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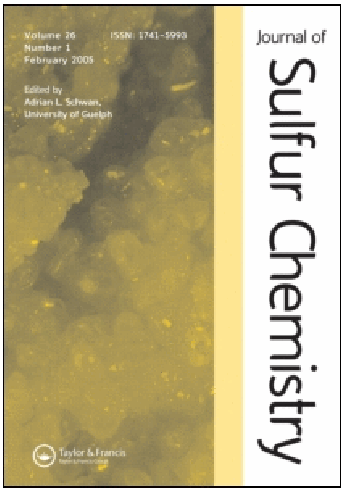

**Journal of Sulfur Chemistry**

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926081

# *Status Paper*: NMR and Crystallographic Study of Some Oxide Derivatives of D-t-Butyl Di-, Tri-, and Tetrasulfides

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**To cite this Article** Derbesy, Gérard and Harpp, David N.(1995) '*Status Paper*: NMR and Crystallographic Study of Some Oxide Derivatives of D-t-Butyl Di-, Tri-, and Tetrasulfides', Journal of Sulfur Chemistry, 16: 2, 363 — 369
**To link to this Article: DOI:** 10.1080/01961779508048744
**URL:** http://dx.doi.org/10.1080/01961779508048744

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*Sulfur Reports*, Volume 16, pp. 363–369
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# *STATUS PAPER:* NMR AND CRYSTALLOGRAPHIC STUDY OF SOME OXIDE DERIVATIVES OF DI-*t*-BUTYL DI-, TRI-, AND TETRASULFIDES

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*(Received July 18, 1994)*

The $^1$H and $^{13}$C NMR spectra for 16 di-, tri- and tetrasulfide oxide derivatives have been summarized. In addition, the relevant bond lengths and angles for 5 of these derivatives are reported from the X-ray crystal data.

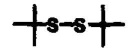
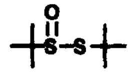
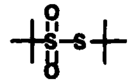
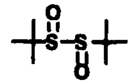
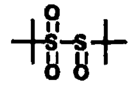
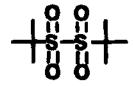
## INTRODUCTION

The characterization of the oxide derivatives of sulfides and disulfides has essentially been performed by $^1$H and $^{13}$C NMR spectroscopy.[1] The identification of the oxide derivatives of higher polysulfides (tri- and tetrasulfides) becomes even more complex because they are relatively less stable and some of them can only be detected at low temperature (~ −40 °C).[1c,d,g,2] Freeman laid the ground work for the analysis of a number of reactions with useful $^{13}$C NMR work.[2a] Our study of the oxidative reactivity of organopolysulfides,[3] strongly confirms that the techniques of choice to study this class of compounds are $^1$H and $^{13}$C NMR spectroscopy because they give extremely reliable chemical shifts and can easily be used at various temperatures.

The chemistry of a variety of oxide derivatives of di-*t*-butyl di-,[2a,4,5] tri-[6,a,b,c] and tetrasulfides[6a,b] has been investigated and we have extended earlier observations.[2b,3,6d] Five key derivatives have had their structures confirmed by X-ray crystallography.[2b] The use of mass spectrometry was not very helpful as only very small parent peaks could be obtained even under chemical ionization conditions. However, the results obtained showed specific fragmentation in some cases.[2b,6a] All of these oxide derivatives readily decompose under gas chromatographic analysis. Finally, the melting points were measured in all appropriate cases. In most situations, the samples melted over a *ca.* 20 °C range suggesting that the compound decomposed in the capillary tube.[2b,6a]

We present here a thorough comparative NMR study of this class of compounds that clearly shows that the chemical shifts of these derivatives can be predictably forecast. The X-ray structures obtained[2b] give new, useful information on bond lengths and angles.

