Organic & Biomolecular Chemistry

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Journal:	*Organic & Biomolecular Chemistry*
Manuscript ID	OB-ART-11-2023-001871.R1
Article Type:	Paper
Date Submitted by the Author:	11-Jan-2024
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ARTICLE

Reductive Dimerization of Benzothiazolium Salts

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Three different types of reaction products were obtained from the reduction of 2-substituted 3-methylbenzothiazolium salts using Na:Hg (1 wt%). Depending on the 2-substituents, two types of dimeric compounds were obtained: the 2-cyclohexyl-, 2-phenyl-, and 2-(*p*-tolyl)-substituted species are reduced to the corresponding 2,2′-bibenzo[*d*]thiazoles, while their 2-((*p*-OMe)C_6H_4)- and 2-(*p*-NMe_2)C_6H_4)-substituted derivatives afford cis-[1,4]benzothiazino[3,2-*b*][1,4]benzothiazines. Furthermore, in the presence of molecular O_2, new disulfide derivatives were obtained from the bibenzo[*d*]thiazoles. The products were obtained in a moderate to good yield, and the structures were confirmed using single-crystal X-ray diffraction. The electro-chemistry and further reactivity towards different oxidants of the dimeric compounds were studied; the 2,2′-bibenzo[*d*]thiazoles show oxidation potentials similar to that of ferrocene and are converted back to the corresponding benzothiazolium cations by mild oxidants such as TCNQ. In contrast, the benzothiazino-benzothiazines show no oxidations in the solvent window of THF.

Introduction

N,S-Based 5- and 6-membered heterocyclic compounds, such as benzothiazoles and benzothiazines, respectively, have gathered enormous interest in the past few decades. Notably, a number of reactions have been studied related to benzothiazoles and benzothiazines and their derivatives due to interest in a wide range of pharmacological effects and in their use as synthetic intermediates.[1–4] An important feature of benzothiazoles, from both chemical and biochemical points of view, is that the 3-alkylbenzothiazolium salts **1**$^+$ undergo a myriad of chemical transformations.[2] Depending on the substituents at C-2 and/or N-atom of the 1,3-thiazole ring and the reaction conditions, the chemical reduction of benzothiazolium salts result in a variety of products, including hydrogen-reduced species (**1H**, Figure 1) and dimers of the corresponding radicals (**1_2**, this work).[5] In particular, reduction using $NaBH_4$ results in hydride donors, 2,3-dihydrobenzo[d]thiazoles (**1H**, Figure 1), useful for many important chemical and biological processes.[6] In addition, examples unsubstituted in the 2-position (Y = H) can be deprotonated; reaction with bases such as NEt_3 or KH affords carbenes, which typically dimerize to bis(benzo-1,3-thiazolyline-2-ylidene) species (**I_2**, Figure 1),[7–9] but have in some cases been isolated when sufficiently sterically hindered, in particular in the case of 3-(2,6-diisopropyl)-4,5-dimethyl-1,3-thiazolyline-2-ylidene (**I**, Figure 1).[8] A wide range of analogous hydrides **2H**, dimers **2_2**, and carbene dimers **II_2** (Figure 1) have also been obtained from the corresponding benzimidazolium cations **2**$^+$ using $NaBH_4$, Na:Hg (1 wt%), or NaH respectively.[6,10–14] All three classes of molecules have proved effective reducing agents in organic syntheses, and **2H** and **2_2** have been used as molecular n-type dopants for various organic electronic devices.[10,11,15,16] Amides, **III**, have been found as a by-product during the synthesis of **2_2**[11] or from the oxidative decomposition of **2_2** or **2H** derivatives.[11,17]

Because of the increased significance of N,S-heterocyclic compounds in pharmaceutical chemistry, possible materials applications analogous to those of their benzimidazolium-derived counterparts, and the diverse reactivities of benzothiazolium salts **1**$^+$, we were interested in exploring their reactivity and began our work with their chemical reduction reactions. Herein, we report the synthesis of some **1_2** derivatives, along with the unexpected finding that reduction of some **1**$^+$ derivatives give, instead, isomers of **1_2** (**1_2′**) involving the opening of the five-membered ring of the heterocycle and formation of a structure consisting of fused six-membered heterocycles.

Results and Discussion

Akiba et al. have previously reported that the reaction of 3-methyl-2-pheny-benzothiazolium salts **1**$^+$**X**$^-$ (X = I/ClO_4/OSO_3Me) with Grignard affords two types of products: 2,2′-diphenyl-3-methylbenzothiazole **1Y′** as the major product, and the dimer 2,2′-diphenyl-3,3′-dimethyl-2,2′,3,3′-tetrahydro-2,2′-bibenzo[d]thiazole **1_2** (Y = Ph) as the minor product (Scheme 1).[18] They attributed the formation of the **1_2** to a transition-metal impurity present in the magnesium used. **1_2**

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†Electronic Supplementary Information (ESI) available: Crystallographic data, electrochemistry, absorption spectra for redox reactions, and NMR spectra. See DOI: 10.1039/x0xx00000x

derivatives (Y = H) can be directly made from the reaction of N-methyl-2-aminothiophenol with glyoxal,[19] and another has also been prepared by the addition of an electrophile, specifically $HP(O)(OMe)_2$ to the C=C bond of a $\mathbf{I_2}$ (R = Me) derivative.[20]

