



Crystal structure of tetraisobutylthiuram disulfide

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Received 29 August 2017

Accepted 17 October 2017

Edited by A. J. Lough, University of Toronto, Canada

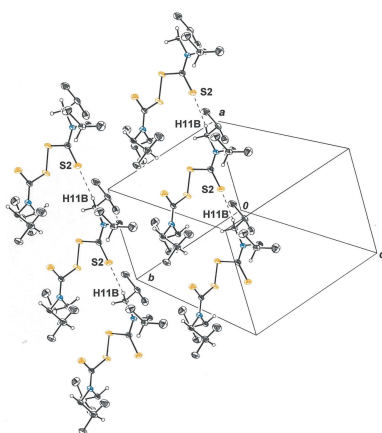
Keywords: crystal structure; tetrathium disulfide; dithiocarbamate; precursor; weak S...H—C interaction.**CCDC reference:** 1580550**Supporting information:** this article has supporting information at journals.iucr.org/e

Tetrakis(2-methylpropyl)thioperoxydicarbonic diamide, or tetraisobutylthiuram disulfide, $C_{18}H_{36}N_2S_4$, crystallizes in a general position in the triclinic space group $P\bar{1}$ but shows pseudo- C_2 symmetry about the disulfide bond. The C—S—S—C torsion angle [$-85.81(2)^\circ$] and the dihedral angle between the two NCS_2 mean planes [$85.91(5)^\circ$] are within the range observed for this compound type. Multiple intra- and intermolecular S...H—C close contacts appear to play a role in assisting the specific conformation of the pendant isobutyl groups and the packing arrangement of molecules within the cell. Tetraisobutylthiuram disulfide molecules of one optical configuration form sheets in the plane of the a and b axes. Inversion centers exist between adjoining sheets, which stack along the c axis and alternate in the handedness of their constituent molecules.

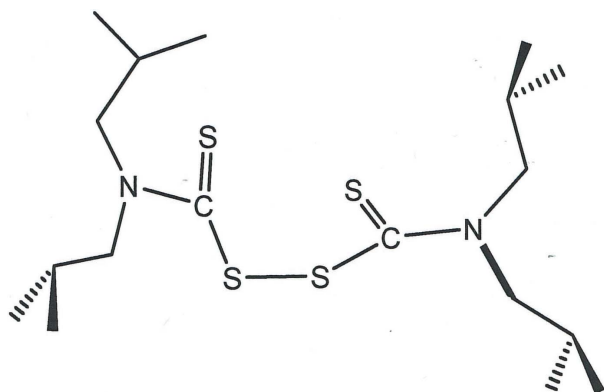
1. Chemical context

N,N,N,N-Tetraalkylthioperoxydicarbonic diamides, commonly called tetrathium disulfides, comprise a class of organosulfur compounds with applications that are both diverse and long-standing. Tetramethylthiuram disulfide, known by the commercial name thiram, is broadly useful both as a fungicide (Sharma *et al.*, 2003) and as a repellent against animals that feed upon seedling trees (Radwan, 1969). In industry, thiram and related tetraalkylthiuram disulfides find application as vulcanizing agents in the production of synthetic rubber (Datta & Ingham, 2001; Ignatz-Hoover & To, 2016). Tetraethylthiuram disulfide, under the trade name disulfiram, is used for the treatment of chronic alcoholism because of its inhibitory effect upon liver alcohol dehydrogenase (Mutschler *et al.*, 2016). More recently, it has received scrutiny for its ability to sensitize cancer cells to radiotherapy and to the effects of anticancer drugs (Jiao *et al.*, 2016) as well as for its bactericidal action against drug-resistant *Mycobacterium tuberculosis* (Horita *et al.*, 2012). Tetraalkylthiuram disulfides function both as chelating ligands themselves (Chieh, 1977; Chieh, 1978; Thirumaran *et al.*, 2000; Saravanan *et al.*, 2005; Prakasam *et al.*, 2009) and as precursors to dithiocarbamate ligands, which are used in the coordination chemistry of both the transition metals (Hogarth, 2005) and main group elements (Heard, 2005).