**TABLE 1** $^1H$ and $^{13}C$ NMR Chemical Shifts (δ ppm) of the Oxide Derivatives of Di-*t*-Butyl Disulfide[a,b,c]

| Entry | R-$S_2O_n$-R′ | C | $CH_3$ | H | C′ | $CH_3'$ | H′ |
|---|---|---|---|---|---|---|---|
| **1a** |  | | | | 45.87 | 30.54 | 1.280 |
| **2a** |  | 59.35 | 24.18 | 1.531 | 48.65 | 32.21 | 1.353 |
| **5a** |  | 68.01 | 23.65 | 1.596 | 56.31 | 31.45 | 1.441 |
| **6a**[d] |  | 57.08 | 22.95 | 1.294 | | | |
| **7a**[d] |  | 69.28 | 23.74 | 1.499 | 63.68 | 23.80 | 1.474 |
| **8a** |  | 72.67 | 24.60 | 1.633 | | | |

[a] Recorded using deuterated chloroform ($CDCl_3$) as NMR solvent; [b] Relaxation time ($t_1$) used: $t_1$ =2 s; [c] **4b** and **4b'** represent the two diastereoisomers of **4**; [d] The spectra were obtained at −40 °C and do not represent a specific diastereoisomer.

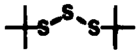
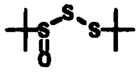
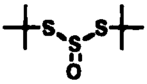
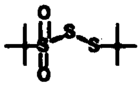
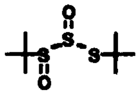
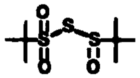
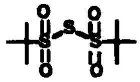
## COMPARATIVE NMR STUDY

The structure, $^1H$ and $^{13}C$ NMR chemical shifts of the oxide derivatives[2b] of di-*t*-butyl di- (compounds **a**) tri- (compounds **b**), and tetrasulfide (compounds **c**) are listed in Tables 1, 2 and 3, respectively. When the structures of one series of oxide derivatives had been confirmed by crystallography (*vide infra*), the structures of the oxide derivatives of the other series were able to be defined by NMR spectroscopy as there is a very good correlation among the compounds of this class.[3]

For unsymmetric molecules (**2**, **5**, **6b**, **7**), the more deshielded tertiary carbon (C in Table 1, 2 and 3) is bonded to the sulfur of higher oxidation state in $^{13}C$ NMR and the related methyl groups (H and $CH_3$ in Table 1, 2 and 3) are the more shielded in both $^1H$ and $^{13}C$ NMR.[2a]

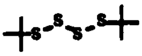
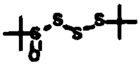
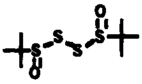
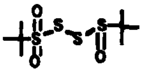
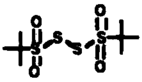
The analysis of the $^{13}C$ NMR data shows that the addition of one oxygen on a sulfur α to a *t*-butyl group has a great deshielding effect (11–13 ppm when a sulfinyl group is formed and 9–10 ppm when a sulfonyl group is formed) on the tertiary carbon and a moderate to small shielding effect (5–6 ppm when there is an adjacent sulfinyl group and 0–1 ppm when there is a sulfonyl group) on the corresponding methyl group. When the added oxygen is on the sulfur in the β position to the *t*-butyl group, it has a weak (<3 ppm) deshielding effect on the tertiary carbon and a small (<2 ppm) shielding effect on the methyl group. When the oxygen atom is added on the sulfur in the γ position to the *t*-butyl group, it has a weak shielding or deshielding (−1 to +1 ppm) effect on the tertiary carbon and methyl groups depending on the molecule. These shielding and deshielding effects are also observed in proton NMR but they are more difficult to see as the scale is much smaller.

**TABLE 2** $^1$H and $^{13}$C NMR Chemical Shifts (δ ppm) of the Oxide Derivatives of Di-*t*-Butyl Trisulfide[a,b]

| Entry | R-S$_3$O$_n$-R' | C | CH$_3$ | H | C' | CH$_3$' | H' |
|---|---|---|---|---|---|---|---|
| **1b** |  | 48.91 | 29.88 | 1.347 | | | |
| **2b** |  | 60.67 | 23.79 | 1.385 | 48.73 | 29.80 | 1.390 |
| **3b** |  | 52.10 | 31.80 | 1.545 | | | |
| **4b** |  | 62.39 | 24.17 | 1.410 | | | |
| **4b'** | | 62.02 | 24.18 | 1.422 | | | |
| **5b** |  | 70.06 | 24.18 | 1.465 | 49.95 | 29.86 | 1.395 |
| **6b**[d] |  | 59.34 | 23.06 | 1.393 | 52.77 | 31.91 | 1.293 |
| **7b** |  | 71.38 | 23.99 | 1.551 | 63.08 | 24.51 | 1.463 |
| **8b** |  | 73.45 | 24.15 | 1.545 | | | |