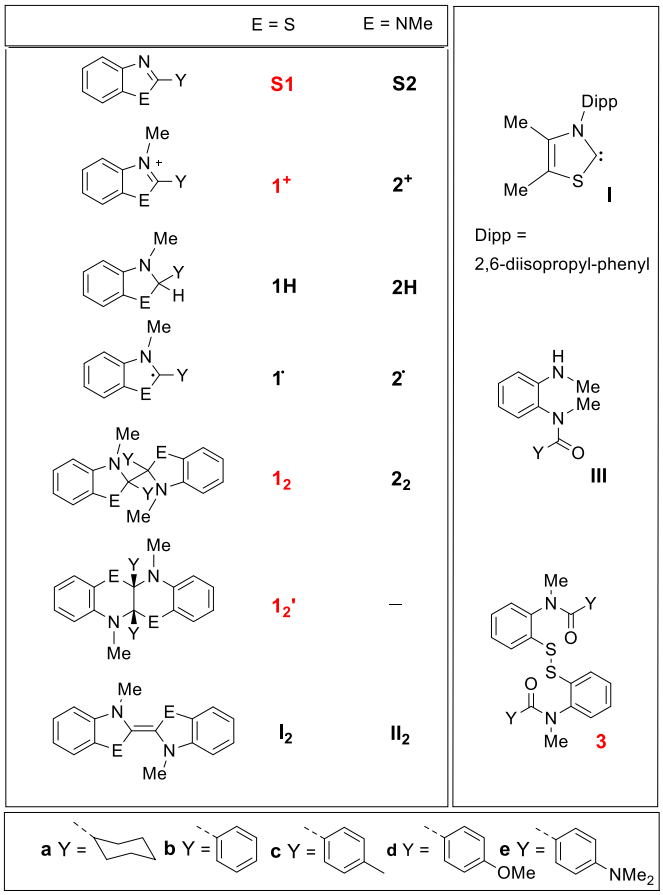
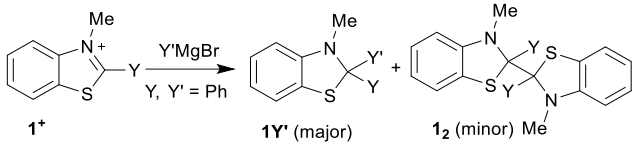
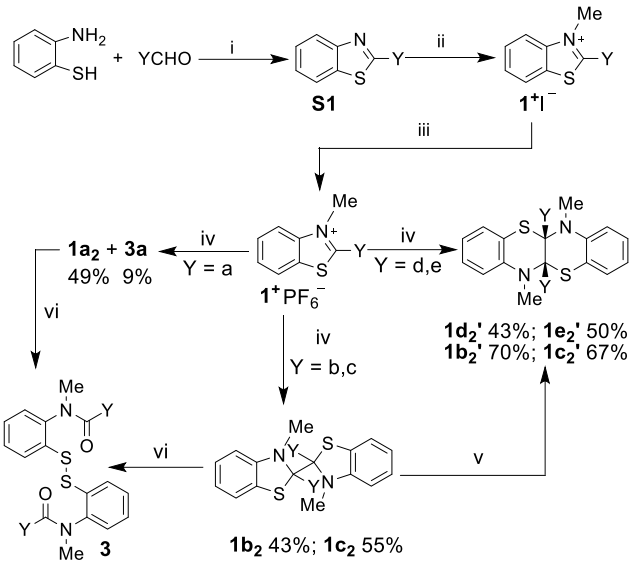


Figure 1. Structures of benzothiazolium and benzoimidazolium-based products obtained from the reduction or deprotonation reaction of their corresponding salts, as well as their decomposition products (**3** and **III**). Compounds synthesized in this paper are marked as red.



Scheme 1. Previously reported reactivity studies of benzothiazolium salts $\mathbf{1}^+X^-$ (X = I/ClO_4/OSO_3Me).

At first, we carried out the reduction reaction of a range of 2-substituted benzothiazolium salts $\mathbf{1}^+PF_6^-$, where Y = cyclohexyl (a), phenyl (b), *p*-tolyl (c), (*p*-OMe)C_6H_4 (d), (*p*-NMe_2)C_6H_4 (e), using Na:Hg (1 wt%) in dry THF. When the PF_6^- salts of $\mathbf{1a}^+$ – $\mathbf{1c}^+$ were subjected to 5 eq. of 1 wt% Na:Hg for 2 h, we obtained the benzothiazole-based dimers $\mathbf{1a_2}$ – $\mathbf{1c_2}$ in yields of 43 – 55 % (Scheme 2). The ^{1}H-NMR spectra of the crude reaction solids indicated single isomers of the relevant $\mathbf{1_2}$ derivatives as the sole product in the cases of phenyl and tolyl. However, in the case of cyclohexyl, we found three products, identified from the spectroscopic and X-ray analysis as *rac*-$\mathbf{1a_2}$ (49%), *meso*-$\mathbf{1a_2}$ (trace amount) and a disulfide **3a** (N,N'-(disulfanediylbis(2,1-phenylene))bis(N-methylcyclohexanecarboxamide)) (9%), and which could be easily separated using a short column using NEt_3-treated silica gel and n-hexane under a nitrogen atmosphere.

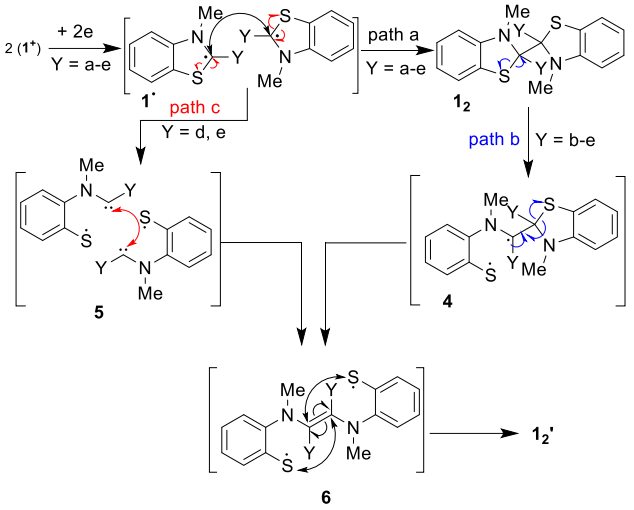


i) $Na_2S_2O_5$, EtOH, H_2O, reflux, 2 h; ii) MeI, CH_3CN/DMF, 100 - 120 ^{0}C, 24 h; iii) NH_4PF_6, acetone, H_2O, 30 min; iv) 1 wt% Na-Hg, THF, 2 h; v) Light (254 nm), THF, 2 h; vi) O_2, THF, 2 h.

Scheme 2. Products obtained from the reduction reaction of benzothiazolium salts $\mathbf{1}^+PF_6^-$ using Na:Hg (1 wt%), as well as the products obtained upon treatment with UV light and molecular O_2.

We further extended our investigation by incorporating π-donor substituents at the C-2-position in $\mathbf{1}^+$: (*p*-OMe)C_6H_4 $\mathbf{1d}^+$ and (*p*-NMe_2)C_6H_4 $\mathbf{1e}^+$. Surprisingly, upon reducing $\mathbf{1d}^+PF_6^-$ and $\mathbf{1e}^+PF_6^-$ in THF solution using 1 wt % Na:Hg, completely different products were obtained (Scheme 2). Though the reduction reaction conditions were identical to those used for $\mathbf{1a}^+$–$\mathbf{1c}^+$ salts, no 5-bibenzothiazoles, $\mathbf{1_2}$, or any **3**-type by-products were obtained; instead only 5a,11a-bis(substituted)-6,12-dimethyl-5a,6,11a,12-tetrahydro[1,4]benzothiazino[3,2-*b*][1,4]benzothiazines, $\mathbf{1_2'}$, consisting of two fused six-membered benzothiazine rings, were obtained in 43-50 % yield. The moderate yields of both $\mathbf{1_2}$ and $\mathbf{1_2'}$ are attributed to the poor solubility of $\mathbf{1}^+PF_6^-$ in THF; indeed, it was possible to recover the unreacted salts for later reuse. A $\mathbf{1_2'}$ derivative (Y = H) has previously been reported as the photolysis product of the corresponding $\mathbf{1_2}$ derivatives (Figure 1),[19] while a related compound with Y = CF_3 and NH (rather than NMe) groups has been obtained from the reaction of 2-aminobenzene thiol with 2,3-bis(trifluoromethyl)oxirane.[21] Hence, we examined the

