Biomolecular Chemistry

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 2336

www.rsc.org/obc

PAPER

In search of a new class of stable nitroxide: synthesis and reactivity of a *peri*-substituted *N*,*N*-bissulfonylhydroxylamine†‡

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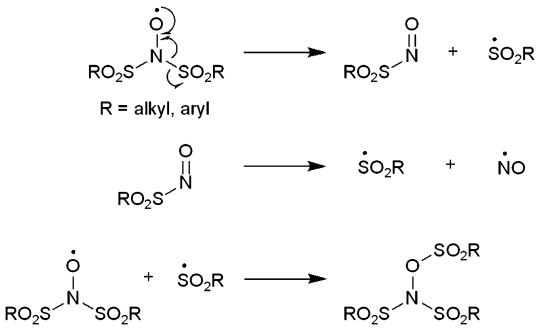
Received 3rd November 2010, Accepted 20th December 2010
DOI: 10.1039/c0ob00976h

Acyclic bissulfonylnitroxides have never been isolated, and degrade through fragmentation. In an approach to stabilising a bissulfonylnitroxide radical, the cyclic, *peri*-substituted *N*,*N*-bissulfonylhydroxylamine, 2-hydroxynaphtho[1,8-*de*][1,3,2]dithiazine 1,1,3,3-tetraoxide (**1**), has been prepared by formal nitrogen insertion into the sulfur–sulfur bond of a sulfinylsulfone, naphtho[1,8-*cd*][1,2]dithiole 1,1,2-trioxide. The heterocyclic ring of **1** is shown to adopt a sofa conformation by X-ray crystallography, with a pseudo-axial hydroxyl group. *N*,*N*-Bissulfonylhydroxylamine **1** displays high thermal, photochemical and hydrolytic stability compared to acyclic systems. EPR analysis reveals formation of the corresponding bissulfonylnitroxide **2** upon oxidation of **1** with the Ce(IV) salts CAN and CTAN. Although **2** does not undergo fragmentation, it cannot be isolated, since hydrogen atom abstraction to reform **1** occurs *in situ*. The stability and reactivity of **1** and **2** are compared with the known cyclic benzo-fused *N*,*N*-bissulfonylhydroxylamine, *N*-hydroxy-*O*-benzenedisulfonimide (**6**), for which the X-ray data, and EPR of the corresponding nitroxide **10**, are also reported for the first time.

Introduction

Although nitroxides are often regarded as long-lived "persistent" radicals, their stability is highly dependent on the nature and substitution on the atoms bonded to nitrogen.[1] Fremy's salt (potassium nitrosodisulfonate), one of the earliest reported and synthetically useful nitroxide radicals, contains a nitrogen attached to two sulfonate anions, and is sufficiently stable for it to be commercially available. In contrast, bis(organosulfonyl)-substituted nitroxides have not been isolated, and have been reported to readily fragment through β-elimination to form sulfonyl radicals ($RSO_2^{\bullet}$) and nitroso-species, which undergo further fragmentation and addition reactions to give *N*,*N*,*O*-trissulfonylhydroxylamines as the major decomposition product (Scheme 1).[2–4]



Scheme 1 Major decomposition pathway of acyclic bissulfonylnitroxides.

We are interested in the use of *peri*-(1,8)-substituted naphthalenes for the generation and stabilisation of reactive sulfur species,[5,6] and as profluorescent nitroxide probes for polymer degradation.[7] In the present study, we report the synthesis of the novel *peri*-substituted *N*,*N*-bissulfonylhydroxylamine **1**, and studies on its subsequent transformation to the nitroxide **2** (Fig. 1).

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† Dedicated to the memory of Professor Athel Beckwith, pioneer in free radical chemistry.

‡ Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR of all new compounds, X-ray experimental and additional information, and EPR decay curves. X-ray data for **1**·H_2O, **1**·EtOAc, **9**, **12** and **6**·H_2O in CIF format. The CIFs for these crystal structures have been deposited with the CCDC, CCDC reference numbers 798806–798810. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ob00976h

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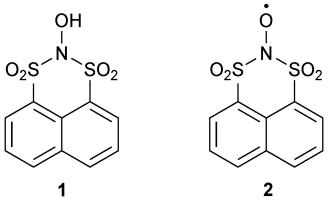


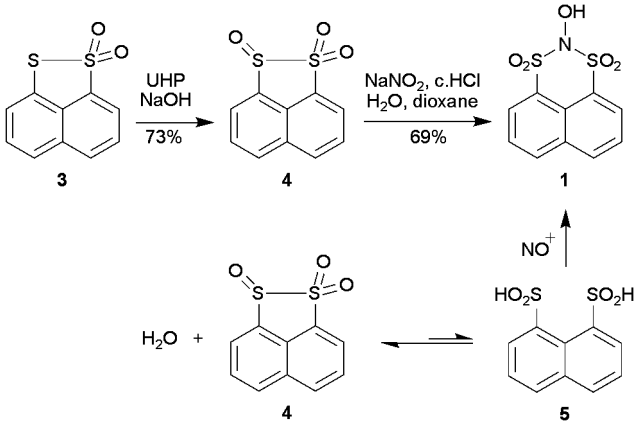
Fig. 1 *peri*-Substituted bissulfonylhydroxylamine **1** and bissulfonylnitroxide **2**.

On the one hand the constrained cyclic system was anticipated to stabilise the bissulfonylnitroxide moiety: the initial fragmentation should be less entropically favourable, and because the sulfonyl radical and nitroso species cannot diffuse apart, the reverse reaction[4] should be favoured as it is now an intramolecular cyclisation. However, it was also recognized that fragmentation to release nitric oxide might also be favoured due to the potential reduction in the *peri*-interaction between the two sulfonyl groups through S–S bond formation.[5]

Results and discussion

Synthesis and analysis of 1,8-bissulfonylhydroxylamine 1

Peri-substituted bissulfonylhydroxylamine **1** was prepared in two steps from the known thiosulfonate **3** (Scheme 2).[6,8] Oxidation of **3** to the sulfinyl sulfone **4** has been previously carried out using basic hydrogen peroxide,[9] and we found that urea–hydrogen peroxide (UHP) is equally effective in this respect, providing **4** in more reproducible yields. Treatment of **4** under nitrosylating conditions gave formal nitrogen insertion into the sulfur–sulfur bond. This reaction is presumed to occur through the capture of nitrosonium with the bissulfinic acid **5**, present through the known equilibrium with **4** in the acidic, aqueous media.[10]



Scheme 2 Synthesis of *peri*-substituted bissulfonylhydroxylamine **1** and proposed mechanistic intermediates.

The *N*,*N*-bissulfonylhydroxylamine **1** is a white crystalline solid, and crystals suitable for X-ray diffraction analysis were obtained by slow recrystallisation from hot H_2O (Fig. 2).¶‖ One molecule of the solvent is present in the unit cell, hydrogen bonding to the hydroxyl group of **1**. The heterocyclic ring adopts a sofa conformation, with the two *peri*-sulfur atoms essentially coplanar with the naphthalane ring and the nitrogen 0.60 Å below the mean plane of the naphthalene ring. The hydroxyl group resides in a pseudo-axial orientation (O(5)–N(1)–S(1)–C(1) and O(5)–N(1)–S(2)–C(10) torsion angles –60.0(2)° and 61.7(2)° respectively). In this arrangement, the nitrogen lone-pair bisects (*gauche*) the two sulfur–oxygen bonds on each adjacent sulfur. This conformation is also seen to a lesser extent in the four known X-ray crystal structures of acylic *N*-hydroxybissulfonamide derivatives found in a search of the CCDC,[11–13] and is commonly observed about the S–N bond in sulfonamides.[14] Selected bond lengths and angles are reported in Table 1.

We also obtained the X-ray crystal structure of **1**·EtOAc by recrystallisation from hot EtOAc (Fig. S1, ESI‡).¶‖ The same conformation is adopted in the solid state, and bond lengths and angles are comparable to those in **1**·H_2O (Table 1).

