Novel Sulfurated Five-, Seven- and Nine-membered Heterocycles: Unusual Products derived from Potential Bisthionitroxide Precursors

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We report the synthesis of three examples of new classes of sulfurated heterocycles: dithiadiazaphospholidine **3**, benzothiadiazacycloheptene **6a** and benzotrithiadiazacyclononene **6b** arising from strained cyclic *N,N*-disubstituted diazadisulfides (**2** and **5**) *via* oxidation or disproportionation; single-crystal X-ray structural analyses are reported for the phospholidine and the benzocycloheptene.

A topic of some current interest[1] is the search for new materials with potential magnetic properties. Nitroxides have featured strongly in this area[2] but to date there have been no reports involving their sulfur analogues. We have generated cyclic systems (**2a** and **5a**) which were expected to serve as precursors for close-proximity bisthionitroxides (**2b** and **5b**) at elevated temperatures or under photolysis. We have found that these highly reactive species defy isolation and instead rapidly undergo transformation *in situ* to the novel heterocycles 1,4-dioxo-4-phenyl-3,5-di-*tert*-butyl-1,2,3,5,4-dithiadiazaphospholidine **3**, 3,6-dioxo-2,7-di-*tert*-butyl-1,2,7-benzo[4,5]thiadiazacycloheptene **6a** and 5,8-dioxo-4,9-di-*tert*-butyl-1,2,3,4,9-benzo[6,7]trithiadiazacyclononene **6b** (Schemes 1 and 2).

The dithiadiazaphospholidine **3**, a stable, colourless, crystalline material which we have fully characterised† by NMR, MS, X-ray (Fig. 1)‡ and elemental analysis, represents the first known example of this ring system and completes a series of these novel carbon-free heterocycles we have synthesised with ring size ranging from five to eight.[3,4] Its precursor **2a** is the only species in this series that is so susceptible to oxidation. This result can be attributed to the ring strain and the repulsive lone pair–lone pair interactions[5] present in this unique heterocycle. The heterocycles **6** are also unique, this being the first report of such cyclic nitrogen and sulfur containing systems. Again lone pair–lone pair repulsions and strain would lead to the high reactivity of **5a**. The major product isolated (**6a**) still shows considerable distortion of the amide moieties from coplanarity with the aromatic ring, commensurate with the difficulties of incorporating the single large sulfur atom (Fig. 2).

The synthesis of the cyclic disulfide precursors to these novel heterocycles involves the simple addition of sulfur(I) chloride (S_2Cl_2) to suitable diamides and phosphonic diamides in pyridine. With di-*tert*-butylphenylphosphonic diamide **1**, transitory NMR signals attributable to **2** can be detected in the reaction mixture at ambient temperatures, however only the *S*-oxide **3** could be isolated. Analogously strained dithiirane rings are known to readily oxidise.[5] The production of **3** is very temperature, concentration and time dependent. At more elevated temperatures, higher concentrations of S_2Cl_2 or longer reaction times, a seven-membered tetrathia heterocycle predominates,[3] although the reaction mixture becomes very complex.[4]§ Lower temperatures result in poor conversions and other bases/solvents also give poor results.

The reaction of S_2Cl_2 with benzene di-*tert*-butyldicarboxamide **4** in pyridine on the other hand is much cleaner, but again the dithia heterocycle **5** cannot be isolated and only a transient species is detected *in situ* by NMR. Presumably rapid disproportionation of **5** gives rise to the unusual thia and trithia