effect of UV irradiation (254 nm) on deoxygenated solutions of pure $\mathbf{1_2}$ derivatives in THF for 2 h. In the case of *rac*-$\mathbf{1a_2}$, we didn't see any change in the reaction product and got back the *rac*-$\mathbf{1a_2}$. However, $\mathbf{1b_2}$ and $\mathbf{1c_2}$ afforded the phenyl-, and tolyl-based 1,4-benzothiazine derivatives $\mathbf{1b_2'}$ (70%) and $\mathbf{1c_2'}$ (67%). During the exposure, all three dimeric molecules $\mathbf{1_2}$ afforded the disulfide derivatives **3** (10–25%) as a side product during the irradiation; these were separated chromatographically.



Scheme 3. Possible pathway for the formation $\mathbf{1_2}$ (path a), and $\mathbf{1_2'}$ from $\mathbf{1_2}$ (path b) or $\mathbf{1^\bullet}$ (path c).

The formation of $\mathbf{1_2}$ is analogous to that of $\mathbf{2_2}$ and the dimers of many 19-electron sandwich compounds; the cation is reduced to an odd-electron species, which then dimerizes (path a, scheme 3).[11,22] Possible mechanisms for $\mathbf{1_2'}$ formation are shown in scheme 3; as in the previously reported rearrangement of a $\mathbf{1_2}$ (Y = H) derivative to its $\mathbf{1_2'}$ analog (Figure 1),[19] these might be formed from $\mathbf{1_2}$ either directly (path b) or from $\mathbf{1^\bullet}$ (path c); in the case of $\mathbf{1d_2'}$ and $\mathbf{1e_2'}$ they could also be formed via path c from $\mathbf{1^\bullet}$ formed directly on reduction of $\mathbf{1^+}$. Both paths b and c are consistent with the formation of $\mathbf{1_2'}$ occurring more readily when Y is more electron-donating (*p*-OMe)C_6H_4 and (*p*-NMe_2)C_6H_4) and, thus, better able to stabilize intermediates in which a radical (**4**) or carbene (**5**) is formed on the carbon adjacent to Y following C–S bond cleavage.

Since $\mathbf{2_2}$ derivatives undergo irreversible oxidations (ultimately reforming $\mathbf{2^+}$), we were interested firstly in how $\mathbf{1_2}$ and $\mathbf{1_2'}$ derivatives compare, so we investigated the electrochemical potentials of $\mathbf{1^+}$, $\mathbf{1_2}$, and $\mathbf{1_2'}$ using cyclic voltammetry in THF / 0.1M ^{n}Bu$_4$NPF$_6$ at a scan rate of 50 mV s^{-1} vs $FeCp_2^{+/0}$. The cyclic voltammograms of $\mathbf{1a^+}$ and $\mathbf{1a_2}$ are shown in Figure 2, qualitatively similar to those of $\mathbf{1b^+/1b_2}$, $\mathbf{1c^+/1c_2}$ (see SI), and $\mathbf{2^+/2_2}$,[16] and their redox potentials are summarized in Table 1. The reduction potentials $E_{red}(\mathbf{1^+/1^\bullet})$ indicate cathodic shifts with increasingly electron-rich 2-aryl substituents, consistent with the expected effects of the aryl substituents on the cation stability. However, $\mathbf{1a^+}$ is the hardest to reduce of all the salts; this is consistent with the behaviour of $\mathbf{2^+}$ analogues,[23] indicating that the stabilizing effect of aryl vs. alkyl groups on the radicals is greater than that on the cations. From the electrochemical oxidation potentials E_{ox}, $\mathbf{1a_2}$ was found to be less readily oxidized than its benzimidazole analogue ($\mathbf{2_2}$ with Y = cyclohexyl), for which the corresponding value is –0.64 V,[11] but somewhat easier to oxidize than $\mathbf{1b_2}$ or $\mathbf{1c_2}$. The $\mathbf{1_2'}$ derivatives were substantially harder to oxidize, exhibiting no peaks in the range –1.0 to +1.0 V (see SI). Solution reactions with oxidants (monitored through absorption spectroscopy, see SI) are consistent with the electrochemistry; $\mathbf{1_2}$ species readily reduce TCNQ ($E_{1/2}^{0/-}$= –0.2; $E_{1/2}^{-/2-}$ = –0.7 V vs $FeCp_2^{+/0}$ in CH_3CN) to $TCNQ^{\bullet-}$ (and $TCNQ^{2-}$ in the case of excess $\mathbf{1a_2}$) and $FeCp_2^+PF_6^-$ (0 V by definition), while no sign of any reaction was seen for the $\mathbf{1_2'}$ derivatives. The facile oxidation of $\mathbf{2_2}$ derivatives (and that of corresponding organometallic dimers) has previously been attributed to destabilization of the molecular HOMO by overlap of phenylene-diamine-like π-orbitals with the relative shallow central C–C σ bonding orbital;[23] the less facile oxidation of $\mathbf{1_2}$ derivatives can be attributed to the poorer π-donor abilities of S vs. NMe, while in $\mathbf{1_2'}$ derivatives, the σ -π overlap is likely much less efficient.