In the course of some studies of diisobutyldithiocarbamate coordination complexes of molybdenum, we have noted a report describing an 1H NMR spectrum of $[Ni(S_2CN^iBu_2)_2]$ that was more complex than anticipated, even considering the hindered rotation about the $^-S_2-CN^iBu_2$ bond (Raston & White, 1976). This complexity was attributed to intraligand S...H interactions involving the tertiary hydrogen of the



isobutyl group. Although the room temperature ^1H NMR spectrum of N,N,N',N' -tetrakis(2-methylpropyl)thioperoxydicarbonyl diamide (tetraisobutylthiuram disulfide) itself does not show evidence of such intramolecular interaction, several recent studies of tetrathuram disulfides have suggested such interactions in the crystalline state (Raya *et al.*, 2005; Srinivasan *et al.*, 2012; Nath *et al.*, 2016). This possibility of similar weak interaction(s) in the crystal structure of tetraisobutylthiuram disulfide has motivated a determination of its structure by X-ray diffraction, reported herein.



2. Structural commentary

Tetraisobutylthiuram disulfide crystallizes upon a general position in $P\bar{1}$ but has pseudo- C_2 symmetry across the disulfide bond, strict C_2 symmetry being disrupted by conformational differences among the pendant isobutyl groups (Fig. 1*a*). Despite the lack of strict C_2 symmetry, tetraisobutylthiuram disulfide is nevertheless chiral. The image in Fig. 1*a* presents the molecule with a left-handed configuration to the core $-\text{H}_2\text{CNC}(\text{S})\text{S}-\text{SC}(\text{S})\text{NCH}_2-$ portion. If Fig. 1*a* were to be viewed from above, along the pseudo C_2 axis that bisects the $\text{S}3-\text{S}4$ bond, the $\text{C}1-\text{S}1$ and $\text{C}2-\text{S}2$ thione bonds would project forward and backward, respectively, from the plane of the paper and thereby define a left-handed propeller. The right-handed counterpart is necessarily the other occupant of the unit cell, as required by the racemic space group. Among the structurally characterized thiuram disulfides, crystallographically imposed C_2 symmetry is also common (Fig. 3).

The $\text{S}3-\text{S}4$ bond length is 1.9931 (10) Å, while the thione $\text{C}=\text{S}$ bonds are essentially identical at 1.642 (3) and 1.643 (3) Å. The $\text{C}1-\text{S}3-\text{S}4-\text{C}2$ torsion angle, τ , is -85.81 (2)° and, as is typical of tetrathuram disulfides, very similar in magnitude to the angle of 85.91 (5)° between the mean planes defined by the S_2CN fragments, θ .

Multiple intramolecular $\text{S}\cdots\text{H}-\text{C}$ contacts that are shorter than, or close to, the 2.92 Å sum of the van der Waals radii (Rowland & Taylor, 1996) for sulfur and hydrogen are calculated for the structure of tetraisobutylthiuram disulfide. Each of the four sulfur atoms on the molecule is a participant in such a close contact, as illustrated in Fig. 1*b* and shown in Table 1. Although weak individually, particularly since these $\text{D}-\text{H}\cdots\text{A}$ angles are closer to 90° than to 180° (Table 1), these interactions may act cooperatively with packing forces

to decide the specific molecular conformation that is adopted. Weak intermolecular $\text{S}\cdots\text{H}-\text{C}$ contacts are also calculated for molecules that stack along the a axis of the cell (Fig. 2). While angles for these contacts are larger (145.6 , 159.5°), the $\text{D}\cdots\text{A}$ separations are longer [3.834 (3), 3.810 (3) Å]. The geometric parameters for both these intramolecular and intermolecular $\text{S}\cdots\text{C}-\text{H}$ contacts fall within the range defined as consistent with a weak $\text{D}-\text{H}\cdots\text{A}$ interaction (Desiraju & Steiner, 1999). These features of the molecular packing in the crystal structure of tetraisobutylthiuram disulfide suggest that the crystal structures of coordination complexes with the diisobutylthiocarbamate ligand be considered for similar $\text{S}\cdots\text{H}-\text{C}$ contacts and, importantly, that variable temperature ^1H NMR spectroscopy be used to assess the importance of any such interactions in solution.