We have previously reported release and *in situ* capture of the reactive diatomic molecule sulfur monoxide upon thermolysis of a *peri*-substituted trisulfide-2-oxide.[5] We therefore undertook a study on the thermal stability of **1**, a potential source of nitroxyl (HNO)[15] or hydroxynitrene (HON).[16] Solutions of **1** in DMSO and D_2O remained unchanged after 3 months. Heating **1** in solvents at increasing temperatures (*t*-BuOH at 83 °C, DMSO at 100 °C, toluene at 110 °C, chlorobenzene at 132 °C) over extended periods quantitatively returned starting material in all

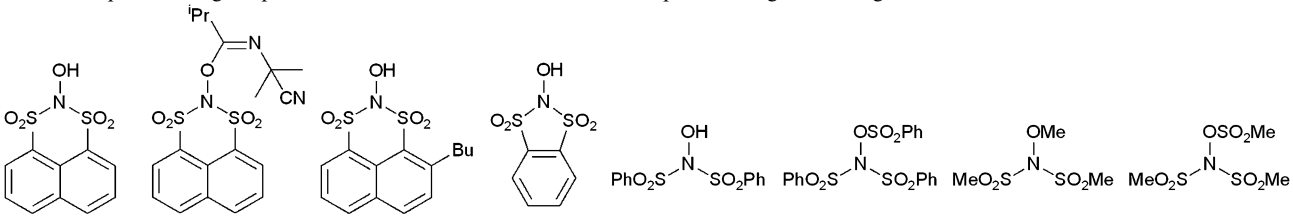
¶ Crystallographic data:**1**·H_2O: $C_{10}H_7NO_5S_2·H_2O$, M = 303.30, monoclinic, space group $P2_1/n$, T = 120 K, a = 6.9698(2) Å, b = 9.4671(3) Å, c = 17.7500(4) Å, α = 90°, β = 94.399(2)°, γ = 90°, V = 1167.76(6) Å^3, Z = 4, 16422 reflections measured, 2668 unique (R_{int} = 0.0898) which were used in all calculations. Final R1 ($I > 2\sigma(I)$) = 0.0552, wR_2 (all data) = 0.1599, goodness of fit = 1.082 on F^2.**1**·EtOAc: $C_{10}H_7NO_5S_2$, $C_4H_8O_2$, M = 373.39, monoclinic, space group $P2_1/n$, T = 296(2) K, a = 14.1894(3) Å, b = 7.1236(2) Å, c = 18.0588(4) Å, α = 90°, β = 112.627(1)°, γ = 90°, V = 1684.87(7) Å^3, Z = 4, 10441 reflections measured, 3067 unique (R_{int} = 0.0385) which were used in all calculations. Final R1 ($I > 2\sigma(I)$) = 0.0388, wR_2 (all data) = 0.1083, goodness of fit = 1.040 on F^2.**9**: $C_{18}H_{19}N_3O_5S_2$, M = 421.48, monoclinic, space group $P2_1/c$, T = 173(2) K, a = 15.1983(15) Å, b = 8.5889(7) Å, c = 15.6813(15) Å, α = 90°, β = 95.42(1)°, γ = 90°, V = 2037.8(3) Å^3, Z = 4, 14029 reflections measured, 4719 unique (R_{int} = 0.0522) which were used in all calculations. Final R1 ($I > 2\sigma(I)$) = 0.0476, wR_2 (all data) = 0.1069, goodness of fit = 1.080 on F^2.**12**: $C_{14}H_{15}NO_5S_2·H_2O$, M = 359.41, triclinic, space group $P\bar{1}$, T = 120(2) K, a = 12.042(1) Å, b = 13.397(1) Å, c = 21.306(3) Å, α = 72.268(7)°, β = 81.717 (4)°, γ = 74.535(7)°, V = 3148.0(6) Å^3, Z = 8, 28727 reflections measured, 10075 unique (R_{int} = 0.1065) which were used in all calculations. Final R1 ($I > 2\sigma(I)$) = 0.1509, wR_2 (all data) = 0.3157, goodness of fit = 1.094 on F^2. The structure contains four crystallographically-independent nitroxide molecules. The crystal was the best quality that could be obtained but in spite of this the diffraction data were weak, especially at higher angles and the agreement statistics are rather high. These facts can be at least partially attributed to the substantial levels of disorder in the structure.**6**·H_2O: $C_6H_5NO_5S_2·H_2O$, M = 253.25, triclinic, space group $P\bar{1}$, T = 120(2) K, a = 7.2877(3) Å, b = 8.1680(3) Å, c = 8.3571(2) Å, α = 93.740(2)°, β = 107.823(2)°, γ = 92.785(2)°, V = 471.35(3) Å^3, Z = 2, 8728 reflections measured, 2171 unique (R_{int} = 0.0425) which were used in all calculations. Final R1 ($I > 2\sigma(I)$) = 0.0391, wR_2 (all data) = 0.0918, goodness of fit = 1.076 on F^2.

‖ There is evidence of π–π stacking between aromatic ring systems in the solid state X-ray crystal structure of **1**·H_2O, **1**·EtOAc, **9**, **12** and **6**·H_2O (average interplanar separations 3.3–3.6 Å. Figs. S3–S7 ESI‡). Changes in the chemical shifts of the aromatic protons in the ^{1}H NMR of **1** observed upon dilution between 0.1 M and 0.01 M may be related to increased intermolecular aromatic-aromatic interactions in solution at higher concentration (see experimental for details).

Table 1 Selected bond lengths (Å) and angles (°) for bissulfonylhydroxylamine derivatives from X-ray crystallographic data

Compound	**1**·H_2O	**1**·EtOAc	**9**	**12**·H_2O[a]	**6**·H_2O	**14** (ref. 11)	**15** (ref. 11)	**16** (ref. 12)	**17** (ref. 13)
Bond lengths									
S–N	1.699(2)	1.703(2)	1.714(2)	1.66(1–3)	1.7215(19)	1.71	1.73	1.71	1.75
	1.718(2)	1.711(2)	1.719(2)	1.68(1–2)	1.7411(19)	1.72	1.75	1.71	1.72
N–O	1.425(3)	1.423(2)	1.435(2)	1.41(1–7)	1.422(2)	1.41	1.42	1.33	1.42
Bond angles									
S–N–S	114.7(1)	115.4(1)	115.4(1)	118(1–3)	105.61(10)	124.2	123.5	120.5	119.6
O–N–S(1)	106.2(1)	107.3(1)	105.2(1)	100(1–3)	106.77(13)	111.0	110.7	111.5	109.3
O–N–S(2)	108.1(2)	107.5(1)	106.6(1)	110(1–4)	105.51(13)	108.1	107.9	111.5	110.0
$\sum N^b$	329.0(1–2)	330.2(1)	327.2(1)	328(1–4)	317.89(10–13)	343.3	342.1	347.4	338.9
Torsion angles									
O–N–S–O	57.3(2)	54.0(2)	54.2(1)	61(1–4)	−42.00(15)	69.1	69.3	−31.6	100.0
	−175.9(1)	−177.1(1)	−177.1(1)	174(1–3)	−172.38(13)	−163.4	−162.4	97.1	−28.8
	−53.4(2)	−51.2(2)	−56.2(1)	53(1–4)	39.85(15)	−168.1	−167.9	50.4	59.1
	178.4(1)	−179.9(1)	176.6(1)	177(1–4)	169.36(13)	−41.0	−40.9	178.5	−173.9
A···nap_{plane}[c,d]									
S(1)···nap_{plane}	0.17	0.15	0.05	0.1	0.08[d]				
S(2)···nap_{plane}	0.09	0.03	0.04	0.3	0.01[d]				
N(1)···nap_{plane}	0.60	0.64	0.70	0.6	0.62[d]				

[a] Averages of parameters from the four crystallographically-independent molecules given. [b] Sum of bond angles at nitrogen. [c] Perpendicular distances from mean plane through naphthalene. [d] For **6**·H_2O distances from mean plane through benzene given.