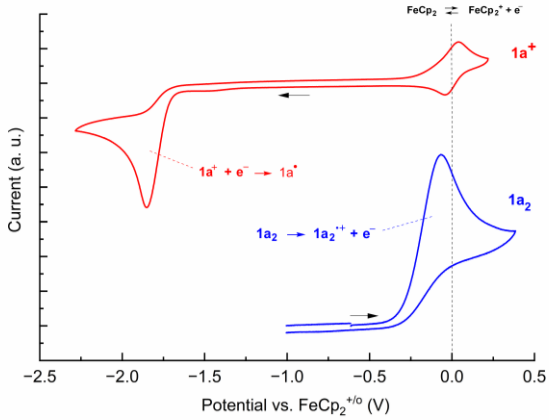


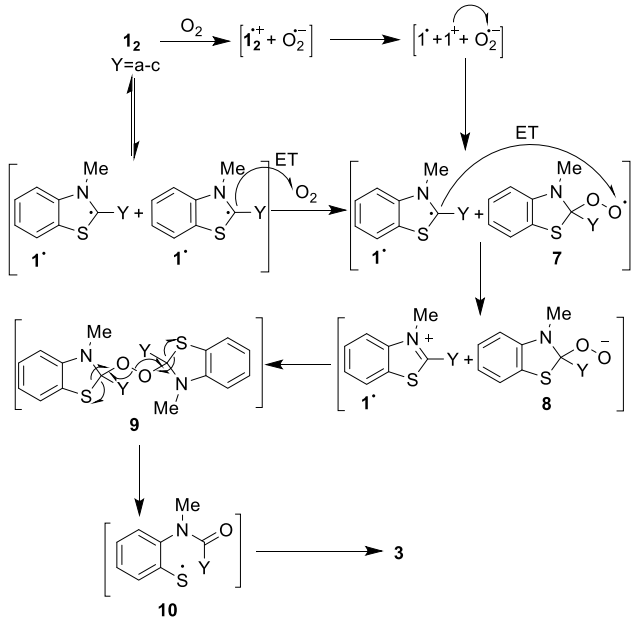
Figure 2. Cyclic voltammograms of $\mathbf{1a^+}$ (red, top) and $\mathbf{1a_2}$ (blue, bottom), recorded at a scan rate of 50 mV s^{-1} in THF / 0.1 ^{n}Bu$_4$NPF$_6$ with Ferrocene as an internal standard. The black arrow shows the starting point and the scanning direction in each voltammogram.

Table 1. Electrochemical potentials (V vs. $FeCp_2^{+/0}$ in THF/0.1M ^{n}Bu$_4$NPF$_6$) for 2-substituted benzothiazolium derivatives and the corresponding dimers.

	$E_{red}(\mathbf{1^+/1^\bullet})$	$E_{ox}(\mathbf{1_2^{\bullet+}/1_2})$
1a (Y = Cyc)	–1.85	–0.07
1b (Y = Ph)	–1.32	+0.04
1c (Y = p-Tol)	–1.45	+0.04
1d (Y= (p-OMe)C_6H_4)	–1.47	–
1e (Y= (p-NMe_2)C_6H_4)	–1.68	–

As noted above, we encountered **3a** as a side-product alongside $\mathbf{1a_2}$, presumably due to the high reactivity of $\mathbf{1a_2}$

relative to that of **1b$_2$**, **1c$_2$**, and **1$_2$'** derivatives and/or of **1a$^•$** relative to that of the other monomer radicals (consistent with both E_{ox}(**1$_2$**) and E_{red}(**1$^+$**) values, see above). We investigated this further by exposing THF solutions of **1$_2$** and **1$_2$'** species to an O_2 atmosphere for 2 h: **1a$_2$** quantitatively converted into **3a**, about 75% of **1b$_2$** and **1c$_2$** were converted into **3b** and **3c**, respectively, while the **1$_2$'** derivatives did not undergo any reaction or show any decomposition (even over 24 h)



Scheme 4. Possible mechanism for forming **3** (Y = a, b, c).

Similar disulfides have previously been found to be formed from **1H** and **I$_2$** derivatives in the presence of O_2,[24,25] and have been directly prepared by treating **1$^+$** salts with KO_2 / 18-crown-6 or electrogenerated superoxide.[26] In the present case, **1$_2$** species likely react with O_2 to form **1$^+$** and $O_2^{•-}$, which can then react further to afford a 2,2'-peroxybis(3-methyl-2,3-dihydrobenzo[*d*]thiazole), the O–O bond (**9**) of which can then dissociate with ring-opening to afford a S-radical (**10**), which dimerizes to **3** (Scheme 4). This behaviour can be contrasted to that of **2$_2$** derivatives, which form **2$^+$** and **III** derivatives (Figure 1) in air;[11] an N-centred radical intermediate would likely be more reactive than the S-radical and presumably abstracts H$^•$ from solvent rather than dimerizing. The formation of **2$^+$** may reflect the stronger π-donor character of NMe vs. S disfavouring nucleophilic attack by $O_2^{•-}$, and/or the aromaticity and/or bond-strength effects disfavouring ring opening vs. re-formation of the aromatic cation.

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All the compounds discussed in this report were fully characterized by ^{1}H, ^{13}C NMR, and elemental analysis. However, structures of type **1$_2$** and **1$_2$'** cannot be unambiguously distinguished by these methods. Moreover, both bridgehead carbons of **1$_2$** and **1$_2$'** are chiral, and thus, in principle, both *rac* (±) and *meso* diastereomers are possible and although ^{1}H and ^{13}C NMR data for all dimers except **1a$_2$** are consistent with formation of only single diastereomers, they do not unambiguously identify which specific isomers are formed. Fortunately, we were able to grow crystals suitable for single-crystal X-ray diffraction (SCXRD); ORTEP plots for **1a$_2$**–**1c$_2$**, **1b$_2$'**–**1e$_2$'**, and **3a**–**3c** are shown in Figure 3, and their crystallographic numbering schemes are given in SI (Figure S1). A few crystal structures of **2$_2$** derivatives have been reported,[11,16] but only one has been reported for a **1$_2$** derivative (Y = Me),[5] one of a molecule related to **1$_2$'** (Y = CF_3, but with H, rather than Me, substitution at N),[21] and two of *N*,*O*-heterobicyclics related to **1$_2$'**.[27,28] For each **1$_2$** derivative SCXRD revealed the majority or only products to be the *rac* isomers; in each case these crystallize in centrosymmetric space groups and thus the crystals contains equal numbers of RR and SS stereoisomers. For **1a$_2$** we were also able to isolate trace amounts of the minor isomer and confirm this by SCXRD to be the *meso* (RS) isomer; the molecule in this structure is located on a crystallographic inversion centre and thus is staggered about the central C2–C2' bond (bond length 1.616(3) Å); i.e., the Y– C2–C2'–Y torsion angle is 180^o. The molecules in the structure of *rac*-**1a$_2$** and *rac*-**1b$_2$** have approximate C2 symmetry, while that of *rac*-**1c$_2$** has crystallographic C2 symmetry. Y–C2–C2'–Y torsion angles are 152.7, 60.8, and 61.7^o respectively and and C2-C2' distances are 1.622(3), 1.590(3), and 1.575(5) Å[27]. The central C–C bonds are rather long, as in those of previously reported related dimeric molecules of types **2$_2$** and **1$_2$**.[5,11] The thiazole rings of both isomers of **1a$_2$** are almost flat, whereas those of *rac*-**1b$_2$** and *rac*-**1c$_2$** have puckered envelope conformation. All four **1$_2$'** derivatives are confirmed to be *cis*, i.e., *rac* diastereomers. The Y–C5a–C11a–Y torsion angles are 41.2, 35.6 / 39.8 (two molecules in the asymmetric unit), 36.6 / 36.3 (two molecules in the asymmetric unit), and 41.5^o for **1b$_2$'**, **1c$_2$'**, **1d$_2$'** and **1e$_2$'**, respectively. The 6-membered heterocycles of **1$_2$'** have boat-like conformations. The average central C5a–C11a bond distance is 1.572 Å, slightly longer than those of [1,4]benzoxazino[3,2-b][1,4]benzoxazines (1.506(4)–1.550(6) Å).[27] The disulfides **3** have crystallographic (**3a**, **3b**) or

