In search of a new class of stable nitroxide: synthesis and reactivity of a *peri*-substituted

N,N-bissulfonylhydroxylamine

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Electronic Supplementary Information

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Supplementary Material (ESI) for Organic & Biomolecular Chemistry This journal is © The Royal Society of Chemistry 2011 Copies of ¹H and ¹³C NMR spectra

¹H NMR in CDCl₃ (300 MHz) for compound **4**





10.0 9.5 7.5 4.0 3.5 2.5 2.0 1.5 1.0 0.5 9.0 8.5 8.0 7.0 6.5 6.0 5.5 5.0 4.5 3.0 0.0 -0.5

¹³C NMR in CDCl₃ (75 MHz) for compound **4**









¹H NMR in CD_2Cl_2 (300 MHz) for compound **1**



¹H NMR in DMSO-d₆ (300 MHz) for compound **1**





¹³C NMR in CD₃CN (100 MHz) for compound **1**









¹H NMR in CDCl₃ (300 MHz) for compound **7**



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 9.0	۲۲۲ ۲۲ 	7.0	6.0	5.0	4.0	3.0	2.0	1.0	0.0

13 C NMR in CDCl₃ (100 MHz) for compound **7**



¹H NMR in CDCl₃ (400 MHz) for compound **9**



^{13}C NMR in CDCl₃ (100 MHz) for compound **9**



¹H NMR in CDCl₃ (300 MHz) for compound **11a**

¹³C NMR in CDCl₃ (100 MHz) for compound **11a**

-10

¹³C NMR in CDCl₃ (100 MHz) for compound **11b**

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200	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0	-10

¹H NMR in CDCl₃ (300 MHz) for compound **11c**

¹³C NMR in CDCl₃ (100 MHz) for compound **11c**

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210	200	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	3	0	20	10	0		-10

¹H NMR in CDCl₃ (300 MHz) for compound **11d**

¹³C NMR in CDCl₃ (100 MHz) for compound **11d**

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210	200	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0	-10

¹³C NMR in CDCl₃ (100 MHz) for compound **11e**

¹H NMR in CDCl₃ (300 MHz) for compound **12**

13 C NMR in CDCl₃ (100 MHz) for compound **12**

0

Single Crystal X-ray Diffraction Analyses

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Compound reference	1.H2O	1.EtOAc	9	12	6.H2O
Chemical formula	$C_{10}H_7NO_5S_2 \cdot H_2O$	$C_{10}H_7NO_5S_2 \cdot C_4H_8O_2$	$C_{18}H_{19}N_3O_5S_2$	$C_{14}H_{15}NO_5S_2 \cdot H_2O$	C ₆ H ₅ NO ₅ S ₂ •H ₂ O
Formula Mass	303.30	373.39	421.48	359.41	253.25
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
a/Å	6.9698(2)	14.1894(3)	15.1983(15)	12.0422(14)	7.2877(3)
b/Å	9.4671(3)	7.1236(2)	8.5889(7)	13.3971(13)	8.1680(3)
c/Å	17.7500(4)	18.0588(4)	15.6813(15)	21.306(3)	8.3571(2)
$\alpha / ^{\circ}$	90.00	90.00	90.00	72.268(7)	93.740(2)
$\beta/^{\circ}$	94.399(2)	112.6270(10)	95.420(10)	81.717(4)	107.823(2)
γ/°	90.00	90.00	90.00	74.535(7)	92.785(2)
Unit cell volume/Å ³	1167.76(6)	1684.87(7)	2037.8(3)	3148.0(6)	471.35(3)
Temperature/K	120(2)	296(2)	173(2)	120(2)	120(2)
Space group	$P2_1/n$	$P2_1/n$	$P2_{1}/c$	Pİ	Pİ
No. of formula units per unit cell, Z	4	4	4	8	2
Radiation type	ΜοΚα	CuKa	ΜοΚα	ΜοΚα	ΜοΚα
Absorption coefficient, μ/mm^{-1}	0.479	3.207	0.295	0.369	0.574
No. of reflections measured	16422	10441	14029	28727	8728
No. of independent reflections	2668	3067	4719	10075	2171
R _{int}	0.0898	0.0385	0.0522	0.1065	0.0425
Final R_I values $(I > 2\sigma(I))$	0.0552	0.0388	0.0476	0.1509	0.0391
Final $wR(F^2)$ values $(I > 2\sigma(I))$	0.1506	0.0992	0.1021	0.2496	0.0871
Final R_1 values (all data)	0.0645	0.0515	0.0732	0.2695	0.0465
Final $wR(F^2)$ values (all data)	0.1599	0.1083	0.1069	0.3157	0.0918
Goodness of fit on F^2	1.082	1.040	1.080	1.094	1.076
CCDC Deposition Number	798806	798807	798808	798809	798810