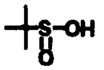
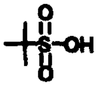
[a] Recorded using deuterated chloroform (CDCl$_3$) as NMR solvent; [b] Relaxation time ($t_1$) used: $t_1$ = 2 s; [c] **4b** and **4b'** represent the two diastereoisomers of **4**; [d] The spectra were obtained at −60 °C and do not represent a specific diastereoisomer.

**TABLE 3** $^1$H and $^{13}$C NMR Chemical Shifts (δ ppm) of the Oxide Derivatives of Di-*t*-Butyl Tetrasulfide[a,b,c]

| Entry | R-S$_4$O$_n$-R' | C | CH$_3$ | H | C' | CH$_3$' | H' |
|---|---|---|---|---|---|---|---|
| **1c** |  | | | | 49.01 | 30.16 | 1.382 |
| **2c** |  | 60.60 | 23.82 | 1.330 | 49.91 | 29.76 | 1.321 |
| **4c** |  | 61.51 | 23.50 | 1.410 | | | |
| **4c'** | | 61.20 | 23.77 | 1.368 | | | |
| **7c** |  | 71.16 | 23.72 | 1.519 | 62.33 | 23.84 | 1.453 |
| **8c** |  | 72.10 | 24.18 | 1.527 | | | |

[a] Recorded using deuterated chloroform (CDCl$_3$) as NMR solvent; [b] Relaxation time ($t_1$) = 2 s; [c] **4c** and **4c'** represent the two diastereoisomers; [d] The spectrum was obtained at low temperature and does not represent a specific diastereoisomer; [e] Partially soluble in CDCl$_3$.

**TABLE 4** $^{1}$H and $^{13}$C NMR Chemical Shifts (δ ppm) of Related *t*-Butyl Oxide Derivatives[a,b]

| Entry | Compound | C | $CH_3$ | H |
|---|---|---|---|---|
| 9 |  | 57.46 | 21.42 | 1.196 |
| 10[c] |  | 58.07 | 24.49 | 1.432 |
| 11[d] |  | 60.52 | 21.37 | 1.284 |
| 11' | | 60.07 | 21.53 | 1.261 |

[a] Recorded using deuterated chloroform ($CDCl_3$) as NMR solvent; [b] Relaxation time ($t_1$) used: $t_1$ = 2 s; [c] Partially soluble in $CDCl_3$; [d] **11** and **11'** represent the two diastereoisomers.

It can be seen that the α effect is by far the most important. The quantification of these effects can be a very good predictive tool. For example, di-*t*-butylsulfinyl anhydrosulfide (**4b**) should show a tertiary carbon signal between 61 and 63 ppm and a corresponding methyl signal between 24 and 25 ppm. The actual values (62.02, 62.39/24.17, 24.18) lie exactly in the range predicted and this confirm the existence of **4b** which was subject to controversy[6c] (Figure 1).

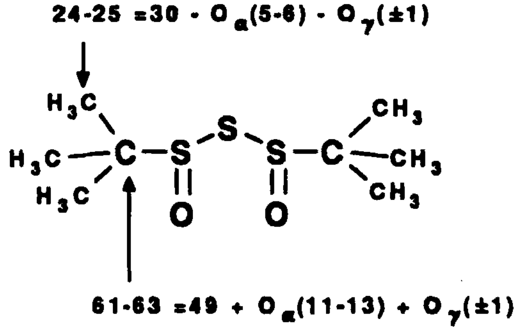


FIGURE 1

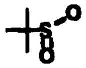
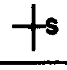
The $^{1}$H and $^{13}$C NMR chemical shifts of some related t-butyl derivatives[1d,2b,3] are presented in Table 4.

