In search of a new class of stable nitroxide: synthesis and reactivity of a peri-substituted \(N,N\)-bissulfonylhydroxylamine

Bhaven Patel, Julie Carlisle, Steven E. Bottle, Graeme R. Hanson, Benson M. Kariuki, Louise Male, John C. McMurtrie, Neil Spencer and Richard S. Grainger

\(a\) School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK
Fax: +44 (0)121 4144403; Tel: +44 (0)121 4144465; E-mail: r.s.grainger@bham.ac.uk

\(b\) Department of Chemistry, King’s College London, Strand, London WC2R 2LS, UK

\(c\) ARC Centre of Excellence for Free Radical Chemistry and Biotechnology, Queensland University of Technology, Brisbane, Queensland, 4001, Australia

\(d\) Centre for Advanced Imaging, The University of Queensland, Brisbane, Queensland, 4072, Australia

\(e\) Present address: School of Chemistry, Cardiff University, Park Place, Cardiff CF10 3AT, UK

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$^1$H NMR in CDCl$_3$ (300 MHz) for compound 4

Copies of $^1$H and $^{13}$C NMR spectra
$^{13}$C NMR in CDCl₃ (75 MHz) for compound 4
$^1$H NMR in CD$_3$CN (300 MHz) for compound 1 (0.1M)
$^1$H NMR in CD$_3$CN (300 MHz) for compound 1 (0.01M)
$^1$H NMR in CD$_2$Cl$_2$ (300 MHz) for compound 1
$^{1}$$H$ NMR in DMSO-$d_6$ (300 MHz) for compound 1
$^{13}$C NMR in CD$_3$CN (100 MHz) for compound 1
HSQC-1/J(CC)-ADEQUATE NMR in CD$_3$CN (500 MHz) for compound 1

- 2 x H(2)
- 2 x H(4)
- 2 x H(3)
- 2 x C(3)
- 2 x C(1)
- 2 x C(2)
- C(5)
- 2 x C(4)

ppm
HSQC NMR in CD$_2$CN (500 MHz) for compound 1

- 2 x H(2)
- 2 x H(4)
- 2 x H(3)
- 2 x C(3)
- 2 x C(1)
- 2 x C(2)
- C(5)
- 2 x C(4)

ppm

8.55 8.50 8.45 8.40 8.35 8.30 8.25 8.20 8.15 8.10 8.05 8.00 7.95 7.90 7.85 ppm
$^1$H NMR in CDCl$_3$ (300 MHz) for compound 7
$^{13}$C NMR in CDCl$_3$ (100 MHz) for compound 7
$^1$H NMR in CDCl$_3$ (400 MHz) for compound 9
$^{13}$C NMR in CDCl$_3$ (100 MHz) for compound 9
$^1$H NMR in CDCl$_3$ (300 MHz) for compound 11a
$^{13}$C NMR in CDCl$_3$ (100 MHz) for compound 11a
$^1$H NMR in CDCl$_3$ (300 MHz) for compound 11b

Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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$^{13}$C NMR in CDCl$_3$ (100 MHz) for compound 11b
$^1$H NMR in CDCl$_3$ (300 MHz) for compound 11c
$^{13}$C NMR in CDCl$_3$ (100 MHz) for compound 11c
$^1$H NMR in CDCl$_3$ (300 MHz) for compound 11d
$^{13}$C NMR in CDCl$_3$ (100 MHz) for compound 11d
$^1$H NMR in CDCl$_3$ (300 MHz) for compound 11e
$^{13}$C NMR in CDCl$_3$ (100 MHz) for compound 11e
$^1$H NMR in CDCl$_3$ (300 MHz) for compound 12
$^{13}$C NMR in CDCl$_3$ (100 MHz) for compound 12
Single Crystal X-ray Diffraction Analyses