Table S1 Crystallographic Details for the X-ray Crystal Structures of 1.H₂O, 1.EtOAc, 9, 12 and 6.H₂O

Suitable crystals were selected and datasets were measured on a Bruker SMART 6000 diffractometer for **1.EtOAc**, on an Oxford Diffraction Gemini Ultra diffractometer for **9**, and by the UK National Crystallography Service on a Bruker KappaCCD diffractometer for **1.H**₂**O** and a Bruker APEXII CCD diffractometer for **12** and **6.H**₂**O**, both at the windows of a Bruker FR591 rotating anode. The data collections were driven by SMART¹ and processed by SAINTPLUS² for **1.EtOAc**, were driven by CrysAlis CCD³ and processed by CrysAlis RED³ for **9** and were driven by COLLECT⁴ and processed by DENZO⁵ for **1.H**₂**O**, **12** and **6.H**₂**O**. Absorption corrections were applied using SADABS⁶ for **1.H**₂**O**, **1.EtOAc**, **12** and **6.H**₂**O**, and **12** were solved in SHELXS-97,⁷ the structure of **9** was solved in SIR97⁸ and that of **6.H**₂**O** was solved in SIR204.⁹ All five structures were refined by a full-matrix least-squares procedure on F² in SHELXL-97.⁷ All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms belonging to water molecules in **1.H**₂**O**, **12** and **6.H**₂**O** were located in the electron density and their positions refined subject to O-H (0.88 (2) Å) and H...H (1.41 (4) Å) bond distance restraints. The remaining hydrogen atoms in all structures were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on the equivalent isotropic displacement parameter (U_{eq}) of the parent atom. Figures were produced using OLEX2¹⁰ and Mercury 2.3.¹¹

The structure of 12 contains four crystallographically-independent nitroxide molecules with one molecule of water per nitroxide molecule. Two of the O₂SN(OH)SO₂ groups are disordered over two positions with the percentage O(201)O(202)S(201)N(201)(O(205))S(202)O(203)O(204) occupancy ratio of and O(21')O(22')S(21')N(21')(O(25'))S(22')O(23')O(24') 79(1):21(1) being and that of O(301)O(302)S(301)N(301)(O(305))S(302)O(303)O(304) and O(31')O(32')S(31')N(31')(O(35'))S(32')O(34') being 80(1):20(1). In addition, the terminus of the butyl group C(111)-C(114) is disordered over two positions with the percentage occupancy ratio of C(113)-C(114) and C(13')-C(14') being 80:20. 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.

Fig. S1 X-ray crystal structure of 1.EtOAc (hydrogen atoms and solvent omitted for clarity).

Fig. S2 X-ray crystal structure of one of the four crystallographically-independent molecules of 12 (hydrogen atoms and solvent omitted for clarity).

Fig. S3 π - π Stacking interactions in **1.H**₂**O**. The average interplanar separation is 3.4 Å. (Hydrogen atoms and solvent omitted for clarity).

Fig. S4 π - π Stacking interactions in **1.EtOAc**. The average interplanar separation is 3.4 Å. (Hydrogen atoms and solvent omitted for clarity).

Fig. S5 π - π Stacking interactions in 9. The interplanar separation is 3.6 Å. (Hydrogen atoms omitted for clarity).

Fig. S6 π - π Stacking interactions in 12 involving the four crystallographically-independent molecules. The average interplanar separation is 3.3 Å. (Minor parts of disordered groups, hydrogen atoms and solvent omitted for clarity).

Fig. S7 π - π Stacking interactions in **6.H**₂**O**. The average interplanar separation is 3.5 Å. (Hydrogen atoms and solvent omitted for clarity).

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EPR decay curves for nitroxides 2 and 10

Fig. S8 Decay of EPR signals for solutions of nitroxide 2 (green line) generated with CAN in bromobenzene and nitroxides 2 (blue line) and 10 (red line) generated with CTAN in dichloromethane over time.