3. Supramolecular features

Molecules of tetraisobutylthiuram disulfide are linked by $\text{C}-\text{H}\cdots\text{S}$ hydrogen bonds (Table 1) to form linear chains

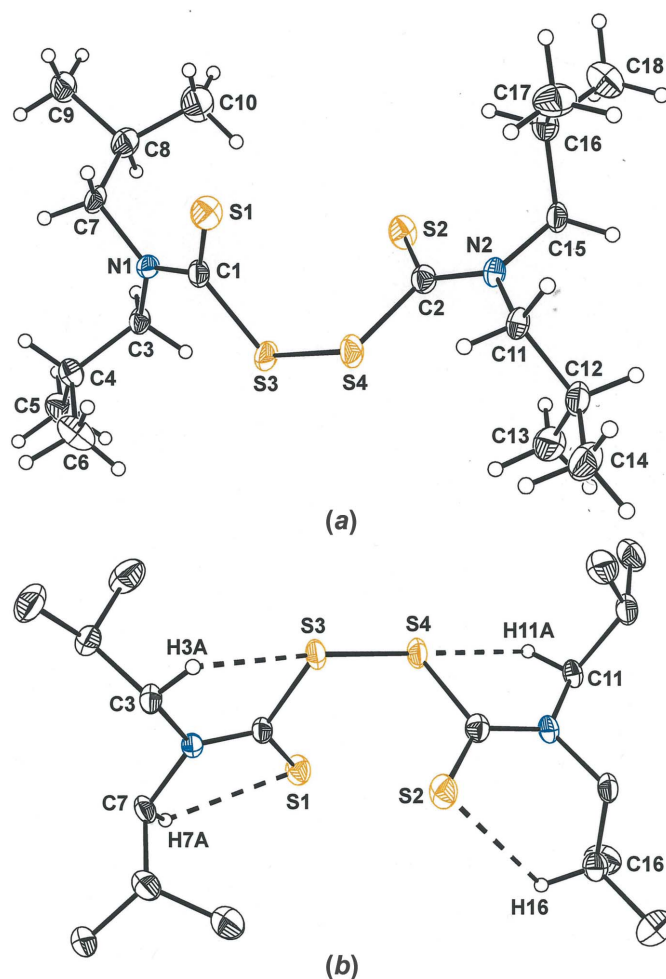


Figure 1
(*a*) Displacement ellipsoid plot (50%) of tetraisobutylthiuram disulfide with complete labeling for the non-H atoms. (*b*) Displacement ellipsoid plot (50% probability) of tetraisobutylthiuram disulfide illustrating close intramolecular $\text{S}\cdots\text{H}-\text{C}$ contacts (dashed lines).

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3–H3A \cdots S3	0.99	2.34	2.907 (3)	115
C7–H7A \cdots S1	0.99	2.60	3.084 (3)	110
C8–H8 \cdots S1 ⁱ	1.00	2.97	3.834 (3)	146
C11–H11A \cdots S4	0.99	2.33	2.896 (3)	115
C11–H11B \cdots S2 ⁱⁱ	0.99	2.87	3.810 (3)	160
C16–H16 \cdots S2	1.00	2.91	3.473 (3)	117

Symmetry codes: (i) $x + 1, y, z$; (ii) $x - 1, y, z$.

directed along the a axis of the cell, and parallel chains then align within the ab plane to form sheets (Fig. 2). Because the molecules within a single sheet are related, one from another, only by translations along a or b , they all have the same optical configuration. The sheets in the ab plane then stack along the c