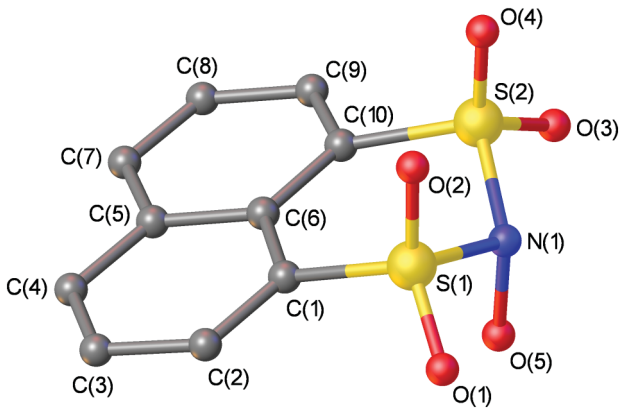


Fig. 2 X-ray crystal structure of **1**·H_2O (hydrogen atoms and solvent omitted for clarity).

cases. Refluxing for 24 h in the presence of *t*-BuOK in *t*-BuOH, or Et_3N in dichloromethane, followed by reacidification again returned starting material, suggesting **1** is stable to base. Finally, **1** proved to be hydrolytically stable in water, 1 M HCl and 1 M NaOH over 24 h at reflux.

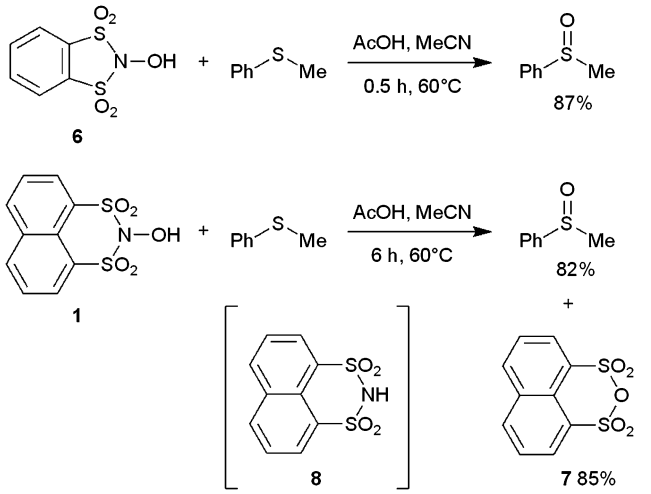
The high thermal and hydrolytic stability of **1** can be contrasted with that of known *N*,*N*-bissulfonylhydroxylamines reported in the literature. *N*,*N*-Bis(tolylsulfonyl)hydroxylamine has been reported to be hydrolytically unstable, and breaks down slowly at room temperature in $CDCl_3$, accelerated in an oxygen atmosphere, *via* the corresponding bissulfonylnitroxide radical.[4] Other acyclic *N*,*N*-bissulfonylhydroxylamines, both aryl and alkyl, have also been reported to be thermally, base and water sensitive at room temperature.[2,17,18]

The closely related cyclic, benzo-fused *N*,*N*-bissulfonylhydroxylamine, *N*-hydroxy-*O*-benzenedisulfonimide (**6**), has been reported to degrade upon prolonged standing at room temperature and to slowly decompose in boiling water.[19] This compound was studied by Degani and Fochi *et al.* as an oxidising reagent for organic synthesis.[20] To further gauge the relative reactivity of **1** and **6**, we ran a comparative sulfur oxidation under the conditions reported for **6** (Scheme 3). Consistent with the literature,[20] we found that **6** effectively oxidises methyl phenyl sulfide to the sulfoxide in 87% yield. In contrast, the naphthalene system **1** is a less reactive oxidant, requiring 6 h to achieve a comparable 82% yield of methyl phenyl sulfoxide. The novel sulfonic anhydride **7** was also isolated from this reaction, which presumably results from hydrolysis of bissulfonamide **8**, the expected product of oxygen transfer from **1** to the sulfide.

The UV spectrum of *N*,*N*-bissulfonylhydroxylamine **1** shows an absorbance at 298 nm (ε 17700). However, **1** also proved stable to irradiation in MeCN solution with a variety of light sources in both quartz and Pyrex glassware (5 W low pressure and 125 W medium pressure mercury arc lamps and a 500 W halogen lamp).

Nitroxide radical generation

The oxidation of hydroxylamines is a common method for the synthesis of nitroxides, and has been successfully applied in the study of acyclic *N*,*N*-bissulfonylhydroxylamines.[2–4] However, TLC analysis of the reaction of hydroxylamine **1** with a

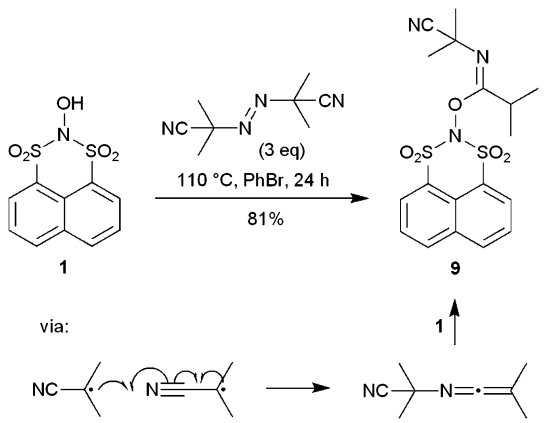


Scheme 3 Comparative oxidation of methyl phenyl sulfide using cyclic bissulfonylhydroxylamines.

wide variety of oxidants (Pd/C, PbO_2,[2,3,21] MnO_2,[22] $Cu(OAc)_2$,[23] $Ce(NH_4)_4(SO_4)_4$,[4] $Na_2WO_4{\cdot}2H_2O/H_2O_2$,[7] *m*CPBA) showed only starting material, which could be reisolated in essentially quantitative yield.

We also attempted formation of the nitroxide **2** through radical-mediated hydrogen atom abstraction. Heating **1** with benzoyl peroxide (benzene, reflux), di-*tert*-butoxydiazene (MeCN, 65 °C), or di-*tert*-butyl peroxydicarbonate (bromobenzene, 70 °C), or photoactivation of isoindoline nitroxide 1,1,3,3-tetramethylisoindolin-2-yloxyl (TMIO) (benzene, 150 W medium pressure Hg-arc lamp, pyrex, 7 h, rt)[24] again did not show formation of a new compound by TLC analysis. Use of Fenton conditions ($FeSO_4{\cdot}7H_2O$, DMSO, H_2O_2) to both generate the nitroxide by hydrogen atom abstraction and trap it with methyl radical also gave only starting material.

In only one case was a new product observed, when **1** was heated with an excess of AIBN. Formation of the unusual imidate **9** can be rationalized by addition of **1** to the ketenimine formed by the combination of two isobutyronitrile radicals (Scheme 4).[25] The structure of **9** was confirmed by X-ray diffraction analysis (Fig. 3).¶‖ The location of the imino double bond is indicated by the N(2)–C(11) bond length (1.255(3) Å). The heterocyclic ring again adopts a sofa conformation with a pseudo-axial oxygen



Scheme 4 Reaction of **1** with AIBN.