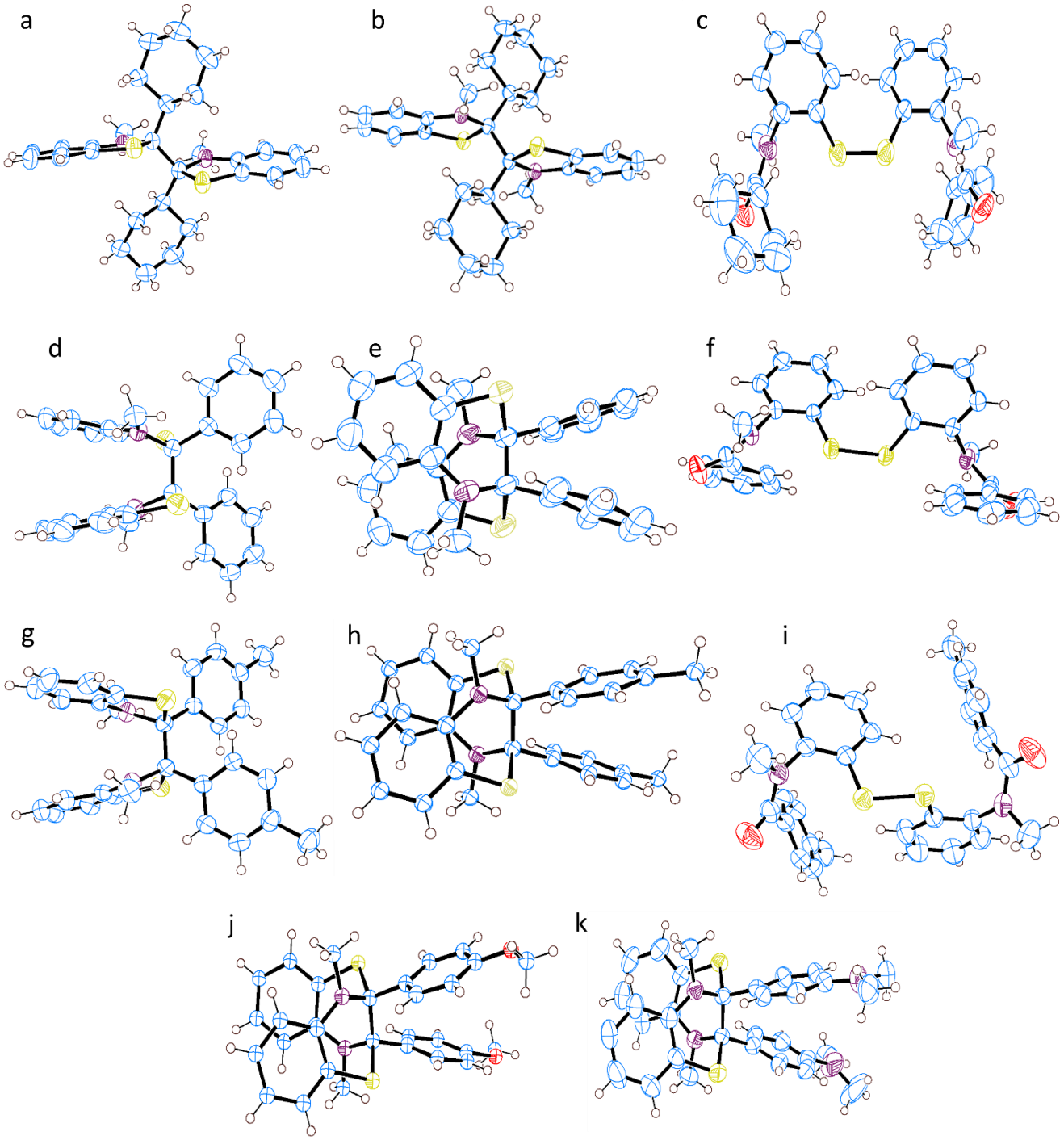

Figure 3. Molecular structures of (a) *rac*-**1a**$_2$, (b) *meso*-**1a**$_2$, (c) **3a**, (d) **1b**$_2$, (e) **1b**$_2$**'**, (f) **3b**, (g) **1c**$_2$, (h) **1c**$_2$**'**, (i) **3c**, (j) **1d**$_2$**'**, (k) **1e**$_2$**'** with anisotropic displacement ellipsoids drawn at 50 % probability. In the case of **1c**$_2$**'** and **1d**$_2$**'**, two similar crystallographic independent molecules are present in the asymmetric unit. Blue – C, purple – N, yellow – S, red – O.

approximate (**3c**) C2 symmetry, with C–S–S–C torsion angles in the range 81.6–86.2° and central S–S bond distances (2.0156(14)–2.0293(9) Å) within the range of usual disulfides.

Conclusion

We have developed syntheses for two classes of dimeric N,S-based heterocyclic compounds, 5-membered 2,2'-bibenzo[*d*]thiazoles, and 6-membered cis-[1,4]benzothiazino[3,2-*b*][1,4]benzothiazines. Thus, this approach to the dimeric compounds 1_2 and 1_2' and the ease of

synthesis of these and related derivatives (ongoing work) may stimulate interest in biological and pharmaceutical applications.

Experimental Section

1. General Details:

All operations were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Unless otherwise stated, all commercially available chemicals were used without further purification. Toluene, THF, and n-hexane were dried over sodium and freshly distilled before use. Other solvents used were purified by standard distillation technique immediately before use. Sodium amalgam (1 wt%) was prepared immediately before use by adding small pieces of Na metal to vigorously stirred Hg (electronic grade, 99.99%). After the reaction, the Na-Hg is carefully treated with methanol under an atmosphere of N_2 to destroy the unreacted Na. The remaining Hg is isolated and stirred in a solution of methanol:water (8:2). The liquid layer is decanted, and the Hg is isolated. The same procedure is repeated twice in pure methanol and THF. Finally, the Hg is dried using a high vacuum and re-used for similar reduction reactions. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Bruker Advance 400 MHz spectrum. They were referenced to tetramethylsilane using the residual proton signal of the solvent and the carbon resonances of the deuterated solvent, respectively. Elemental analyses were carried out by EAS vario MICRO CHNS elemental analyzer. Electrochemical data were obtained using cyclic voltammetry in 0.1 M ^{n}Bu$_4$NPF$_6$ in THF under nitrogen, using a BAS potentiostat, a glassy carbon working electrode, a platinum wire auxiliary electrode, and a silver wire as a pseudo-reference electrode. A scan rate of 100 mV s^{-1} was used, and the potentials were referenced to ferrocene as an internal standard. UV-Vis absorption spectra were recorded in a JASCO V-770 UV-Vis spectrophotometer.

