131.3(5), 131.3(8), 132.5, 133.8 (16 C, arene and alkene C; one signal covered). – MS (70 eV): m/z (%) = 182 (5) $[M]^+$, 166 (3) $[M - O]^+$, 134 (100) $[M - SO]^+$. – IR (nujol): $\tilde{\nu}$ = 1092 (s, S=O) cm^{-1}.

18: Red oil. – UV (MeCN): λ_{max} (lg ε) = 250 (3.81), 281 (4.05, sh), 293 (4.12), 449 (2.84) nm. – ^{1}H NMR ($CDCl_3$): δ = 7.25-7.41 (m, 4 H, arene H), 7.55 (s, 1 H, alkene H), 9.56 (s, 1 H, -CHO). – ^{13}C NMR ($CDCl_3$): δ = 128.7, 128.8, 130.5, 131.4, 132.5, 134.5, 141.2, 145.8 (8 C, arene and alkene C), 187.4 (-CHO). – IR (nujol): $\tilde{\nu}$ = 2823, 2723 (w, C-H [-CHO]), 1673 (s, C=O) cm^{-1}.

[a] Satisfactory elemental analyses were obtained for all compounds. – [b] Cf. 1,4-benzodithiin (**E**)[7a]; UV (EtOH): λ_{max} (lg ε) = 253 (4.23), 262 (3.81), 301 (2.91) cm^{-1}; 6,7-dimethyl-1,4-benzodithiin[7b]: UV (*n*-hexane): λ_{max} (lg ε) = 237 (3.95), 252 (3.70), 299 (3.31) nm.

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Dedicated to Professor Manfred Schulz on the occasion of his 65th birthday

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14 In light sulfur extrusion is slow compared to **A**. The quantum yield of decolourization (sulfur extrusion) for **13** in EtOH (λ_{irr} = 405 nm) was 0.20, whereas for 3,6-diphenyl-1,2-dithiin[1b] (λ_{max} = 460 nm; λ_{irr} = 436 nm) the quantum yield was 0.91 (*G. Israel*, University of Halle, unpublished results).

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