

**(*N,N*-Diisobutyldithiocarbamoylsulfinato)zinc(II)****Günter Reck\* and Roland Becker**Bundesanstalt für Materialforschung und  
-prüfung, Richard-Willstätter-Straße 11,  
D-12489 Berlin, Germany

Correspondence e-mail: guenter.reck@bam.de

Zinc dialkyl dithiocarbamoylsulfinate have been proposed as intermediates in the antioxidant action of the respective zinc dialkyl dithiocarbamate additives in hydrocarbon-based plastics and lubricants. As a model compound, zinc diisobutyl dithiocarbamoylsulfinate,  $[\text{Zn}(\text{C}_9\text{H}_{18}\text{NO}_2\text{S}_2)_2]$ , has been prepared and its crystal structure determined.

Received 4 April 2003

Accepted 12 June 2003

Online 24 June 2003

**Key indicators**

Single-crystal X-ray study

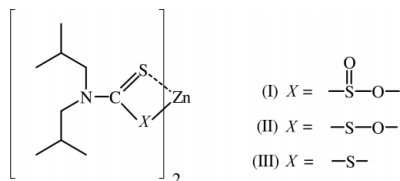
 $T = 293 \text{ K}$ Mean  $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$  $R$  factor = 0.032 $wR$  factor = 0.093

Data-to-parameter ratio = 12.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

**Comment**

Zinc dialkylthiocarbamoylsulfinate and zinc dialkyldithioper-carbamates have been discussed as possible oxidation products in the antioxidant action of zinc dialkyldithiocarbamate additives in plastics and liquid hydrocarbons. Compound (II) has been identified as a derivative of (III) in model systems using auto-oxidizing liquid hydrocarbons (Al-Malaika *et al.*, 1985; Shelkova *et al.*, 1990) and vegetable-oil-based lubricants (Becker *et al.*, 1996) and could be shown to display antioxidant activity itself. Although it has been demonstrated that the title compound, (I), exhibits antioxidant activity (Shelkova *et al.*, 1990), there is no evidence that it accumulates in these materials in significant amounts during auto-oxidation.



While the solid-state structure of (II) has been reported (Reck *et al.*, 1995), structural proposals for (I), to the best of our knowledge, are based on their IR spectra only. Here, the solid-state structure of zinc diisobutyldithiocarbamoylsulfinate, (I), is reported.

**Experimental**

Zinc diisobutyldithiocarbamoylsulphinate, (I), was prepared following the method reported by Shelkova *et al.* (1990) for the di-*n*-butyl isomer. A stirred solution of sodium diisobutyldithiocarbamate (1 molar equivalent) in acetone was treated with hydrogen peroxide (2 molar equivalents) in small portions and kept at 273–278 K. The yellow precipitate formed after dilution with water was purified by fractionatal crystallization from ethanol/*n*-hexane to yield colourless crystals of (I). IR spectrum ( $\text{cm}^{-1}$ ): 2975, 2960, 2940, 1530, 1460, 1445, 1435, 1380, 1365, 1350, 1330, 1290, 1275, 1255, 1170, 1165, 1155, 1090, 970, 955, 920, 855, 825, 815, 805, 645.

Crystal data

[Zn(C<sub>9</sub>H<sub>18</sub>NO<sub>2</sub>S<sub>2</sub>)<sub>2</sub>]  
*M<sub>r</sub>* = 538.10  
 Tetragonal, *P*4̄<sub>2</sub>*c*  
*a* = 12.557 (2) Å  
*c* = 16.600 (3) Å  
*V* = 2617.5 (8) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.365 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 25 reflections  
 $\theta = 12\text{--}20^\circ$   
 $\mu = 1.28\text{ mm}^{-1}$   
*T* = 293 (2) K  
 Prism, colourless  
 0.36 × 0.33 × 0.29 mm

Data collection

Enraf–Nonius CAD-4 diffractometer  
 2θ–ω scans  
 2940 measured reflections  
 1695 independent reflections  
 1523 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.042

$\theta_{\text{max}} = 25.0^\circ$   
*h* = 0 → 14  
*k* = -14 → 14  
*l* = 0 → 19  
 3 standard reflections  
 frequency: 120 min  
 intensity decay: 0.5%

Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.032  
*wR* (*F*<sup>2</sup>) = 0.093  
*S* = 1.11  
 1695 reflections  
 133 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0545P)^2 + 0.3208P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

(Δ/σ)<sub>max</sub> = 0.001  
 Δρ<sub>max</sub> = 0.53 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.31 e Å<sup>-3</sup>  
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.0101 (10)  
 Absolute structure: Flack (1983),  
 386 Friedel pairs  
 Flack parameter = -0.02 (3)

The molecule of (I) consists of two equivalent parts related by the twofold axis of the space group. The Zn atom occupies a special position on this twofold axis. Atoms C6 and C7 have very large anisotropic displacement parameters, indicating a disorder of the corresponding isobutyl group.

Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977); cell refinement: *CAD-4 Operations Manual*; data reduction: *PROCESS* in *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL97*.

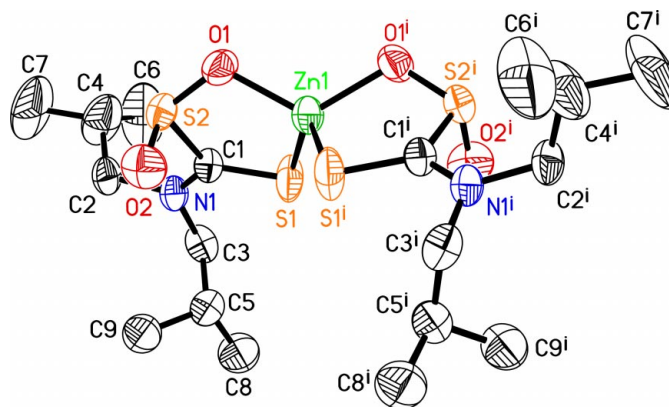


Figure 1

The molecular structure of (I), showing 50% probability displacement ellipsoids (*SHELXTL*; Sheldrick, 1999). H-atom labels have been omitted for clarity. [Symmetry code: (i) -*x*, -*y* - 1, *z*.]

The authors cordially thank Mrs G. Bannier for technical assistance.

References

Al-Malaika, S. A., Marogi, A. & Scott, G. (1985). *Polym. Degrad. Stabil.* **10**, 237–245.  
 Becker, R., Knorr, A. & Kelm, J. (1996). *Oxidation Commun.* **19**, 33–43.  
 Enraf–Nonius (1977). *CAD-4 Operations Manual*. Enraf–Nonius, Delft, The Netherlands.  
 Fair, C. K. (1990). *MolEN*. Enraf–Nonius, Delft, The Netherlands.  
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
 Reck, G., Becker, R. & Walther, G. (1995). *Z. Kristallogr.* **210**, 769–774.  
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.  
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.  
 Sheldrick, G. M. (1999). *SHELXTL-NT*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Shelkova, R. G., Kuzmina, G. N., Dzyubina, M. A., Ilin, K. V. & Parenago, O. P. (1990). *Nefkimiya*, **30**, 244–251.