From the results presented in Table 1, 2 and 3, it can be seen that the chemical shifts of each of these compounds are very consistent with the others. As a consequence, the chemical shifts of a given *t*-butyl group can be unambiguously interpreted depending on which sulfur it is bonded to (sulfenyl, sulfinyl, sulfonyl or sulfinate) (Table 5).

The only exception encountered is thiosulfonate **5a** where one of the tertiary carbon signals is out of the normal range. Four types of *t*-butyl groups have been defined according to the degree of oxidation of its bonded sulfur atom (sulfenyl, sulfinyl, sulfonyl or sulfinate). Specific ranges of chemical shifts are given for each type of *t*-butyl group.

The results presented in Table 5 clearly show that the structure of other analogs can be easily determined by comparing the chemical shifts observed with the ranges reported

**TABLE 5** $^1H$ and $^{13}C$ NMR Chemical Shifts Ranges (δ ppm) of the *t*-Butyl Groups Bonded to Differently Oxidized Sulfur

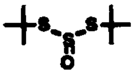
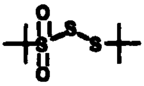
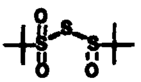
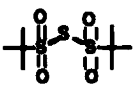
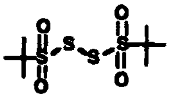
| Functionality | C | $CH_3$ | H | C′ | $CH_3'$ | H′ |
|---|---|---|---|---|---|---|
|  | 60–61 | 21–22 | 1.1–1.2 | | | |
|  | 59–64 | 24–26 | 1.3–1.6 | | | |
|  | 68–74 | 23–26 | 1.4–1.6 | | | |
|  | | | | 48–53 | 29–33 | 1.3–1.5 |

here. The preparation and characterization of a wide variety of isopropyl analogs revealed that similar ranges can be applied to other alkyl analogs.

## CRYSTALLOGRAPHY STUDY

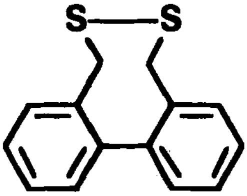
The X-ray analysis of some oxide derivatives of di-*t*-butyl tri- and tetrasulfides[2b] allowed the unambiguous characterization of these materials. Although nothing has been reported on the structures of this class of compounds, there are a few publications on trisulfides,[7] disulfides,[5d,8] and disulfide polyoxides[9] that could give some likely values as to their S-S bond lengths and valency angles. The S-S bond lengths of different disulfides, trisulfides, thiosulfinates and thiosulfonates vary from 2.02 Å to 2.098 Å, the longest one being that of the thiosulfinates. The corresponding S-S-S bond angles lie between 90° and 107°. The S-S bond lengths and angles observed in the present study are gathered in Table 6.

**TABLE 6** S-S Bond Lengths and Angles of di-*t*-Butyl Tri/Tetrasulfide Polyoxides[a]

| Entry | S(1)-S(2)-S(3) | S(1)-S(2) (Å) | S(2)-S(3) (Å) | S(1)-S(2)-S(3) (°) |
|---|---|---|---|---|
| 3b |  | 2.066(9) | 2.045(10) | 89.8(4) |
| 5b |  | 2.1159(24) | 2.0093(24) | 105.31(10) |
| 7b |  | 2.095(3) | 2.136(4) | 100.23(14) |
| 8b |  | 2.1175(12) | 2.1175(12) | 109.52(7) |
| 8c |  | 2.1293(16) | 2.0037(22) | 104.30(7) |

[a] Estimated values refer to the last digits.

