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Non-bonded S···N Interactions in Organosulfur Derivatives: Crystal and Molecular Structures of [2-(4,4-Dimethyl-2-oxazolinyl)phenyl] Benzyl Sulfide and Bis[2-(4,4-dimethyl-2-oxazolinyl)phenyl] Sulfide

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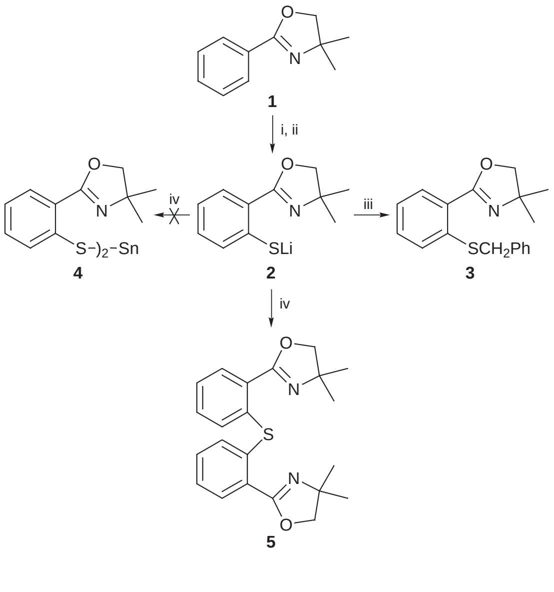
The synthesis and structural characterisation of two low-valent sulfur derivatives stabilised by S···N intramolecular non-bonded interactions are described.

The chemistry of organochalcogen derivatives stabilised by intramolecular non-bonded E···X (E = Se, Te; X = H, N, O, S, Se, F, Cl) interactions has attracted considerable current interest. In contrast, very few compounds with S···X interactions have been reported.[9] Schultz *et al.* showed strong S···O interactions in *o*-nitrobenzene sulfenyl chloride[9c] and Mollier and coworkers have shown the existence of partial bonding between oxygen and the neighbouring sulfur in carbonyl derivatives of dithiole and thiopyran.[10] However, the existence of S···N non-bonded interactions has not been studied extensively. We report here the synthesis, crystallographic study and spectroscopic analysis of two aryl sulfides stabilized by intramolecular S···N interactions.

Reaction of OxS^-Li^+ **2** with benzyl chloride gave **3** in moderate yield (Scheme 1). The novel diaryl sulfide **5** was obtained unexpectedly during the attempts to synthesise the tin(II) thiolate **4**. Reaction of OxS^-Li^+ **2** with anhydrous $SnCl_2$ afforded the unexpected sulfide **5**. Although the mechanism of the reaction has not been established, we however, postulate that the monosulfide **5** probably results from the thermal dissociation of complex **4**. The reactions of $SnCl_2$ with lithium selenolate and tellurolate afforded the corresponding diselenide and ditelluride, respectively.



Scheme 1 *Reagents and conditions*: i, Bu^nLi, THF, 0 °C, 1 h; ii, S powder, 0 °C, 1 h; iii, $PhCH_2Cl$, room temp., 2 h; iv, anhydrous $SnCl_2$, 0 °C, 1 h, room temp., 24 h

Diffraction measurements for **3** and **5** were performed at 293 K on a Siemens R3m/V diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.7170$ Å). In view of the low absorption coefficient, absence of heavy atoms and Mo-Kα source, no absorption correction was applied. Crystallographic data for **3**: triclinic, space group $P\bar{1}$, $a = 8.0200(10)$, $b = 9.1090(10)$, $c = 12.112(2)$ Å, $\alpha = 85.58(1)$, $\beta = 70.83(1)$, $\gamma = 68.52(1)^\circ$, $V = 776.8(2)$ Å^3, $Z = 2$, $D_c = 1.272$ Mg m^{-3}, $R(R_w) = 0.0432(0.1047)$. **5**: monoclinic, space group $P2_1/c$, $a = 20.982(2)$, $b = 8.8026(7)$, $c = 11.490(2)$ Å, $\beta = 98.378(9)^\circ$, $V = 2099.6(4)$ Å^3, $Z = 4$, $D_c = 1.204$ Mg m^{-3}, $R(R_w) = 0.0788(0.1879)$.

An ORTEP view of **3** is shown in Fig. 1. The S–C bond distances [S–C(1) 1.765(2), S–C(12) 1.822(2) Å] are comparable with normal S–C(Ph) bond distances.[9] Of particular interest in the structure is the nature of the S···N interaction and the arrangement of S–C(12) *trans* to the S···N bond. The S···N separation [2.827(2) Å] is significantly shorter than the sum of van der Waals radii (3.35 Å) for these two atoms.[14] The N···S–C(12) bond angle 179.05° indicates a linear arrangement of N···S–C atoms.

The crystal structure of **5** is shown in Fig. 2. Out of the two nitrogen atoms present which can interact with the sulfur, only one nitrogen atom, N(1), interacts with sulfur whereas the other nitrogen, N(2), is twisted away from the sulfur. Although the S···N(1) interaction in **5** is found to be weak, the S···N(1) bond length (2.782 Å) is considerably lower than the sum of the van der Waals radii (3.35 Å)[14] and comparable to the corresponding values observed for the disulfide (2.815 and 2.787 Å).[16]

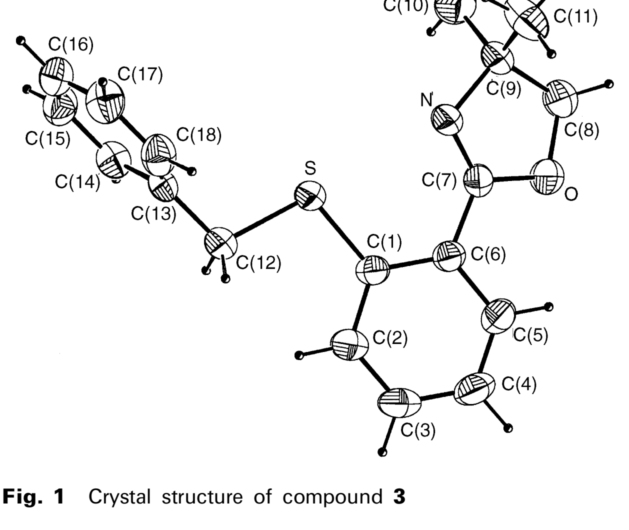


Fig. 1 Crystal structure of compound **3**

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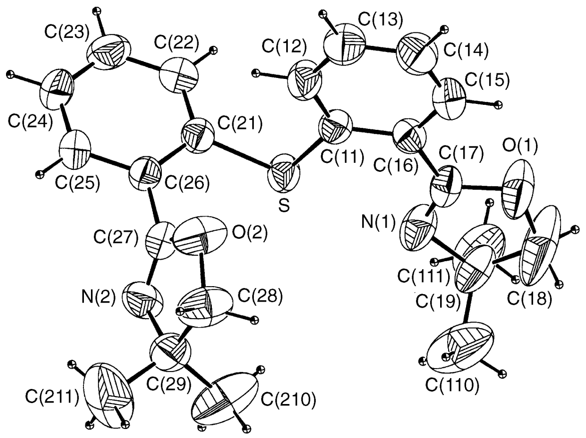

Fig. 2 Crystal structure of compound **5**

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Techniques used: ^{1}H and ^{13}C NMR, MS, X-ray diffraction

References: 20

Table 1: Crystal and structure refinement data for **3** and **5**

Table 2: Significant bond lengths and angles for **3**

Table 3: Significant bond lengths and angles for **5**

Appendix: Crystallographic details

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