The first isolation and structure analysis of a crystalline tetrathiolane

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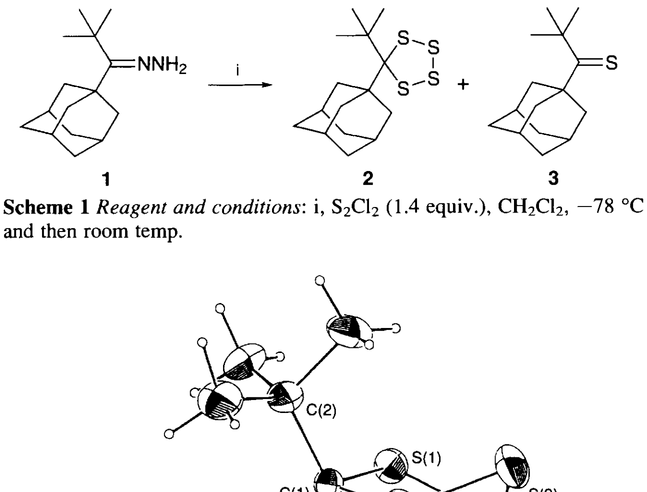
1-Adamantyl *tert*-butyl ketone hydrazone reacts with disulfur dichloride in dichloromethane to give 5-(1-adamantyl)-5-*tert*-butyltetrathiolane.

The chemistry of cyclic polysulfides, RR′CS$_n$, has drawn much attention because of their structures and reactivities. In addition, they have recently been detected in the sulfur metabolite of hyperthermophilic archaea,[1] sediments collected from hydrothermal fields in the Gulf of California[2] and from an inshore industrial site in the Great Lakes,[3] and some kinds of pyrolysates.[4] Of the cyclic polysulfides with n from 2 to 34,[5–9] tetrathiolane (n = 4)† and trithietane (n = 3) are the only two missing links since we recently succeeded in the synthesis and structure analysis of dithiirane (n = 2).[10] This is in contrast with the Group 14 elements heavier than carbon, where the tetrathiametallolanes (ArAr′MS$_4$; M = Si, Ge, Sn) are the most stable forms of ArAr′MS$_n$.[11] Here we report on the first isolation of a crystalline tetrathiolane by reaction of a sterically congested hydrazone with S_2Cl_2,[6c,‡] which was discovered during the course of our work on the chemistry of dithiiranes.



Scheme 1 *Reagent and conditions*: i, S_2Cl_2 (1.4 equiv.), CH_2Cl_2, −78 °C and then room temp.

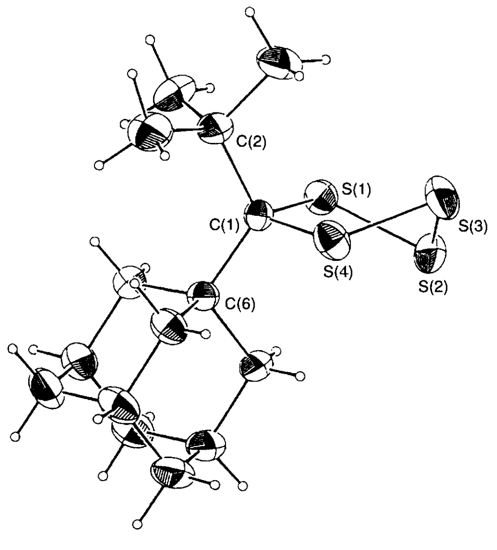


Fig. 1 ORTEP drawing (50% ellipsoids) of **2**. Selected bond lengths (Å), bond angles (°) and torsion angles (°): C(1)–S(1) 1.884(3), S(1)–S(2) 2.042(2), S(2)–S(3) 2.052(2), S(3)–S(4) 2.048(2), S(4)–C(1) 1.875(3), C(1)–C(2) 1.605(4), C(1)–C(6) 1.604(4); S(1)–C(1)–S(4) 108.4(2), C(1)–S(1)–S(2) 102.6(1), S(1)–S(2)–S(3) 93.9(1), S(2)–S(3)–S(4) 94.1(1), S(3)–S(4)–C(1) 102.8(1), C(2)–C(1)–C(6) 120.3(3), S(4)–C(1)–C(6) 103.6(2), S(1)–C(1)–C(2) 102.7(2); C(1)–S(1)–S(2)–S(3) 49.4(1), S(1)–S(2)–S(3)–S(4) 57.3(1), S(2)–S(3)–S(4)–C(1) 48.7(1).