The S-S bond lengths of this class of compounds vary by more than 0.12 Å depending on the molecule. This amplitude is more than twice the variation observed for the thiosulfinate and thiosulfonate derivatives of *5H,8H*-dibenzo[*d,f*][1,2]-dithiocin (12).[9] However, the length of the S-S(O) bond is the longest as reported for the disulfide analogs.[9]



12

When the oxygen is on S(2) (**3b**) there is a difference in the S-S bond lengths of 0.021 Å possibly showing some asymmetry in the molecule. However, these two bond lengths lie in the range of regular trisulfides.[7] Meanwhile, the valency angle of the sulfinyl sulfur is much smaller than the one reported for trisulfides,[7] but it is very close to the one of disulfides (90°).[8] Consequently, the addition of an oxygen atom on the internal sulfur of a trisulfide does not affect much the S-S bond lengths but it considerably decreases its valency angle. The addition of an oxygen atom on the external sulfurs has a strong increasing effect (0.12 Å) on the sulfinyl sulfenyl bond and a small decreasing effect (0.02 Å) on the other S-S bond. It also decreases the internal sulfur valency angle by about 5° to 8°. Finally, the addition of two oxygen atoms on the same external sulfur has a moderate increasing affect (0.07 Å) on the S-S bond bearing the sulfur dioxide group and a moderate decreasing effect (0.05 Å) on the other S-S bond; it has virtually no effect on the bond angles.

By analogy with the shielding and deshielding effects of oxygen in the $^1H$ and $^{13}C$ NMR (*vide supra*), this X-ray analysis could be used to predict the bond lengths and angles of other oxide derivatives of di-*t*-butyl polysulfides which could also be compared to molecular modeling calculations. For instance, the addition of two oxygen atoms on the internal sulfur should even more decrease its valency angle and therefore facilitate the extrusion of sulfur dioxide as has been shown.[3,10] The fact that the sulfinyl sulfenyl (S(O)-S) bond length is the longest, confirms the preferred breaking of that bond. It could also explain why the oxide derivatives of trisulfides that bear a sulfinyl sulfur are less stable than the others.[2b] As a result, the sulfonyl sulfenyl (S-S(O)$_2$) bond is shorter than the sulfinyl sulfenyl (S-S(O)) bond for di- and trisulfide derivatives. Considering that the valency angle of the sulfonyl moiety is about 130° (O=S=O), these results suggest that the dipole-dipole interaction of the two oxygen atoms reduces their individual influence on the corresponding S-S bond (Figure 2).

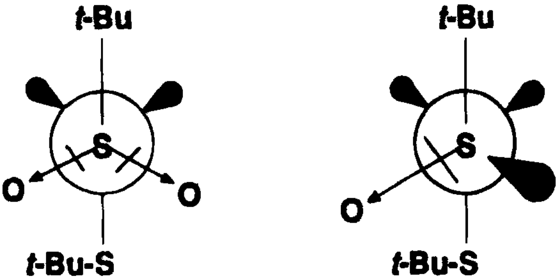


FIGURE 2 Dipole-dipole interaction.

## EXPERIMENTAL SECTION

Di-*t*-Butyl Polysulfides (**1a**, **1b**, **1c**). The synthesis of these polysulfides has been reported.[11]

Oxide Derivatives of Disulfides (**2a**, **5a**, **6a**, **7a**, **8a**, **9**, **10**, **11**). The preparation, behavior and characterization of these compounds has already been described.[2]

Monoxide Derivatives of Tri- and Tetrasulfides (**2b**, **3b**, **2c**). The preparation, behavior and characterization of these compounds has been reported.[2,6a,b]

Dioxide Derivatives of Tri- and Tetrasulfides (**4b**, **5b**, **6b**, **4c**). The preparation, behavior and characterization of these compounds has been described.[2,6a,b]

Tri- and Tetraoxide Derivatives of Tri- and Tetrasulfides (**7b**, **8b**, **7c**, **8c**). The preparation, behavior and characterization of these compounds has already been described.[2b,6a,b]

The X-ray structures of compounds **3b**, **5b**, **7b**, **8b** and **8c** have been reported[2b] and have been deposited at the Cambridge Crystallographic Data Centre.

## ACKNOWLEDGEMENTS

We thank Elf Aquitaine (France) and Atochem North America, King of Prussia and the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

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