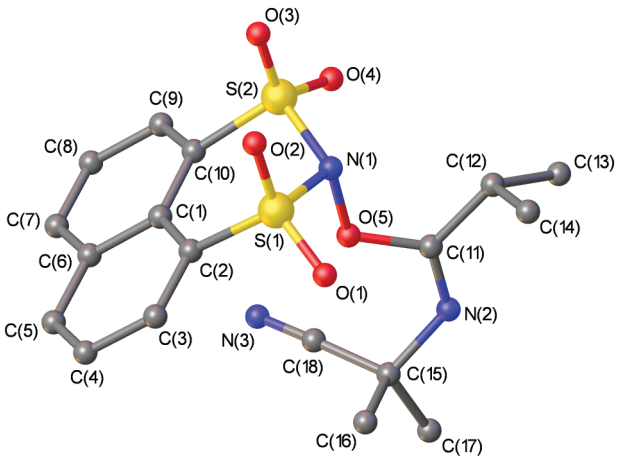


Fig. 3 X-ray crystal structure of **9** (hydrogen atoms omitted for clarity).

substituent, similar to **1**. Selected bond lengths and angles are reported in Table 1.

Notably, when the same conditions were applied to the benzo-fused ring system **6**, no compound analogous to **9** was isolated and instead extensive decomposition of **6** occurred, again suggesting that *N*,*N*-bissulfonylhydroxylamine **1** has a higher thermal stability than **6**.

In order to determine whether recovered starting material **1** in these reactions was a consequence of a failure of the nitroxide **2** to form, or a result of *in situ* hydrogen atom abstraction by **2**, the reaction of **1** with excess CAN was monitored by EPR. A three line spectrum was observed, consistent with formation of nitroxide **2** (Fig. 4). Oxidation of **6** under the same conditions gave a comparable a_N value, which we assign to the novel nitroxide **10**. The narrow spectral linewidths ($\Delta B_{1/2}$ = 0.32 G) enables

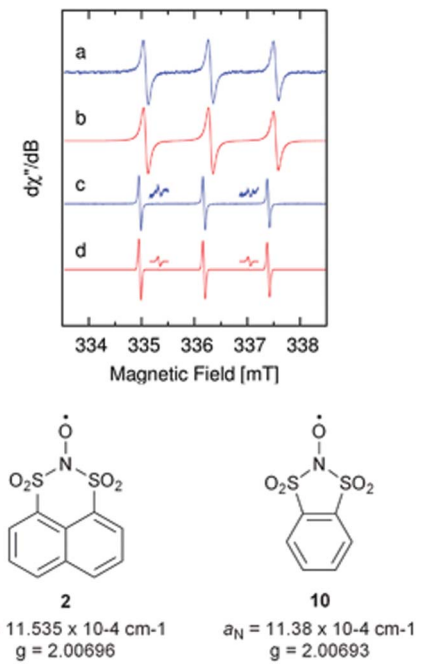


Fig. 4 (a) EPR spectra of **2** at 298 K in PhBr υ = 9.446851 GHz; (b) simulated EPR spectra of **2**; (c) EPR spectra of **10** at 298 K in PhBr υ = 9.440798 GHz; (d) simulated EPR spectra of **10**.

the observation of hyperfine coupling to the ^{15}N nucleus (0.36% natural abundance) as seen in Fig. 4 (expanded resonances). The a_N values for the cyclic nitroxides **2** and **10** lie in the range of EPR data reported for acyclic bis(arylsulfonyl)nitroxides ($a_N/g\beta = 10 - 12G$).[2,4,26]

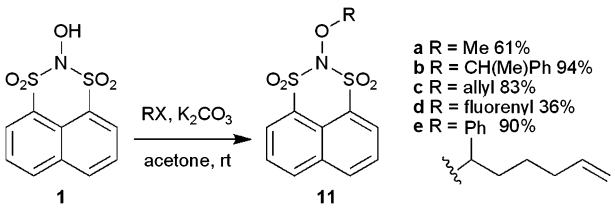
The conversion of **1** to **2** was estimated to be 10% by EPR after a single scan using TMIO as an internal standard.** Nevertheless, repetition of these conditions on a preparative scale with 10 equiv. of CAN in PhBr or benzene over extended time periods and at temperatures up to reflux did not reveal the formation of any new compound, with hydroxylamine **1** recovered qualitatively.

CAN is essentially insoluble in PhBr and benzene, and hence the EPR experiment was repeated using the more soluble ceric tetra-*n*-butylammonium nitrate[27] (CTAN) in CH_2Cl_2 as solvent. The initial conversion of **1** to **2** increased to 24%,** but on a preparative scale (2 equiv. CTAN in CH_2Cl_2 or MeCN, rt–reflux) only starting material **1** was recovered. Application of the same conditions to **6** showed an 85% initial conversion to nitroxide **10** by EPR,** but again only starting material was obtained on scale-up.

The EPR signals for **2** and **10** decayed over time (Fig. S8, ESI‡), more rapidly when using CTAN in CH_2Cl_2, presumably due to a more facile hydrogen abstraction from solvent or ammonium salt. No EPR signal for **2** is observed with CAN in PhBr at 100 °C.

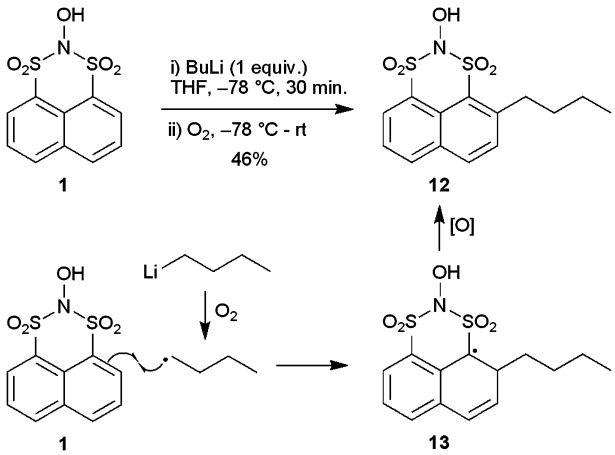
The reversible homolytic fission of *O*-benzylic alkoxy amines to nitroxides and benzylic radicals is a widely used technique for initiation of living radical polymerization,[28] and has also been applied by Studer *et al.* in small molecule synthesis,[29] both methodologies based on exploitation of the persistent radical effect.[30] We therefore undertook a study on the *O*-alkylation of **1** with a range of electrophiles. The resulting systems were envisioned as being potential precursors to nitroxide **2**.

O-Alkylation of **1** proceeded readily in acetone at rt in the presence of K_2CO_3 (Scheme 5). The *O*-styryl compound **11b** and the *O*-fluorenyl compound **11d** were both investigated as a means to synthesise the nitroxide **2**, through heating in *tert*-butyl benzene in the presence of oxygen,[31] however only starting material was observed. *In situ* generation of nitroxide **2** would be evidenced by the formation of tandem homolytic fission–radical cyclisation–nitroxide capture products[28] in the thermolysis of **11e**, however again no change occurred even upon prolonged heating in a sealed tube of a *t*-BuOH solution at 200 °C for 32 h.



Scheme 5 *O*-Alkylation of **1**.

A final attempt to generate nitroxide **2** through oxidation of the corresponding lithium alkoxide[32] gave an unexpected result. Attempted deprotonation of **1** at −78 °C with BuLi followed by bubbling oxygen through the solution gave the butyl-substituted naphthalene **12** (Scheme 6). When this reaction was carried out in the absence of oxygen, no transformation to **12** occurred, and the starting material was recovered after acidic work-up. The formation of **12** may be rationalized as occurring through a homolytic aromatic substitution reaction.[33] If deprotonation of **1** is slow, formation of a butyl radical by oxidation of BuLi can result. The nucleophilic butyl radical adds to the naphthalene ring, *ortho* to the activating sulfonyl group, and the resulting delocalized radical **13** regains aromaticity through oxidation.[34] The structure of **12** was confirmed by X-ray crystallography (Fig. S2, ESI‡ and Table 1).¶‖ The same product **12** was observed when the reaction was carried out at room temperature, suggesting deprotonation is particularly slow in the case of **1**. An analogous transformation does not occur for the benzo-fused *N*,*N*-bissulfonylhydroxylamine **6**, with starting material returned upon acidic work-up.



Scheme 6 Homolytic aromatic substitution of **1**.