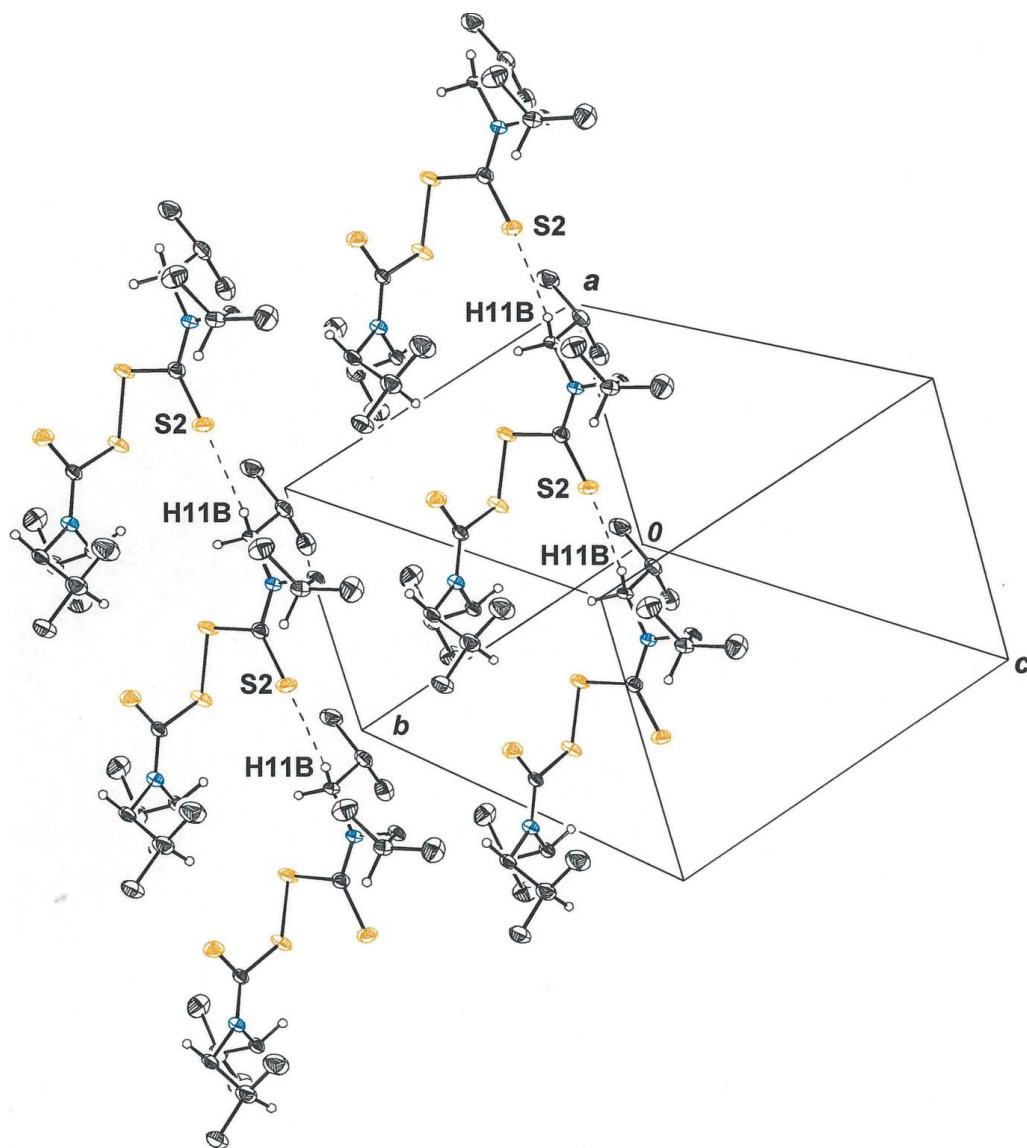


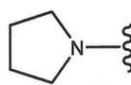
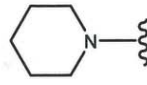
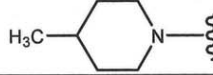
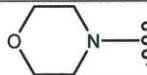
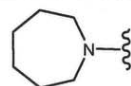
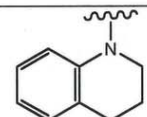
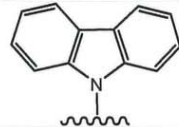
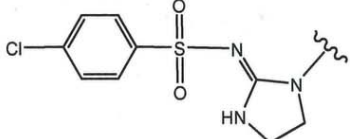
Figure 2
Stacking of tetraisobutylthiuram disulfide molecules along the a axis of the unit cell, showing intermolecular $S\cdots H-C$ close contacts. Displacement ellipsoids are represented at the 50% probability level. Parallel stacks fill in the ab plane to form two-dimensional sheets, as shown. (Symmetry operations: $x + 1, y, z$; $x, y + 1, z$.)