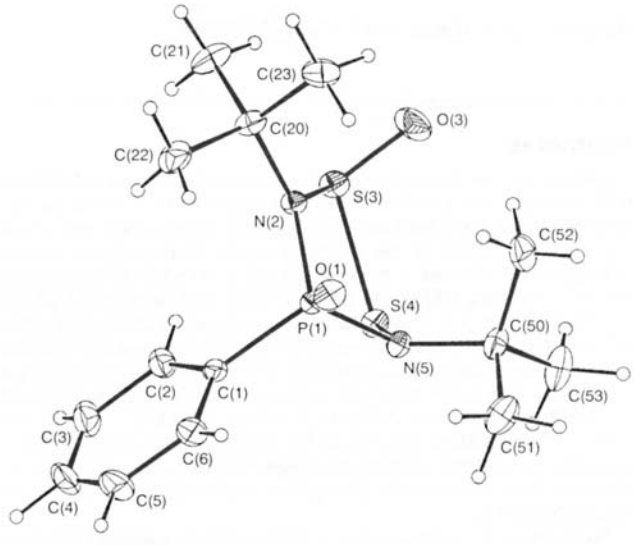

Fig. 1 Molecular configuration and atom numbering scheme for **3**. Unless otherwise indicated, atoms are carbon. Important bond distances (Å) and angles (°) are: P(1)–O(1) 1.468(2), P(1)–N(2) 1.693(2), P(1)–N(5) 1.674(2), N(2)–S(3) 1.693(2), S(3)–O(3) 1.461(2), S(3)–S(4) 2.158(1), S(4)–N(5) 1.699(2), N(2)–P(1)–N(5) 102.2(1), P(1)–N(2)–S(3) 120.5(1), N(2)–S(3)–S(4) 91.0(1), N(2)–S(3)–O(3) 108.9(1), O(3)–S(3)–S(4) 111.7(1), S(3)–S(4)–N(5) 99.0(1), S(4)–N(5)–P(1) 106.1(1).

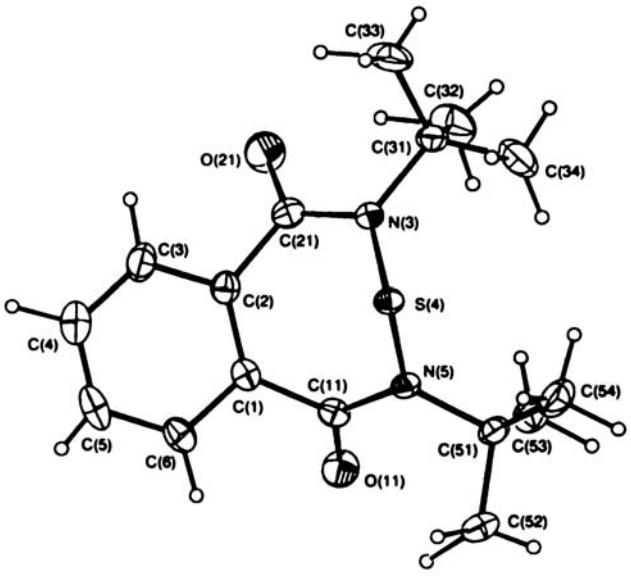

Fig. 2 Molecular configuration and atom numbering scheme for **6a**. Important bond distances (Å) and angles (°) are: N(3)–S(4) 1.691(3), N(5)–S(4) 1.695(3), C(21)–N(3) 1.369(6), C(11)–N(5) 1.382(5), C(31)–N(3) 1.526(5), C(51)–N(5) 1.514(5), C(21)–N(3)–S(4) 116.6(3), C(21)–N(3)–C(31) 120.4(3), C(31)–N(3)–S(4) 122.5(3), N(3)–S(4)–N(5) 104.0(2), S(4)–N(5)–C(11) 116.0(3), S(4)–N(5)–C(51) 123.1(3), C(51)–N(5)–C(11) 120.9(3).

heterocycles **6** along with some elemental sulfur. No other major components are detectable in the reaction mixture¶ and these sulfurated heterocycles were produced in relatively high yield, with the seven-membered sulfurated heterocycle **6a** predominating.‖ For both of the presumed transients (**2a** and **5a**) two *tert*-butyl signals are detected in the NMR, indicating non-equivalence of these groups. It is likely that the constraints of incorporating the large sulfur atoms gives rise to a non-symmetrical ring shape which equilibrates slowly on the NMR time-scale. This effect has also been seen with the seven-[3] and eight-membered[4] carbon-free species.