This final intriguing result led us to determine the X-ray crystal structure of **6** (Fig. 5).¶‖ The heterocyclic ring adopts an envelope conformation, with the two sulfur atoms essentially coplanar with the benzene ring and the nitrogen at the flap of the envelope. The hydroxyl group is pseudo-axial on the 5-membered ring (O(5)–N(1)–S(1)–C(1) and O(5)–N(1)–S(2)–C(6) torsion angles 74.55(14)° and −76.54(14)° respectively), with the nitrogen lone-pair again bisecting the O–S–O dihedral angle (Table 1).

A selection of bond lengths and angles for the novel bissulfonylhydroxylamine derivatives reported herein, along with data for literature compounds **14–17**,[11–13] are reported in Table 1. The degree of pyramidalization at the bissulfonamide nitrogen is reflected in the sum of the bond angles $\sum N$. The nitrogen atom of the bicyclic compounds, most notably **6**, are significantly more pyramidalized than the acyclic systems **14–17**. The idealised O–N–S–O torsion angles where the nitrogen lone-pair bisects (*gauche*) the O–S–O system are 60° and 180°. These are most closely matched in the naphthalene-based systems.

Discussion

The data presented above suggests that although nitroxides **2** and **10** cannot be classified as stable radicals by the Ingold definition,[35] they have sufficient lifetime to be characterized by EPR. The major degradation pathway of **2** and **10** appears to be hydrogen

** Data obtained after a single scan due to the nitroxide signal for **2** or **10** decaying over time. % conversion = A/B × 100, where A = calculated double integration of unknown radical **2** or **10** (obtained by subtracting TMIO standard from spectrum containing both radicals), and B = calculated double integration of total spectrum.

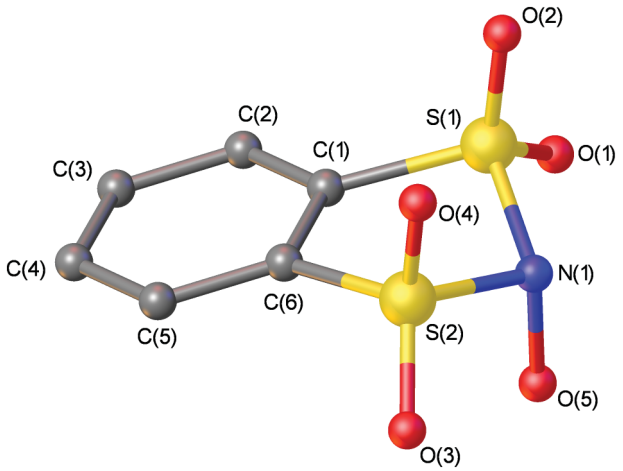
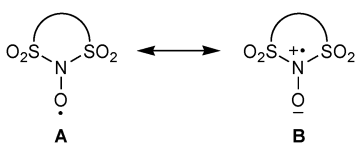


Fig. 5 X-ray crystal structure of **6**·H_2O (hydrogen atoms and solvent omitted for clarity).

abstraction, as evidenced by the complete recovery of the precursor hydroxylamines **1** and **6** under Ce(IV) oxidation conditions. Fragmentation of the nitroxide to an *N*-sulfonylnitroso species is either disfavoured or is rapidly reversible compared to hydrogen abstraction, and so incorporation into a ring system does appear to kinetically stabilise the nitroxide towards those degradation pathways previously observed for this class of radical.[2–4]

The lack of formation of nitroxide **2**, or any products derived thereof, from the attempted thermolysis of **11** reflects the high C–O bond dissociation energy in these alkoxyamines. Since other alkoxylamines undergo homolytic fission with the same benzylic carbon substituents,[28–30] nitroxide **2** must therefore be less thermodynamically stable than a typical alkyl or aryl-substituted nitroxide.

Nitroxide radicals are stabilised by the interaction of the nitrogen lone pair with the SOMO of the oxygen centred radical, which can be represented in the present case by the two resonance forms **A** and **B**. Resonance form **B** is destabilised relative to **A** as a result of the electron-withdrawing nature of the sulfonyl groups. Previous studies on sulfonyl-substituted nitroxides have noted the relatively large a_N values, also seen for **2** and **10**, compared with acyl nitroxides (a_N 4–8). For resonance contributor **B**, delocalisation of the unpaired electron into the sulfonyl group is negligible because of poor orbital overlap. In contrast, with acyl nitroxides, the lone pair of the nitrogen is conjugated with the carbonyl leading to lower spin density on the nitrogen and hence smaller a_N values.[26,36]



A **B**

Nitroxides having electron-withdrawing groups on nitrogen, particularly acyl nitroxides, are generally more reactive than nitroxides flanked by alkyl groups. These systems have high spin density on the nitroxide oxygen and high O–H bond dissociation energies in the corresponding hydroxylamine, which has led to their investigation as oxidants in organic chemistry through C–H abstraction.[37]

Although both nitroxides **2** and **10** behave similarly in undergoing hydrogen atom abstraction in preference to fragmentation, there are notable differences in the chemistry of their precursor hydroxylamines **1** and **6**. Hydroxylamine **1** is notably more stable (less reactive) than **6**, as evidenced by the isolation of **9**, and the more facile *O*-transfer from **6**. The only exception appears to be reaction with butyllithium and oxygen, where in the case of **1** butylation of the naphthalene ring is observed, whereas no analogous reaction occurs with **6**. Here, however, the recovery of **6** may be rationalized in two ways. Deprotonation of **6** may occur, and the resulting alkoxide is oxidised to the nitroxide, which abstracts a hydrogen to return **6** (or if oxidation does not occur, **6** is formed through protonation of the alkoxide on work-up). Alternatively the reaction may proceed initially as for **1**: deprotonation is again slow so that butyl radical formation occurs, however intermolecular homolytic aromatic substitution is less likely for **6** than for **1**, due to the ease of breaking naphthalene aromaticity compared with an isolated benzene ring. Our available data do not allow us to distinguish between these pathways.

At present we do not have a satisfactory explanation for the slow deprotonation of **1** (and possibly **6**) with butyllithium, although the folded conformation of these molecules places the hydroxyl group in the concave face of the molecule and hence deprotonation may be kinetically disfavoured on steric grounds.

Conclusions

The first study on the generation and stability of cyclic bis-sulfonylnitroxides **2** and **10** has been reported. Use of a cyclic system stabilises the radical towards fragmentation, the major decomposition pathway for acyclic bissulfonylnitroxides. Hydrogen atom abstraction by the radicals **2** and **10** is evidenced by the complete recovery of the precursor hydroxylamines under Ce(IV) oxidation conditions, where formation of the nitroxide has been demonstrated by EPR. The high thermal, photochemical and hydrolytic stability of *N*,*N*-bissulfonylhydroxylamine **1**, its ease of functionalisation, and the apparent reactivity of the nitroxides **2** and **10** towards hydrogen atom abstraction, may lead to new applications in organic chemistry.