To a solution of 1-adamantyl *tert*-butyl ketone hydrazone **1**[12] in dichloromethane was added a solution of 1.4 equiv. of S_2Cl_2 in dichloromethane at −78 °C. After being stirred for 1 h at this temperature, the mixture was gradually warmed to room temperature. Aqueous workup followed by chromatographic purification (silica gel) gave 5-(1-adamantyl)-5-*tert*-butyltetrathiolane **2** in 5.5% yield and 1-adamantyl *tert*-butyl thioketone **3** as the main product (46%). When a larger excess of S_2Cl_2 was used (2.5 equiv.), 1-adamantyl-*tert*-butyldichloromethane was obtained in 16% yield along with **3** (16%).

The tetrathiolane **2** is a yellow, crystalline material melting at 110 °C with decomposition to thione **3**. The structure of **2** was elucidated from its spectroscopic data and elemental analysis§ and finally confirmed by X-ray single-crystal structure analysis.¶ In the ^{1}H NMR spectrum, the *tert*-butyl protons and the methylene protons at the 2-position of the 1-adamantyl group appear as broad singlets, indicating that the free rotation of *tert*-butyl and 1-adamantyl groups in **2** is disturbed due to steric hindrance among the two bulky alkyl groups and the sulfur atoms. In the crystal, the tetrathiolane **2** takes a half chair conformation and the steric hindrance causes lengthening of bonds around C(1) and widening of the angle C(2)–C(1)–C(6) (Fig. 1). It is significant to note that the torsion angles C(1)–S(1)–S(2)–S(3), S(1)–S(2)–S(3)–S(4) and S(2)–S(3)–S(4)–C(1) are 49.4, 57.3 and 48.7°, respectively, where deviations from the C–S–S–C 90° torsion angle in the most stable conformation of disulfides[13] reach to 32.7–41.3°. These values are considerably larger than those for the torsion angles at S–S bonds in pentathiane (18.0–20.2°),[5b] hexathiepane (0.9–19.2°),[5b] heptathiocane (0.1–7.7°)[7c] and octathionane (1.2–25.6°).[8]

Desulfuration of the tetrathiolane **2** with an equimolar amount of PPh_3 in benzene at room temperature gave a 1 : 2.5 mixture of thione **3** and tetrathiolane **2**, where neither the corresponding trithietane nor dithiirane was detected.

Footnotes

† Detection of the parent tetrathiolane by GC–MS analysis has been reported, see refs. 2 and 4(*c*).

‡ The reaction of hydrazones with S_2Cl_2 giving thiones (Okazaki reaction) was originally run in the presence of an amine to trap the hydrogen chloride generated, where thiocarbonyl *S*-sulfides and dithiiranes were proposed as precursors for the thiones.[6c] In the expectation of the isolation of dithiiranes by the Okazaki reaction, we carried out the reaction in the absence of amines since we now know that dithiiranes in our hands are unstable to basic materials.[10b]

§ *Selected data* for **2**: (Found: C, 54.36; H, 7.33; $C_{15}H_{24}S_4$ requires C, 54.17; H, 7.27%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.40 (br s, 9 H, Bu^t), 1.63 (br s, 6 H), 2.00 (br s, 3 H), 2.14 (br s, 6 H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 29.3, 32.7, 36.5, 43.7, 45.5, 47.7, 115.4 (S–C–S). MS (EI): m/z 332 (M$^+$).

¶ *Crystal data* for **2**: $C_{15}H_{24}S_4$, yellow columns, 0.36 × 0.22 × 0.24 mm, monoclinic, space group $P2_1/n$ (no.14), a = 13.740(2), b = 18.049(3), c = 6.480(1) Å, β = 93.25(2)°, U = 1604.3(5) Å^3, D_c = 1.38 g cm^{-3}, Z = 4, F(000) = 711, μ(Cu-Kα) = 52.320 cm^{-1}. Mac Science MXC3K diffractometer with graphite-monochromated Cu-Kα radiation (λ = 1.54178), ω–2θ scan method in the range 3 < 2θ < 140°, 3745 reflections measured, 3030 unique reflections. The structure was solved by direct methods using SIR92 in the CRYSTAN GM program system and refined by a full-matrix least-squares method using 2820 reflections [$I \geqslant$

$2\sigma(I)$] for 268 parameters. The final R, R_w $\{w = 1/[\sigma^2(F_0) + 0.002|F_0|^2]\}$ and S values are 0.0500, 0.0721 and 2.4969, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/270.