axis of the cell. The cell's inversion center resides within the center of the cell and relates molecules from neighboring sheets. Consequently, the sheets alternate in the handedness of the molecules from which they are comprised.

4. Database survey

Values for τ and θ for structures in the Cambridge Structural Database (Web CSD v1.1.1; Groom *et al.*, 2016) were determined using Mercury (Macrae *et al.*, 2008). These structures are: METHUS (Marøy, 1965), METHUS01 (Ymén, 1983), METHUS02 (Wang *et al.*, 1986), METHUS03 (Wang & Liao, 1989), METHUS04 (Wang & Liao, 1989), ETHUSS (Karle *et al.*, 1967) ETHUSS01 (Wang *et al.*, 1986), ETHUSS02 (Wang & Liao, 1989), ETHUSS03 (Wang & Liao, 1989), ETHUSS04 (Shi & Wang, 1992), ETHUSS05 (Hu, 2000), HIQJUM (Jian *et al.*, 1999), HIQJUM01 (Yu & Wang, 2003), JECYAZ (Kumar *et al.*, 1990), TIBFEQ (Zhai *et al.*, 2007), ZEMPUC (Hall & Tiekink, 1995), KAZHEA (Karim *et al.*, 2012), NELTUT (Fun *et al.*, 2001), XEBJOF (Ajibade *et al.*, 2012), JAXPOO (Raya *et al.*, 2005), CAPLEK (Williams *et al.*, 1983), CAPLEK01 (Ymén, 1983), CAPLEK02 (Yamin *et al.*, 1996), CAPLEK03 (Bai *et al.*, 2010), RISNEN (Quan *et al.*, 2008), ULOXIC (Bodige & Watson, 2003), PIPTHS (Dix & Rae, 1973), PIPTHS01 (Shi & Wang, 1992), EWESUW (Nath *et al.*, 2016), BOMPAU (Rout *et al.*, 1982), VOHFIH (Polyakova & Starikova, 1990), VOHFIH01 (Ivanov *et al.*, 2003), PECWOL (Uludağ *et al.*, 2013), ZIJLOV (Srinivasan *et al.*, 2012) and MEMFUG (Sączewski *et al.*, 2006).

The C–S–S–C torsion angle (τ) and the dihedral angle (θ) between S_2CN mean planes are closely comparable to values observed for the analogous features in most other tetra-thiuram disulfides, as summarized in Fig. 3. Positive and negative values of τ occur with approximately equal frequency for tetra-