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Footnotes

† *Synthetic and spectroscopic data*: To synthesise **3** a solution of **1** (200 mg, 0.75 mmol) in dry pyridine (7 ml) was cooled to 0 °C under an inert atmosphere and S_2Cl_2 (440 mg, 3.2 mmol) was added slowly with stirring *via* a syringe. NMR of the *tert*-butyl region of the reaction mixture ([$^2H_5$]pyridine) showed a transient species [^{1}H NMR ([$^2H_5$]pyridine), δ 1.42 (s, 9H, Bu^t), 1.52 (s, 9H, Bu^t); ^{13}C NMR ([$^2H_5$]pyridine); δ 30.3 (d, 3 × Me), 31.7 (d, 3 × Me)], estimated $t_{1/2}$ < 5 min at 20 °C. After 2 h at 0 °C chromatography gave 215 mg (83%) of a white powder. Recrystallisation from MeOH gave colourless needles. [^{1}H NMR ([$^2H_5$]pyridine), δ 1.47 (s, 9H, Bu^t), 1.51 (s, 9H, Bu^t), 7.22–7.32 (m, 3H, Ar H), 7.78 (m, 2H, Ar H); ^{13}C NMR ([$^2H_5$]pyridine), δ 30.0 (d, 3 × Me), 31.6 (d, 3 × Me), 62.8 (d, *C*Me$_3$), 62.9 (d, *C*Me$_3$), 128.3 (d, Ar C), 132.0 (d, Ar C), 132.3 (d, Ar C)]. Doublets (d) indicate coupling to phosphorus, the *ipso* carbon was not detected. Mass spectrometry (EI) gave a molecular ion at *m/z* = 346 ($C_{14}H_{23}N_2O_2PS_2$).

To synthesise **6** a solution of **4** (2 g, 7.2 mmol) in dry pyridine (20 ml) was cooled to 0 °C under an inert atmosphere and S_2Cl_2 (1.95 g, 22 mmol) was added slowly with stirring *via* a syringe. NMR of the *tert*-butyl region of the reaction mixture in [$^2H_5$]pyridine showed a transient species [^{1}H NMR ([$^2H_5$]pyridine), δ 1.29 (s, 9H, Bu^t), 1.51 (s, 9H, Bu^t), ^{13}C NMR ([$^2H_5$]pyridine): δ 28.9 (3 × Me), 31.8 (3 × Me)], estimated $t_{1/2}$ < 10 min at 20 °C. After 48 h at room temp. chromatography gave a mixture of **6a** and **6b** (1.8 g) as a slightly yellow powder. Two recrystallisations from acetonitrile gave **6a** (1.53 g, 69%) as colourless needles of analytical purity. [^{1}H NMR ($CDCl_3$), δ 1.63 (s, 18H, 2 × Bu^t), 7.52 (dd, 2H, Ar H), 7.67 (dd, 2H, Ar H), ^{13}C NMR ($CDCl_3$), d 29.5 (6 × Me), 63.4 (2 × *C*Me$_3$), 127.8 (Ar C), 130.4 (Ar C), 135.6 (Ar C), 173.7 (2 × C=O)]. Mass spectrometry (EI) gave a molecular ion at *m/z* 306 ($C_{16}H_{22}N_2O_2S$). Further chromatography of the mother-liquors gave poorly crystalline **6b** (0.252 g, 9.4%). [^{1}H NMR ($CDCl_3$), δ 1.57 (s, 18H, 2 × Bu^t), 7.39 (s, 4H, Ar H); ^{13}C NMR ($CDCl_3$), δ 29.1 (6 × Me), 63.2 (2 × *C*Me$_3$), 126.7. (Ar C), 129.3 (Ar C), 137.4 (Ar C), 174.5 (2 × C=O)]. Mass spectrometry (EI) gave a molecular ion at *m/z* = 370 ($C_{16}H_{22}N_2O_2S_3$). All products isolated gave satisfactory elemental analyses.

‡ *Crystallography*: Both crystal specimens used for X-ray analysis were cleaved from larger crystals.