References

1 M. Ritzau, M. Keller, P. Wessels, K. O. Stetter and A. Zeeck, *Liebigs Ann. Chem.*, 1993, 871.

2 O. E. Kawka and B. R. T. Simoneit, *Org. Geochem.*, 1987, **11**, 311.

3 D. L. Fabacher, J. M. Besser, C. J. Schmitt, J. C. Harshbarger, P. H. Peterman and J. A. Lebo, *Arch. Environ. Contam. Toxicol.*, 1991, **20**, 17.

4 (*a*) Y. Zhang and C.-T. Ho, *J. Agric. Food Chem.*, 1991, **39**, 1145; (*b*) O. Hincelin, J. M. Ames, A. Apriyantono and J. S. Elmore, *Food Chem.*, 1992, **44**, 381; (*c*) W. J. Cole, M. Kaschke, J. A. Sherringham, G. B. Curry, D. Turner and M. J. Russell, *Marine Chemistry*, 1994, **45**, 243.

5 Pentathianes (n = 5): (*a*) F. Fehér, B. Degen and B. Söhngen, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 301; (*b*) F. Fehér and J. Lex, *Z. Anorg. Allg. Chem.*, 1976, **423**, 103; (*c*) F. Fehér and K. Glinka, *Z. Naturforsch. B, Chem. Sci.*, 1979, **34**, 1031; (*d*) N. Tokitoh, N. Takeda and R. Okazaki, *J. Am. Chem. Soc.*, 1994, **116**, 7907; (*e*) N. Takeda, N. Tokitoh, T. Imakubo, M. Goto and R. Okazaki, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 2757.

6 Hexathiepanes (n = 6): (*a*) K. Morita and S. Kobayashi, *Chem. Pharm. Bull.*, 1967, **15**, 988; (*b*) F. Fehér, J. Lex and K.-H. Linke, *Z. Naturforsch. B, Chem. Sci.*, 1969, **24**, 1485; (*c*) R. Okazaki, K. Inoue and N. Inamoto, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 3541 and ref. 5(*b*).

7 Heptathiocanes (n = 7): (*a*) F. Fehér and W. Becher, *Z. Naturforsch. B, Chem. Sci.*, 1965, **20**, 1125; (*b*) W. Lutz, T. Pilling, G. Rihs, H. R. Waespe and T. Winkler, *Tetrahedron Lett.*, 1990, **31**, 5457; (*c*) F. W. Heinemann, H. Hartung, N. Maier and H. Matschiner, *Z. Naturforsch. B, Chem. Sci.*, 1994, **49**, 1063 and ref. 1.

8 Octathionanes (n = 8): N. Tokitoh, N. Takeda, T. Imakubo, M. Goto and R. Okazaki, *Chem. Lett.*, 1992, 1599.

9 Me_2CS_n ($5 \leqslant n \leqslant 34$): R. Steudel, R. Strauss and D. Jensen, *Chemiker-Zeitung*, 1985, **109**, 349.

10 (*a*) A. Ishii, T. Akazawa, M.-X. Ding, T. Honjo, J. Nakayama, M. Hoshino and M. Shiro, *J. Am. Chem. Soc.*, 1993, **115**, 4914; (*b*) A. Ishii, T. Akazawa, T. Maruta, J. Nakayama, M. Hoshino and M. Shiro, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 777.

11 N. Tokitoh, H. Suzuki, T. Matsumoto, Y. Matsuhashi and R. Okazaki, *J. Am. Chem. Soc.*, 1991, **113**, 7047; N. Tokitoh, M. Saito and R. Okazaki, *J. Am. Chem. Soc.*, 1993, **115**, 2065; H. Suzuki, N. Tokitoh, S. Nagase and R. Okazaki, *J. Am. Chem. Soc.*, 1994, **116**, 11 578.

12 A. Ishii, R. Okazaki and N. Inamoto, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 861.

13 N. L. Allinger, M. J. Hickey and J. Kao, *J. Am. Chem. Soc.*, 1976, **98**, 2741; J. P. Snyder and L. Carlsen, *J. Am. Chem. Soc.*, 1977, **99**, 2931 and references cited therein.

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