Experimental

General

^{1}H and ^{13}C NMR data were recorded on a Bruker AC300, Bruker AVIII300, Bruker AV400 or a Bruker AMX400 spectrometer. Spectra were recorded in CD_2Cl_2 referenced to residual CH_2Cl_2 (^{1}H, 5.33 ppm), CD_3CN referenced to residual CH_3CN (^{1}H, 1.92 ppm; ^{13}C, 1.2 ppm), DMSO-d_6 referenced to residual DMSO (^{1}H, 2.50 ppm) and $CDCl_3$ referenced to residual $CHCl_3$ (^{1}H, 7.26 ppm; ^{13}C, 77.0 ppm). Chemical shifts are reported in ppm (δ) and coupling constants (J) are reported in Hz. The following abbreviations are used to describe multiplicity; s-singlet, d-doublet, t-triplet, m-multiplet. Mass spectra were recorded on either a LCT spectrometer or an Agilent QTOF LC/MS 6520 utilising electrospray ionisation (recorded in the positive mode) with a methanol mobile phase, or electron impact ionisation, and are reported as (m/z (%)). HRMS were recorded on a LCT spectrometer using lock mass incorporated into the mobile phase. IR spectra were recorded as KBr disks or neat on a Perkin Elmer 1600 series FT-IR Perkin Elmer FT-IR Paragon 1000,

Perkin Elmer 100-series FT-IR or a Nicolet 870 Nexus FT-IR spectrometer. UV/Vis spectra were recorded on a UV-3101PC Shimadzu spectrophotometer. Melting points were determined using open glass capillaries on a Gallenkamp melting point apparatus and are uncorrected. Elemental analyses were carried out by the University of Queensland Microanalytical Service. Analytical TLC was carried out on Merck 60 F245 aluminium backed silica gel plates. Short wave UV (245 nm), $KMnO_4$ or anisaldehyde were used to visualise components. Compounds were purified by flash column chromatography using Merck silica gel 60. Continuous wave X-band EPR spectra were recorded with a Bruker Biospin Elexsys E580 EPR spectrometer fitted with a super high Q cavity or a Bruker EMX-AR spectrometer operating at X-band frequencies (ca 9.2–9.8 GHz) with 100 kHz field modulation. Magnetic field and microwave frequency calibration were achieved with a Bruker ER 036M Teslameter and a Bruker microwave frequency counter, respectively or a Bruker ER 035M NMR gaussmeter and a Hewlett–Packard 5350B frequency counter respectively. Spectrometer tuning, signal averaging and subsequent spectral comparisons were performed with Bruker's Xepr (version 2.6) software. Computer simulation of the EPR spectra were performed using the XSophe-Sophe-XeprView computer simulation software suite (v 1.1.4) running on PC utilizing Mandriva 2009.1 as the Linux operating system.[38]

Naphthothiosulfonate **3** was prepared by oxidation of the corresponding disulfide.[6,39] (1-Bromohex-5-en-1-yl)benzene was prepared by modification of a literature procedure.[40] CTAN was prepared by the literature procedure.[27] All other compounds are commercially available and were used as received. Reactions were run in oven dried glassware under an argon atmosphere. Solvents were purified and dried using standard methods.

Naphtho[1,8-*c*,*d*][1,2]dithiole 1,1,2-trioxide (4)

Thiosulfonate **3** (604 mg, 2.72 mmol) was dissolved in dioxane (4.34 mL) and a solution of UHP (1.12 mL, 4.08 mmol) and NaOH (331 mg, 8.28 mmol) in water (2.88 mL) was added. The mixture was stirred for 15 min and evaporated to dryness. The resulting disodium salt was dissolved in H_2O (2.17 mL) and acidified slowly with conc. HCl to pH < 1. The resulting white solid was filtered and recrystallised from hot CH_2Cl_2–hexane to give sulfinyl sulfone **4** (470 mg, 73%). R_f 0.61 (8 : 2 CH_2Cl_2–hexane); mp 148–150 °C (CH_2Cl_2–hexane) (lit.,[9] 168–169 °C); ν_{max} (KBr)/cm^{-1} 3077, 1489, 1404, 1345, 1313 (SO_2), 1182, 1152 (SO_2), 1134 (SO_2) and 1083 (SO); δ_H(300 MHz; $CDCl_3$) 7.85–7.92 (2 H, m, Ar*H*), 8.18 (1 H, d, *J* 7.3, Ar*H*) and 8.25–8.28 (3 H, m, Ar*H*); δ_C(75 MHz; $CDCl_3$) 123.9 (CH), 125.8 (C), 2 × 128.6 (CH), 129.8 (CH), 132.4 (C), 132.9 (CH), 133.1 (CH), 135.5 (C) and 137.4 (C); *m*/*z* (ESI) 260.9651 ([M + Na]$^+$, $C_{10}H_6NO_3S_2Na$ requires 260.9656), 260.9 (100%).

2-Hydroxynaphtho[1,8-*de*][1,3,2]dithiazine 1,1,3,3-tetraoxide (1)

Naphtho[l,8-*cd*][l,2]dithiole l,l,2-trioxide (**4**) (258 mg, 1.08 mmol) and $NaNO_2$ (75.0 mg, 1.08 mmol) were dissolved in a mixture of H_2O (4.82 mL) and 1,4-dioxane (4.82 mL). Conc. HCl (386 μL) was added dropwise at room temperature and the solution was stirred overnight. The resulting precipitate was filtered and recrystallised from hot EtOAc (~3 mL) yielding bis(sulfonyl)hydroxylamine **1** (0.212 g, 69%) as a white, crystalline solid. R_f 0.33 (7 : 3 Et_2O–hexane); mp 167–169 °C (EtOAc); λ_{max} (MeCN)/nm 298 (ε/dm^3 mol^{-1} cm^{-1} 17 700); ν_{max} (KBr)/cm^{-1} 3535 (OH), 3092 (CH), 2862, 1497, 1380, 1361 (SO_2N), 1220, 1191, 1174 (SO_2N), 1156, 902, 846 (SO_2) and 829; δ_H(300 MHz; CD_3CN, 0.1 M) 7.91 (2 H, dd, *J* 8.3 and 7.5, SCCHC*H*), 8.44 (2 H, dd, *J* 8.5 and 1.0, SCC*H*), 8.49 (2 H, dd, *J* 7.4 and 1.1, SCCCC*H*) and 9.99 (1 H, s, NO*H*); δ_H(300 MHz; CD_3CN, 0.01 M) 7.93 (2 H, dd, *J* 8.3 and 4.4, Ar*H*), 8.47 (4H, dd, *J* 8.0 and 1.0, Ar*H*), 8.50 (2 H, dd, *J* 7.4 and 1.1, Ar*H*) and 9.85 (1 H, s, NO*H*); δ_H(300 MHz; CD_2Cl_2) 7.90 (2 H, t, *J* 7.8, Ar*H*), 8.37 (2 H, d, *J* 8.4, Ar*H*), 8.49 (2 H, d, *J* 7.4, Ar*H*) and 8.60 (1 H, s, NO*H*); δ_H(300 MHz; DMSO-d_6) 8.62 (2 H, d, *J* 8.3, Ar*H*), 8.60 (2 H, d, *J* 7.4, Ar*H*) and 8.02 (2 H, t, *J* 7.8, Ar*H*); δ_C(100 MHz; CD_3CN) 120.8 (SC*C*), 128.1 (SCCH*C*H), 129.7 (C), 130.9 (SCCC*C*H), 134.1 (C) and 136.9 (SC*C*H); *m*/*z* (ESI) 307.9669 ([M + Na]$^+$, $C_{10}H_7NO_5S_2Na$ requires 307.9663), 308 (100%).

Oxidation of methyl phenyl sulfide with 1. Isolation of 3-oxa-1,3-dithiaphenalene 1,1,3,3-tetraoxide (7)

Thioanisole (8.57 μL, 0.073 mmol) was heated in acetic acid (0.15 mL) at 60 °C. A solution of bissulfonylhydroxylamine **1** (20 mg, 0.070 mmol) in MeCN (0.15 mL) was added dropwise over a period of 30 min. The solution was heated at 60 °C for a 2 h. Additional bissulfonylhydroxylamine **1** (5 mg, 0.017 mmol) was added as a solid to the mixture and heating continued for a further 4 h at 60 °C. The mixture was washed with water (3 × 3 mL), 5% NaOH solution (3 × 3 mL) and extracted with EtOAc (3 × 5 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography (7 : 3 Et_2O–hexane) yielded 3-oxa-1,3-dithiaphenalene 1,1,3,3-tetroxide (**7**) (16 mg, 85%) as a white solid. Further elution (Et_2O) afforded methyl phenyl sulfoxide (8 mg, 82%). **7**: R_f 0.58 (7 : 3 Et_2O–hexane); mp 211–213 °C; ν_{max} (KBr)/cm^{-1} 3076, 1400, 1384, 1370, 1344, 1180 and 1147; δ_H(300 MHz; $CDCl_3$) 7.89 (2 H, dd, *J* 8.3 and 7.5, Ar*H*) and 8.35 (2 H, dd, *J* 8.5 and 1.0, Ar*H*) and 8.43 (2 H, dd, *J* 7.4 and 1.1, Ar*H*); δ_C(100 MHz; $CDCl_3$) 119.9 (C), 127.0 (CH), 128.5 (CH), 130.5 (C), 133.1 (C), and 135.4 (CH); *m*/*z* (ESI) 292.9551 ([M + Na]$^+$, $C_{10}H_6O_5S_2Na$ requires 292.9554), 292.8 (100%). Methyl phenyl sulfoxide: R_f 0.10 (7 : 3 Et_2O–hexane); mp 29–31 °C; δ_H(300 MHz; $CDCl_3$) 2.75 (3 H, s, C*H*$_3$) and 7.54–7.70 (5 H, m); δ_C(75 MHz; $CDCl_3$) 45.9 (CH_3), 127.4 (2 ×CH), 128.9 (2 × CH), 132.7 (CH) and 143.2 (C).