Crystal data **3**: $C_{14}H_{23}N_2O_2PS_2$ M_r = 346.4, monoclinic, space group *Cc*, *a* = 6.501(2), *b* = 19.998(5), *c* = 13.935(6) Å, β = 102.09(3)°, *V* = 1772(1) Å^3, *Z* = 4, D_c = 1.299 g cm^{-3}, *F*(000) = 736, λ = 0.710 73 Å, μ(Mo-Kα) = 4.0 cm^{-1}, *T* = 298(2) K. **6a** $C_{16}H_{22}N_2O_2S$, M_r = 306.4, monoclinic, space group $P2_1/n$, *a* = 8.079(2), *b* = 12.219(3), *c* = 16.634(4) Å, β = 92.59(1)°, *V* = 1640.4(7) Å^3, *Z* = 4, D_c = 1.241 g cm^{-3}, *F*(000) = 656, λ = 0.710 73 Å, μ(Mo-Kα) = 2.0 cm^{-1}, *T* = 293(2) K.

Data collection, structure solution and refinement: X-Ray diffraction data were collected from crystals measuring 0.30 × 0.28 × 0.20 mm (**3**), and 0.38 × 0.25 × 0.12 mm (**6a**) on an Enraf-Nonius CAD-4 diffractometer, using graphite-crystal monochromatized Mo-Kα radiation (λ = 0.710 73 Å). Of 3359 (**3**), and 3103 (**6a**) reflections collected up to $2\theta_{max}$ = 50° [collection ranges: *h*, −7–0; *k*, −23–23; *l*, −16–16 (**3**) and *h*, 0–9; *k*, 0–24; *l*, −19–19 (**6a**)], 1708 (R_{int} = 0.041) and 2886 (R_{int} = 0.024) respectively were unique. Data were corrected for absorption using semi-empirical methods.[6] Both structures were solved using direct methods (SHELXS-86)[7] and refined (on F^2) by full-matrix least squares (SHELXL 93)[8] to residuals *R*, *wR* and *S* of 0.022, 0.052, 1.05 (**3**) and 0.054, 0.147, 1.03 (**6a**) for 1653 and 1761 observed data with $I > 2.0\,\sigma I$. For **3**, *A* = 0.033, *B* = 0 and for **6a**, *A* = 0.090, *B* = 1.26 were used in the weighting scheme $w = 1/\sigma^2[(F_o^2) + (AP)^2 + BP]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$. Hydrogen atoms were included in the respective refinements at calculated positions with both positional and thermal parameters refined. The largest peaks in the final electron density maps for **3** and **6a** were 0.29 and 0.32 e Å^{-3}. Important bond distances and angles are included in Figs. 1 and 2. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ There are over ten components detectable by ^{13}C and ^{31}P NMR spectroscopy.

¶ As detectable by ^{1}H and ^{13}C NMR.

‖ A ratio of 85 : 15 for **6a** : **6b** was determined by analytical C_{18} HPLC of the crude reaction mixture.

References

1 T. Ishida and H. Iwamura, *J. Am. Chem. Soc.*, 1991, **113**, 4238; *Jap. Pat.*, JP 03,100,006; Chem. Abstr., 1991, **115**, 184225z.

2 K. Inoue and H. Iwamura, *J. Chem. Soc., Chem. Commun.*, 1994, 2273; R. Chiarelli, Y. Dromzee, Y. Jeannin, M. A. Novak, A. Rassat and J. L. Tholence, *Phys. Scr.*, 1993, **49**, 706; L. Dulog and W. Wang, *Adv. Mater.*, 1992, **4**, 349.

3 S. E. Bottle, R. C. Bott, I. D. Jenkins, C. H. L. Kennard, G. Smith and A. D. Wells, *J. Chem. Soc., Chem. Commun.*, 1993, 2273.

4 S. E. Bottle, R. C. Bott, C. H. L. Kennard, G. Smith, U. Wermuth, submitted to *Acta Crystallogr., Sect. C.*

5 A. Ishii, T. Akazawa, T. Maruta, J. Nakayama, M. Hoshini and M. Shiro, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 777; A. Ishii, T. Akazawa, M. X. Ding, T. Honjo, J. Nakayama and M. Hoshini, *J. Am. Chem. Soc.*, 1993, **115**, 4914.

6 C. K. Fair, MolEN. An intelligent interactive program for crystal structure analysis. Enraf-Nonius, Delft, 1990.

7 G. M. Sheldrick, SHELXS-86. Structure solution package, University of Göttingen, 1986.

8 G. M. Sheldrick, SHELXL-93. Program for crystal structure determination, University of Göttingen, 1993.