2. General synthetic procedures of 2-Substituted benzo[*d*]thiazoles, S1a – S1e:

A mixture of 2-aminothiophenol (15.9 mmol), an appropriate aldehyde (Y-CHO, 17.5 mmol), and sodium metabisulfite (32 mmol) was taken in 150 mL mixture solution of ethanol and water (9:1 v/v). The reaction mixture was refluxed for 2 h. The progress of the reaction was monitored by TLC. After the consumption of the starting material, the reaction mixture was filtered, and the filtrate was dried using a rotary evaporator. The crude reaction product solid was re-crystallized using n-hexane and then dried under a high vacuum to get the desired product. In the case of **S1a**, the purification was done by passing through a short silica gel column with n-hexane as eluent.[29]

S1a (Y = Cyc): Colourless liquid, yield 80%. ^{1}H, and ^{13}C{^{1}H} NMR are consistent with a previous report.[30]

S1b (Y = Ph): White solid, yield 92%. ^{1}H, and ^{13}C{^{1}H} NMR are consistent with a previous report.[31]

S1c (Y = Tol): White solid, yield 87%. ^{1}H, and ^{13}C{^{1}H} NMR are consistent with a previous report.[32]

S1d (Y = (p-OMe)C$_6$H$_4$): White solid, yield 83%. ^{1}H, and ^{13}C{^{1}H} NMR are consistent with a previous report.[31]

S1e (Y = (p-NMe$_2$)C$_6$H$_4$): Yellow solid, yield 82%. ^{1}H, and ^{13}C{^{1}H} NMR are consistent with a previous report.[33]

3. General synthetic procedure for 2-Substituted-3-methylbenzo[*d*]thiazolium iodides, 1a$^+$I$^-$ – 1e$^+$I$^-$:

A mixture of 2-substituted benzo[*d*]thiazole (8 mmol) and methyl iodide (40 mmol) were taken in acetonitrile (30 mL) in a pressure tube and stirred at 100 °C for 24 h. For the synthesis of **1e**$^+$I$^-$, the reaction was carried out in DMF (20 mL) and stirred at 120 °C for 24 h. The volatiles were removed using a rotary evaporator. The crude solid obtained was recrystallized from CH_2Cl_2 and Et_2O to obtain the pure product.[34]

1a$^+$I$^-$: Off-white solid, yield 83%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.54 – 8.45 (m, Ar, 1H), 8.33 (d, *J* = 8.5 Hz, Ar, 1H), 7.92 (t, *J* = 7.8 Hz, Ar, 1H), 7.82 (t, *J* = 7.6 Hz, Ar, 1H), 4.32 (s, NMe, 3H), 3.73 (m, Cyc, 1H), 2.22 (m, Cyc 2H), 1.86 (m, Cyc, 2H), 1.76 (m, Cyc, 1H), 1.54 (m, Cyc, 4H), 1.35 (m, Cyc, 1H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 185.0, 141.9, 129.4, 128.2, 128.1, 124.5, 117.1, 39.1, 36.6, 31.9, 24.9, 24.6. Anal. calcd for $C_{14}H_{18}NSI$: C 46.80, H 5.05, N 3.90, S 8.92; found: C 46.98, H 5.20, N 3.95, S 8.64.

1b$^+$I$^-$: Yellow solid, yield 64%. ^{1}H, and ^{13}C{^{1}H} NMR are consistent with a previous report.[35]

1c$^+$I$^-$: White solid, yield 71%. The characterization data are similar to that reported previously.[36]

1d$^+$I$^-$: Yellow solid, yield 49%. ^{1}H, and ^{13}C{^{1}H} NMR are consistent with a previous report.[35]

1e$^+$I$^-$: Yellow solid, yield 72%. ^{1}H, and ^{13}C{^{1}H} NMR are consistent with a previous report.[33]

4. General synthetic procedures for 2-Substituted-3-methylbenzo[*d*]thiazolium hexafluorophosphates, 1a$^+$PF$_6^-$ – 1e$^+$PF$_6^-$:

1$^+$I$^-$ (1.25 mmol) was dissolved in a minimum amount of a mixture of distilled water and acetone mixture (2:1). An excess of solid NH_4PF_6 (2 mmol) was added to it, and the reaction mixture was stirred for 30 min. The precipitate formed was filtered, washed well with water, and dried under a high vacuum. The compound was further purified by recrystallization from CH_2Cl_2 and Et_2O.[14]

1a$^{+}PF_6^{-}$: White solid, yield 76%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.45 (d, *J* = 8.0 Hz, Ar, 1H), 8.31 (d, *J* = 8.5 Hz, Ar, 1H), 7.97 – 7.89 (m, Ar, 1H), 7.87 – 7.78 (m, Ar, 1H), 4.30 (s, NMe, 3H), 3.68 (s, Cyc, 1H), 2.21 (s, Cyc, 2H), 1.94 – 1.83 (m, Cyc, 2H), 1.77 (d, *J* = 12.1 Hz, Cyc, 1H), 1.54 (t, *J* = 9.7 Hz, Cyc, 4H), 1.42 – 1.30 (m, Cyc, 1H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 185.1, 141.9, 129.4, 128.3, 128.2, 124.5, 117.0, 39.2, 36.4, 31.9, 24.9, 24.6. Anal. calcd for $C_{14}H_{18}NSPF_6$: C 44.56, H 4.81, N 3.71, S 8.50; found: C 44,47, H 4.66, N 3.93, S 8.21.

1b$^{+}PF_6^{-}$: White solid, yield 74%, ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.55 (dd, *J* = 8.2, 2.5 Hz, 1H), 8.43 (dd, *J* = 8.7, 2.6 Hz, 1H), 8.04 – 7.84 (m, 5H), 7.79 (t, *J* = 7.5 Hz, 2H), 4.25 (s, NMe, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 174.2, 142.4, 133.7, 130.4, 129.9, 129.7, 129.7, 128.7, 125.4, 124.5, 117.7, 38.0. Anal. calcd for $C_{14}H_{12}NSPF_6$: C 45.29, H 3.26, N 3.77, S 8.63; found: C 45.58, 3.12, N 3.72, S 8.83.