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

<table>
<thead>
<tr>
<th>Compound reference</th>
<th>1H₂O</th>
<th>1EtOAc</th>
<th>9</th>
<th>12</th>
<th>6H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C₉H₁₀NO₃S₂•H₂O</td>
<td>C₈H₁₀NO₃S₂•C₂H₅O₂</td>
<td>C₈H₁₀NO₃S₂</td>
<td>C₈H₁₀NO₃S₂•H₂O</td>
<td>C₉H₁₀NO₃S₂•H₂O</td>
</tr>
<tr>
<td>Formula Mass</td>
<td>303.30</td>
<td>373.39</td>
<td>421.48</td>
<td>399.41</td>
<td>253.5</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>a/Å</td>
<td>6.9698(2)</td>
<td>14.1894(3)</td>
<td>15.1983(15)</td>
<td>12.0422(14)</td>
<td>7.2877(3)</td>
</tr>
<tr>
<td>b/Å</td>
<td>9.4671(3)</td>
<td>7.1236(2)</td>
<td>8.5889(7)</td>
<td>13.3971(13)</td>
<td>8.1680(3)</td>
</tr>
<tr>
<td>c/Å</td>
<td>17.7500(4)</td>
<td>18.0588(4)</td>
<td>15.6813(15)</td>
<td>21.306(3)</td>
<td>8.3571(2)</td>
</tr>
<tr>
<td>α°</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>72.268(7)</td>
<td>93.740(2)</td>
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<tr>
<td>β°</td>
<td>94.399(2)</td>
<td>112.6270(10)</td>
<td>95.420(10)</td>
<td>81.717(4)</td>
<td>107.823(2)</td>
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<tr>
<td>γ°</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>74.535(7)</td>
<td>92.785(2)</td>
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<tr>
<td>Unit cell volume/Å³</td>
<td>1167.76(6)</td>
<td>1684.87(7)</td>
<td>2037.8(3)</td>
<td>3148.0(6)</td>
<td>471.35(3)</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>120(2)</td>
<td>296(2)</td>
<td>173(2)</td>
<td>120(2)</td>
<td>120(2)</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/n</td>
<td>P2₁/c</td>
<td>P1</td>
<td>P1</td>
<td></td>
</tr>
<tr>
<td>No. of formula units per unit cell, Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>8</td>
<td>2</td>
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<tr>
<td>Radiation type</td>
<td>MoKα</td>
<td>CuKα</td>
<td>MoKα</td>
<td>MoKα</td>
<td>MoKα</td>
</tr>
<tr>
<td>Absorption coefficient, μ/mm⁻¹</td>
<td>0.479</td>
<td>3.207</td>
<td>0.295</td>
<td>0.369</td>
<td>0.574</td>
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<tr>
<td>No. of reflections</td>
<td>16422</td>
<td>10441</td>
<td>14029</td>
<td>28727</td>
<td>8728</td>
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<tr>
<td>No. of independent reflections</td>
<td>2668</td>
<td>3067</td>
<td>4719</td>
<td>10075</td>
<td>2171</td>
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<tr>
<td>Rwp</td>
<td>0.0898</td>
<td>0.0385</td>
<td>0.0522</td>
<td>0.1065</td>
<td>0.0425</td>
</tr>
<tr>
<td>Final Rf values (I &gt; 2σ(I))</td>
<td>0.0552</td>
<td>0.0388</td>
<td>0.0476</td>
<td>0.1509</td>
<td>0.0391</td>
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<tr>
<td>Final wR² values (I &gt; 2σ(I))</td>
<td>0.1506</td>
<td>0.0992</td>
<td>0.1021</td>
<td>0.2496</td>
<td>0.0871</td>
</tr>
<tr>
<td>Final Rf values (all data)</td>
<td>0.0645</td>
<td>0.0515</td>
<td>0.0732</td>
<td>0.2695</td>
<td>0.0465</td>
</tr>
<tr>
<td>Final wR² values (all data)</td>
<td>0.1599</td>
<td>0.1083</td>
<td>0.1069</td>
<td>0.3157</td>
<td>0.0918</td>
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<tr>
<td>Goodness of fit on F²</td>
<td>1.082</td>
<td>1.040</td>
<td>1.080</td>
<td>1.094</td>
<td>1.076</td>
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<tr>
<td>CCDC Deposition Number</td>
<td>798806</td>
<td>798807</td>
<td>798808</td>
<td>798809</td>
<td>798810</td>
</tr>
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</table>

Suitable crystals were selected and datasets were measured on a Bruker SMART 6000 diffractometer for 1EtOAc, on an Oxford Diffraction Gemini Ultra diffractometer for 9, and by the UK National Crystallography Service on a Bruker KappaCCD diffractometer for 1H₂O and a Bruker ApexII CCD diffractometer for 12 and 6H₂O, both at the windows of a Bruker FR591 rotating anode. The data collections were driven by SMART1 and processed by SAINTPLUS2 for 1EtOAc, were driven by CrysAlis CCD3 and processed by CrysAlis RED4 for 9 and were driven by COLLECT5 and processed by DENZO5 for 1H₂O, 12 and 6H₂O. Absorption corrections were applied using SADABS6 for 1H₂O, 1EtOAc, 12 and 6H₂O and in the SCALE3 ABSPACK scaling algorithm with CrysAlis RED7 for 9. The structures of 1H₂O, 1EtOAc and 12 were solved in SHELXS-977, the structure of 9 was solved in SIR978 and that of 6H₂O was solved in SIR20049. All five structures were refined by a full-matrix least-squares procedure on F² in SHELXL-977. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms belonging to water molecules in 1H₂O, 12 and 6H₂O 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 O₃S(NH)SO₂ groups are disordered over two positions with the percentage occupancy ratio of O(201)O(202)S(201)N(201)(O(205))S(202)O(203)O(204) and O(21')O(22')S(21')N(21')(O(25'))S(22')O(23')O(24') being 79(1):21(1) 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(33')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.H₂O. 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 $\pi-\pi$ Stacking interactions in $6\text{H}_2\text{O}$. The average interplanar separation is 3.5 Å. (Hydrogen atoms and solvent omitted for clarity).

References

1. **SMART**, program for instrument control and data acquisition, 1997, Bruker AXS, Inc. 5465 East Cheryl Parkway, Madison, Wisconsin 53711-5373, USA.
2. **SAINTPLUS**, program suite for data processing, 1997, Bruker AXS, Inc. 5465 East Cheryl Parkway, Madison, Wisconsin 53711-5373, USA.
EPR decay curves for nitroxides 2 and 10

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