(*Z*)-1,1,3,3-Tetraoxidonaphtho[1,8-*d*,*e*][1,3,2]dithiazin-2-yl *N*-(2-cyanopropan-2-yl)isobutyimidate (9)

A solution of AIBN (17 mg, 0.105 mmol) and bissulfonylhydroxylamine **1** (10 mg, 0.035 mmol) in bromobenzene (1.06 mL) was heated at reflux for 24 h. The solution was allowed to cool to room temperature and was purified by column chromatography (2 : 1 EtOAc–hexane) to afford **9** (12 mg, 81%) as a white solid. R_f 0.50 (1 : 1 EtOAc–hexane); mp 170–172 °C (CH_2Cl_2); found: C, 51.25; H, 4.4; N, 9.8; S, 15.35. $C_{18}H_{19}N_3O_5S_2$ requires C, 51.3; H, 4.5; N, 10.0; S, 15.2%; ν_{max} (neat)/cm^{-1} 2971, 2925, 2233, 1700, 1559, 1497, 1392, 1373, 1364, 1219, 1189, 1177, 1160, 1151, 1116 and 1076; δ_H(400 MHz; $CDCl_3$) 8.48 (2 H, d, *J* 7.2, Ar*H*), 8.34 (2 H, d, *J* 8.2, Ar*H*), 7.87 (2 H, t, *J* 7.8, Ar*H*), 3.35 (1 H, septet, *J*

6.6, C*H*(CH_3)$_2$), 1.25 (6 H, d, *J* 6.6, CH(C*H*$_3$)$_2$) and 1.17 (6 H, s, NCC(C*H*$_3$)$_2$); δ_C(100 MHz; $CDCl_3$) 161.7 (C), 136.0 (CH), 133.3 (C), 130.2 (CH), 129.6 (C), 126.9 (CH), 121.3 (C), 120.5 (C), 47.9 (C), 29.7 (CH), 28.9 (CH_3) and 20.4 (CH_3); *m*/*z* (ESI) 444.0674 ([M + Na]$^+$, $C_{18}H_{19}N_3O_5S_2Na$ requires 444.0658), 444 (69%), 422 (100), 338 (34) and 282 (25).

O-Alkylation of 1: General procedure

To a solution of **1** (1 eq) in acetone (0.05 M) was added potassium carbonate (1.5 eq) followed by alkyl halide (10 eq) at room temperature. After stirring for 16 h the solvent was removed under reduced pressure. The residue was dissolved in EtOAc and washed with water. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The *O*-alkylated product **11** was purified by column chromatography.

2-Methoxynaphtho[1,8-*de*][1,3,2]dithiazine 1,1,3,3-tetraoxide (11a)

Following the general procedure, **1** (100 mg, 0.35 mmol), potassium carbonate (73 mg, 0.53 mmol) and methyl iodide (0.22 mL, 3.50 mmol) in acetone (7 mL) afforded **11a** (62 mg, 61%) as a white solid after column chromatography (1 : 1 hexane–CH_2Cl_2). R_f 0.78 (1 : 1 hexane–CH_2Cl_2); mp 178–180 °C; λ_{max} (MeCN)/nm 298 (ε/dm^3 mol^{-1} cm^{-1} 31 300); ν_{max} (neat)/cm^{-1} 3094, 1381, 1362, 1188, 1173 and 1153; δ_H(300 MHz; $CDCl_3$) 8.46 (2 H, dd, *J* 7.5 and 1.7, Ar*H*), 8.30 (2 H, dd, *J* 8.5 and 1.1, Ar*H*), 7.86 (1 H, d, *J* 7.5, Ar*H*), 7.84 (1 H, d, *J* 7.5, Ar*H*) and 4.09 (3 H, s, OC*H*$_3$); δ_C(100 MHz; $CDCl_3$) 135.4 (CH), 133.20 (C), 130.0 (C), 129.7 (CH), 126.9 (CH), 120.5 (C) and 67.4 (CH_3); *m*/*z* (EI) 298.9911 (M$^+$, $C_{11}H_9NO_5S_2$ requires 298.9922), 299 (83%), 284 (41), 269 (100), 255 (28), 254 (42), 206 (92), 190 (48), 174 (86), 162 (63), 134 (61), 126 (27), 114 (40) and 102 (28).

2-(1-Phenylethoxy)naphtho[1,8-*de*][1,3,2]dithiazine 1,1,3,3-tetraoxide (11b)

Following the general procedure, **1** (50 mg, 0.18 mmol), potassium carbonate (36 mg, 0.26 mmol) and 1-bromoethylbenzene (0.24 mL, 1.75 mmol) in acetone (3.5 mL) afforded **11b** (64 mg, 94%) as a white solid after column chromatography (1 : 1 hexane–EtOAc). R_f 0.30 (1 : 1 hexane–EtOAc); mp 129–131 °C; ν_{max} (neat)/cm^{-1} 2935, 1496, 1386, 1366, 1189, 1173 and 1149; δ_H(300 MHz; $CDCl_3$) 8.41 (2 H, d, *J* 6.7, Ar*H*), 8.19 (2 H, dd, *J* 8.4 and 0.9, Ar*H*), 7.76 (2 H, t, *J* 7.8, Ar*H*), 7.27–7.37 (5 H, m, Ar*H*), 5.55 (1 H, q, *J* 6.6, OC*H*) and 1.77 (3 H, d, *J* 6.6, OCC*H*$_3$); δ_C(100 MHz; $CDCl_3$) 138.2 (C), 135.20 (CH), 133.1 (C), 130.2 (C), 129.4 (CH), 128.9 (CH), 128.3 (CH), 128.0 (CH), 126.7 (CH), 120.3 (C), 87.7 (CH) and 19.2 (CH_3); *m*/*z* (EI) 412.0295 ([M + Na]$^+$, $C_{18}H_{15}NO_5S_2Na$ requires 412.0289), 482 (30%), 467 (12), 466 (100), 428 (18) and 412 (63).