1c$^{+}PF_6^{-}$: White solid, yield 73%. ^{1}H NMR (400 MHz, Acetone-d_6): δ 8.52 (d, *J* = 8.3 Hz, 1H), 8.43 (dd, *J* = 8.7, 2.5 Hz, 1H), 8.05 (m, 1H), 7.99 – 7.92 (m, 3H), 7.66 (d, *J* = 7.9 Hz, 2H), 4.51 (s, NMe, 3H), 2.54 (s, PhMe, 3H). ^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6): δ 176.1, 146.3, 143.8, 131.5, 131.3, 131.1, 130.7, 129.9, 125.0, 123.6, 118.4, 38.7, 21.7. Anal calcd for $C_{15}H_{14}NSPF_6$: C 46.76, H 3.66, N 3.64, S 8.32; found: C 47.01, H 3.24, N 3.89, S 8.44.

1d$^{+}PF_6^{-}$: White solid, yield 81%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.53 – 8.47 (m, 1H), 8.38 (m, 1H), 8.00 – 7.93 (m, 3H), 7.87 (m, 1H), 7.36 – 7.31 (m, 2H), 4.25 (s, NMe 3H), 3.94 (s, OMe, 3H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 174.1, 163.6, 142.5, 132.6, 129.7, 129.2, 128.4, 124.3, 117.5, 117.3, 115.4, 55.9, 38.0. Anal calcd for $C_{15}H_{14}NOSPF_6$: C 44.89, H 3.52, N 3.49, S 7.99; found: C 45.21, H 3.85, N 3.25, S 7.95.

1e$^{+}PF_6^{-}$: Orange solid, yield 76%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.38 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.91 – 7.75 (m, 4H), 7.02 – 6.95 (m, 2H), 4.25 (s, NMe, 3H), 3.13 (s, NMe, 6H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 173.6, 153.7, 142. 8, 132.3, 129.3, 128.1, 127.7, 123.9, 116.9, 112.0, 110.9, 39.6, 38.2. Anal calcd for $C_{16}H_{17}N_2SPF_6$: C 46.38, H 4.14, N 6.76, S 7.74; found: C 46.19, H 3.99, N 6.74, S 7.99.

5. General synthetic procedure for 2,2′-Disubstituted-3,3′-dimethyl-2,2′,3,3′-tetrahydro-2,2′-bibenzo[*d*]thiazole (1a$_2$ – 1c$_2$) and 5a,11a-bis(substituted)-6,12-dimethyl-5a,6,11a,12-tetrahydro[1,4]benzothiazino[3,2-*b*][1,4]benzothiazine (1d$_2$′ and 1e$_2$′).

A slurry of **1**$^{+}PF_6^{-}$ (0.5 mmol) with an excess of 1 wt % Na:Hg (2.5 mmol, prepared from 60 mg of Na and 6 g of Hg) was stirred in 10 mL of dry THF for 2 h at room temperature under nitrogen. The solution was then carefully decanted from the amalgam using a cannula and evaporated under reduced pressure. The crude product was extracted in toluene, and the solution was then filtered through Celite under nitrogen.[14] The volatiles were removed using a high vacuum. The products obtained in the case of **1b$_2$** and **1c$_2$** were sufficiently pure to be examined using NMR and other analyses. In the case of **1a$_2$**, the crude solid was passed through a short column using NEt_3-treated silica gel and n-hexane under a nitrogen atmosphere. The second spot was collected from the column, later identified as **3a** as a by-product. Interestingly, the second time when we passed the pure **1a$_2$** dimer through another NEt_3-treated silica gel column using n-hexane, we could isolate a new compound (only a trace amount), which we determined to be the 2nd isomer of **1a$_2$** (*meso*). In the case of **1d$_2$′** and **1e$_2$′**, the products were purified by column chromatography using a mixture of ethyl acetate and hexane (2:98).

1a$_2$, mixture of isomers: White solid, yield 49%. ^{1}H NMR (400 MHz, Benzene-d_6): δ 6.98 – 6.87 (br, m, 4H), 6.60 – 6.52 (br, m, 2H), 5.97 – 5.87 (br, m, 2H), 2.59-2.41 (br, s, 6H), 1.81 – 1.00 (br, m, Cyc, 22H). ^{13}C{^{1}H} NMR (101 MHz, Benzene-d_6): δ 149.1 (br), 147.8 (br), 129.4 (br), 128.8 (br), 125.4 (br), 125.2 (br), 119.9 (br), 116.6 (br), 104.6 (br), 103.3 (br), 96.8 (br), 77.4 (br), 47.1 (br), 34.4 (br), 32.1 (br), 29.9 (br), 29.1 (br), 28.2 (br), 27.0 (br), 26.8 (br), 26.6 (br), 26.3 (br). Anal. calcd for $C_{28}H_{36}N_2S_2$: C 72.37, H 7.81, N 6.03; found: C 72.42, H 7.90, N 6.03.

rac-**1a$_2$**, **major isomer**: White solid. ^{1}H NMR (400 MHz, Benzene-d_6): δ 6.95 (t, *J* = 7.9 Hz, 4H), 6.60 (d, *J* = 8.0 Hz, 2H), 5.95 (br, s, 2H), 2.41 (br, s, 6H), 1.73 – 1.00 (br m, Cyc, 22H).

meso-**1a$_2$**, **minor isomer** (trace amount): White solid. ^{1}H NMR (400 MHz, Benzene-d6): δ 6.90 (t, *J* = 7.7 Hz, 4H), 6.55 (t, *J* = 7.4 Hz, 2H), 5.87 (d, *J* = 7.7 Hz, 2H), 2.57 (s, NMe, 6H), 1.65 (br, s, 2H), 1.68 – 1.46 (m, 10H), 1.35 (m, 4H), 1.65 – 1.04 (m, 6H).

3a: Yellow solid, yield 9%. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.44 (t, *J* = 8.4 Hz, 2H), 7.27 – 7.18 (m, 4H), 7.10 (d, *J* = 7.5 Hz, 2H), 3.17 (s, NMe, 6H), 2.05 – 0.73 (m, Cyc, 22H). ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*): δ 176.8, 141.1, 135.3, 129.4, 128.7, 128.0, 126.1, 42.2, 36.1, 29.9, 29.7, 25.7. Anal. calcd for $C_{28}H_{36}N_2O_2S_2$: C 67.70, H 7.31, N, 5.64; found: C, 67.55, H 7.21, N, 5.54.

1b$_2$: White solid, yield 43%. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.66 (s, 4H), 7.29 (d, *J* = 3.7 Hz, 6H), 6.97 – 6.87 (m, 4H), 6.60 (t, *J* = 7.7 Hz, 2H), 5.71 (d, *J* = 7.8 Hz, 2H), 2.46 (s, NMe, 6H). ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*): δ 147.3, 140.6, 131.8, 128.2, 127.3, 126.2, 125.7, 119.1, 117.6, 107.6, 91.5, 36.2. Anal. calcd for $C_{28}H_{24}N_2S_2$: C 74.30, H 5.34, N 6.19; found: C 74.27, H 5.29, N 6.22.

1c$_2$: White solid, yield 55%. ^{1}H NMR (400 MHz, Benzene-d_6): δ 7.66 (d, *J* = 7.7 Hz, 4H), 6.97 – 6.78 (m, 8H), 6.62 (t, *J* = 7.5 Hz, 2H), 5.71 (d, *J* = 7.8 Hz, 2H), 2.49 (s, NMe, 6H), 2.02 (s, PhMe, 6H), ^{13}C{^{1}H} NMR (101 MHz, Benzene-d_6) δ 147.7, 138.0, 137.9, 132.2, 128.2, 126.7, 125.9, 119.2, 117.9, 108.0, 91.9, 36.2, 20.9.

Anal. calcd for $C_{30}H_{28}N_2S_2$: C 74.96, H 5.87, N 5.83; found: C 74.95, H, 5.87, N 5.89.

1d$_2$': White solid, yield 43%. ^{1}H NMR (400 MHz, Benzene-d_6): δ 7.64 (d, *J* = 8.3 Hz, 4H), 6.92 (t, *J* = 8.5 Hz, 4H), 6.63 (t, *J* = 7.3 Hz, 2H), 6.58 (d, *J* = 8.2 Hz, 4H), 5.72 (d, *J* = 7.7 Hz, 2H). 3.25 (s, OMe, 6H), 2.5 (s, NMe, 6H). ^{13}C{^{1}H} NMR (101 MHz, Benzene-d_6): δ 159.6, 147.7, 133.6, 132.5, 126.7, 125.9, 119.2, 117.9, 112.9, 108.1, 92.0, 54.8, 36.1. Anal. calcd for $C_{30}H_{28}N_2O_2S_2$: C 70.28, H 5.51, N 5.46; found: C 70.23, H 5.52, N 5.47.

1e$_2$': Yellow solid, yield 50%. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.73 (d, *J* = 8.7 Hz, 2H), 7.19 (d, *J* = 7.3 Hz, 2H), 6.89 (t, *J* = 8.0 Hz, 2H), 6.65 (m, 4H), 6.21 (dd, *J* = 9.4, 6.1 Hz, 4H), 6.10 (m, 2H), 2.90 (s, NMe_2, 12H), 2.71 (s, NMe, 6H). ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*): δ 150.0, 148.6, 131.0, 129.5, 128.3, 127.5, 119.7, 118.2, 113.0, 110.7, 86.3, 40.7, 36.2. Anal. calcd for $C_{32}H_{34}N_4S_2$: C 71.34, H 6.36, N 10.40; found: C 71.22, H 6.44, N 10.45.

6. General synthetic procedure for 1b$_2$' and 1c$_2$'.

A degassed solution of **1b$_2$** / **1c$_2$** (30 mg) in 2 mL THF was irradiated with UV light (254 nm) for 2 h under constant stirring. The progress of the reaction was monitored using TLC. The THF was removed using a rotary evaporator. The solid was purified by passing through a short silica gel column using n-hexane as eluent.

1b$_2$': White solid, yield 70%. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.03 (d, *J* = 8.0, 2H), 7.30 (t, *J* = 7.7, 2H), 7.21 (m, 2H), 7.19 – 7.12 (m, 2H), 6.90 (dd, *J* = 8.2, 7.3 Hz, 2H), 6.79 (dd, *J* = 8.5, 7.6, 2H), 6.69 (t, *J* = 7.4, 1.2 Hz, 2H), 6.33 (d, *J* = 8.1, 2H), 6.01 (d, *J* = 8.3, 2H), 2.70 (s, NMe, 6H). ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*): δ 148.5, 140.5, 130.2, 129.7, 127.9, 127.9, 126.9, 119.1, 118.7, 113.3, 86.6, 36.2.

1c$_2$': White solid, yield 67%. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.86 (d, *J* = 8.1, 2H), 7.21 (d, *J* = 7.5, 2H), 7.11 (d, *J* = 8.0, 2H), 6.90 (dd, *J* = 8.4, 7.4, 2H), 6.74 – 6.59 (m, 4H), 6.23 (d, *J* = 8.1, 2H), 6.01 (d, *J* = 8.2, 2H), 2.70 (s, NMe, 6H), 2.30 (s, Me, 6H). ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*): δ 148.5, 137. 6, 130.2, 129.9, 127.8, 127.6, 127.4, 119.3, 118.5, 113.1, 86.2, 36.2, 21.1.

7. General synthetic procedure for N,N'-(Disulfanediylbis(2,1-phenylene))bis(N-methyl substituted amides), 3a – 3c:

The dimer **1$_2$** was dissolved in a minimum amount of THF. The solution was then stirred under an atmosphere of pure O_2 (O_2 was purged using a balloon) for 2 h. **1a$_2$** was completely converted into its respective disulfide **3a** after 2 h of stirring (monitored by TLC), whereas almost 75% of the **1b$_2$** and **1c$_2$** were converted into their respective disulfides 3b and 3c. The disulfides were purified by passing through a short silica gel column. The column was eluted first with hexane to collect all the unreacted dimer, then with ethylacetate-hexane mixture (1:5 ratio) to collect the respective disulfides. All the products were obtained as light yellow to yellow-colored solids, and yields were determined using ^{1}H-NMR.

3a: ^{1}H, and ^{13}C{^{1}H} NMR data are as reported above.

3b: ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.37 (m, br, 4H), 7.26 (m, br, 4H), 7.12 (m, br, 10H), 3.40 (s, NMe, 6H). Characterization data are consistent with a previous report.[25,26]

3c: ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.26 (m, 4H), 7.12 (m, 8H), 6.94 (m, 4H), 3.39 (s, NMe, 6H), 2.28 (s, PhMe, 6H). ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 171.3, 142.4, 140.3, 134.6, 132.7, 129.2, 128.6, 128.5, 128.0, 127.8, 127.0, 29.8, 21.5. Anal. calcd for $C_{30}H_{28}N_2O_2S_2$: C 70.28, H 5.51, N 5.46, S 12.51; found: C 70.26, H 5.52, N 5.43, S 12.53.

Author Contributions

The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

This work was supported by the Science & Technology Department, Govt of Odisha, through the grant ST-SCST-MISC-0026-2020. SKM thanks the University Grants Commission, Govt of India, for support through its faculty recharge program (UGC-FRP) D.O No. F.4-5(155-FRP)/2014(BSR).

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