2-(Allyloxy)naphtho[1,8-*de*][1,3,2]dithiazine 1,1,3,3-tetraoxide (11c)

Following the general procedure, **1** (50 mg, 0.18 mmol), potassium carbonate (36 mg, 0.26 mmol) and allyl bromide (0.15 mL, 1.75 mmol) in acetone (3.5 mL) afforded **11c** (47 mg, 83%) as a white solid after column chromatography (1 : 1 hexane–EtOAc). R_f 0.52 (1 : 1 hexane–EtOAc); mp 232–234 °C; ν_{max} (neat)/cm^{-1} 3091, 1496, 1421, 1388, 1368, 1188, 1173 and 1147; δ_H(300 MHz; $CDCl_3$) 8.45 (2 H, dd, *J* 7.4 and 1.2, Ar*H*), 8.29 (2 H, dd, *J* 8.4 and 1.1, Ar*H*), 7.85 (1 H, d, *J* 7.5, Ar*H*), 7.83 (1 H, d, *J* 7.5, Ar*H*), 5.86–6.00 (1 H, m, CH_2C*H*), 5.29–5.39 (2 H, m, OC*H*$_2$) and 4.79 (2 H, dt, *J* 6.8 and 0.9, CH=C*H*$_2$); δ_C(100 MHz; $CDCl_3$) 135.3 (CH), 133.2 (C), 130.5 (C), 130.1 (C), 129.6 (CH), 126.8 (CH), 122.3 (CH_2), 120.4 (CH) and 81.2 (CH_2); *m*/*z* (EI) 347.9980 ([M + Na]$^+$, $C_{13}H_{11}NO_5S_2Na$ requires 347.9976), 488 (100%).

2-((9*H*-Fluoren-9-yl)oxy)naphtho[1,8-*de*][1,3,2]dithiazine 1,1,3,3-tetraoxide (11d)

Following the general procedure, **1** (100 mg, 0.35 mmol), potassium carbonate (73 mg, 0.53 mmol) and bromofluorene (860 mg, 0.35 mmol) in acetone (7 mL) afforded **11d** (56 mg, 36%) as a white solid after column chromatography (1 : 1 hexane–EtOAc). R_f 0.48 (1 : 1 hexane–EtOAc); mp 224–226 °C; ν_{max} (neat)/cm^{-1} 3081, 1494, 1453, 1382, 1367, 1192, 1173 and 1155; δ_H(300 MHz; $CDCl_3$) 8.44 (2 H, dd, *J* 7.4 and 1.1, Ar*H*), 8.24 (2 H, dd, *J* 8.4 and 0.9, Ar*H*), 7.81 (1 H, d, *J* 7.6, Ar*H*), 7.79 (1 H, d, *J* 7.7, Ar*H*), 7.72 (2 H, d, *J* 7.6, Ar*H*), 7.56 (2 H, d, *J* 7.6, Ar*H*), 7.37 (1 H, d, *J* 6.8, Ar*H*), 7.35 (1 H, d, *J* 6.8, Ar*H*), 7.23 (2 H, td, *J* 7.5 and 1.0, Ar*H*) and 6.39 (1 H, s, C*H*); δ_C(100 MHz; $CDCl_3$) 141.2 (C), 139.4 (C), 135.3 (CH), 133.2 (C), 131.7 (C), 130.2 (CH), 129.6 (CH), 127.5 (CH), 127.4 (CH), 126.8 (CH), 120.3 (C), 119.9 (CH) and 89.3 (CH); *m*/*z* (ESI) 472.0293 ([M + Na]$^+$, $C_{23}H_{15}NO_5S_2Na$ requires 472.0289), 472 (100%).

2-((1-Phenylhex-5-en-1-yl)oxy)naphtho[1,8-*de*][1,3,2]dithiazine 1,1,3,3-tetraoxide (11e)

Following the general procedure, **1** (20 mg, 0.07 mmol), potassium carbonate (14 mg, 0.11 mmol) and (1-bromohex-5-en-1-yl)benzene (168 mg, 0.70 mmol) in acetone (1.4 mL) afforded **11e** (28 mg, 90%) as a white solid after column chromatography (1 : 1 hexane–EtOAc). R_f 0.50 (1 : 1 hexane–EtOAc); mp 144–146 °C; ν_{max} (neat)/cm^{-1} 2929, 1496, 1391, 1372, 1221, 1191, 1175 and 1151; δ_H(300 MHz; $CDCl_3$) 8.38–8.43 (2 H, m, Ar*H*), 8.19 (2 H, dd, *J* 8.3 and 0.8, Ar*H*), 7.76 (2 H, t, *J* 7.7, Ar*H*), 7.27–7.34 (5 H, m, Ar*H*), 5.61–5.75 (1 H, m, CH_2=C*H*), 5.29–5.34 (1 H, m, OC*H*), 4.87–4.95 (2 H, m, CH=C*H*$_2$), 2.18–2.30 (1 H, m, 0.5 × OCHC*H*$_2$), 1.97–2.05 (2 H, m, CH_2=CHC*H*$_2$), 1.81–1.89 (1 H, m, 0.5 × OCHC*H*$_2$) and 1.12–1.31 (2 H, m, CH_2C*H*$_2$CH$_2$); δ_C(100 MHz; $CDCl_3$) 138.1 (CH), 136.9 (C), 135.3 (CH), 133.1 (C), 130.4 (C), 129.4 (CH), 129.1 (CH), 128.9 (CH), 128.3 (CH), 126.7 (CH), 120.3 (C), 114.9 (CH_2), 92.1 (CH), 33.4 (CH_2), 32.5 (CH_2) and 24.7 (CH_2); *m*/*z* (ESI) 466.0747 ([M + Na]$^+$, $C_{22}H_{21}NO_5S_2Na$ requires 466.0759), 466 (100%).

4-Butyl-2-hydroxynaphtho[1,8-*de*][1,3,2]dithiazine 1,1,3,3-tetraoxide (12)

A solution of *n*-BuLi in hexanes (1.69 M, 0.04 mL, 0.07 mmol) was added dropwise to a stirred solution of bissulfonylhydroxylamine **1** (20 mg, 0.07 mmol) in THF (0.7 mL) and pentane (0.7 mL) at −78 °C. After stirring for 30 min at the same temperature, O_2 was bubbled through the solution for 5 min. The mixture was stirred under an oxygen atmosphere for 16 h, warming to room temperature. The mixture was washed with water (3 × 3 mL) and

extracted with EtOAc (3 × 5 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography afforded **12** (11 mg, 46%) as a white solid. R_f 0.60 (7 : 3 EtOAc–hexane); mp 86–88 °C (CH_2Cl_2); ν_{max} (neat)/cm^{-1} 3607, 3538, 2961, 2932, 2861, 1498, 1466, 1388, 1368, 1188, 1170, 1161 and 1105; δ_H(300 MHz; $CDCl_3$) 8.44 (1 H, dd, *J* 7.4 and 1.2, Ar*H*), 8.20 (1 H, dd, *J* 8.2 and 1.1, Ar*H*), 8.14 (1 H, d, *J* 8.5, Ar*H*), 7.73 (1 H, t, *J* 7.8, Ar*H*), 7.68 (1 H, d, *J* 8.5, Ar*H*), 3.29–3.34 (2 H, m, CH_2), 1.75–1.86 (2 H, m, CH_2), 1.53 (2 H, sextet, *J* 7.4, CH_2) and 0.99 (3 H, t, *J* 7.4, CH_3); δ_C(75 MHz; $CDCl_3$) 147.4 (C), 135.5 (CH), 134.1 (CH), 132.0 (C), 131.0 (CH), 130.0 (CH), 128.3 (C), 127.9 (C), 125.4 (CH), 121.8 (C), 35.1 (CH_2), 33.4 (CH_2), 22.9 (CH_2) and 13.8 (CH_3); *m*/*z* (EI) 364.0279 ([M + Na]$^+$, $C_{14}H_{15}NO_5S_2Na$ requires 364.0289), 364 (100%).

Acknowledgements

We thank the EPSRC (EP/C543122/1 Advanced Research Fellowship 2005–2010 to RSG, EP/C543130/1 studentship and PhD Plus funding to BP), King's College London and the ARC Centre of Excellence for Free Radical Chemistry and Biotechnology (CEO 561607) for funding. We thank the UK National Crystallography Service for X-ray diffraction data collection for **1**.H_2O, **12** and **6**.H_2O. The NMR spectrometers used in this research were obtained through Birmingham Science City: Innovative Uses for Advanced Materials in the Modern World (West Midlands Centre for Advanced Materials Project 2), with support from Advantage West Midlands (AWM) and part funded by the European Regional Development Fund (ERDF).

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