R	R'	τ^b	θ^c	Position	Ref.	REFCODE
Me	Me	-87.58	87.31	C_2	Marøy, 1965	METHUS
		88.14	87.19	C_2	Ymén, 1983	METHUS01
		88.21	87.00	C_2	Wang <i>et al.</i> , 1986	METHUS02
		87.19	86.27	C_2	Wang & Liao, 1989	METHUS03
		87.15	86.25	C_2	Wang & Liao, 1989	METHUS04
Et	Et	90.22	86.21	general	Karle <i>et al.</i> , 1967	ETHUSS
		-91.00	86.43	general	Wang <i>et al.</i> , 1986	ETHUSS01
		-90.99	86.00	general	Wang & Liao, 1989	ETHUSS02
		-90.82	86.02	general	Wang & Liao, 1989	ETHUSS03
		90.66, -91.16	86.65, 85.75	general	Shi & Wang, 1992	ETHUSS04 ^d
		-	-	general	Hu, 2000	ETHUSS05
ⁿ Pr	ⁿ Pr	85.17	89.95	general	Jian <i>et al.</i> , 1999	HIQJUM
		-	-	general	Yu & Wang, 2003	HIQJUM01
^t Bu	^t Bu	-85.81(2)	85.91(5)	general	This work	-
ⁱ Pr	ⁱ Pr	180	0	<i>i</i>	Kumar <i>et al.</i> , 1990	JECYAZ
Bz	Bz	-85.71	85.08	general	Zhai <i>et al.</i> , 2007	TIBFEQ
Et	Cy	-89.97	88.06	general	Hall & Tickink, 1995	ZEMPUC
CH ₃ OCH ₂ CH ₂	CH ₃ OCH ₂ CH ₂	-89.27	88.39	general	Karim <i>et al.</i> , 2012	KAZHEA
Me	Ph	86.17	87.99	general	Fun <i>et al.</i> , 2001	NELTUT
Et	Ph	-78.00	78.99	C_2	Ajibade <i>et al.</i> , 2012	XEJOF
ⁱ Pr	Ph	78.60	80.53	general	Raya <i>et al.</i> , 2005	JAXPOO
		-93.43	86.01	C_2 in $C2/c$	Williams <i>et al.</i> , 1983	CAPLEK
		93.52	86.05	C_2 in $A2/a$	Ymén, 1983	CAPLEK01
		-87.70	88.85	gen. in $P\bar{1}$	Yamin <i>et al.</i> , 1996	CAPLEK02
		-93.62	86.12	C_2 in $C2/c$	Bai, <i>et al.</i> , 2010	CAPLEK03
		86.88	88.97	general	Quan <i>et al.</i> 2008	RISNEN ^e
		92.8	86.28	general	Bodige & Watson, 2003	ULOXIC ^f
		-90.78	85.43	general	Dix & Rae, 1973	PIPTHS
		-91.55	85.86	general	Shi & Wang, 1992	PIPTHS01
		78.01	83.60, 87.57 ^g	general	Nath <i>et al.</i> , 2016	EWESUW
		99.01	88.37	general	Rout <i>et al.</i> , 1982	BOMPAU
		84.08	83.43	general	Polykova & Starikova, 1990	VOHFIH
		-83.96	82.31	general	Ivanov <i>et al.</i> , 2003	VOHFIH01
		-90.59	86.18	general	Uludağ <i>et al.</i> , 2013	PECWOL
		-131.93	47.81	C_2	Srinivasan <i>et al.</i> 2012	ZIJLOV
		180.00	0.00	<i>i</i>	Sączewski <i>et al.</i> , 2006	MEMFUG

^aValues for τ and θ for structures occurring in the Cambridge Structural Database are determined with *Mercury*, Version 3.3, 2013. ^b $\tau = C-S-S-C$ torsion angle. ^c $\theta =$ dihedral angle between NCS_2 mean planes. ^dThis structure reports $Et_2NC(S)SSC(S)N(Et)_2$ in space group $P2_1$, which has been identified as incorrect in ETHUSS05. ^eThe tetrathium disulfide occurs with $SbCl_2Ph_2$ in the asymmetric unit. ^fThe tetrathium disulfide occurs with 2,3-dibromo-5,6-dimethylbenzoquinone in the asymmetric unit. ^gOne 4-methylpiperidiny group is disordered over two positions and occasions two values for θ .

Figure 3
Summary of structurally characterized tetrathium disulfides, $RR'NC(S)SSC(S)NRR'$.

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₁₈ H ₃₆ N ₂ S ₄
<i>M_r</i>	408.73
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.2449 (11), 9.6102 (14), 17.196 (3)
α , β , γ (°)	98.580 (2), 94.540 (2), 103.409 (2)
<i>V</i> (Å ³)	1143.5 (3)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.42
Crystal size (mm)	0.17 × 0.12 × 0.06
Data collection	
Diffractionmeter	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2016)
<i>T_{min}</i> , <i>T_{max}</i>	0.745, 0.977
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	17180, 4168, 3161
<i>R_{int}</i>	0.057
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.604
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.052, 0.146, 1.07
No. of reflections	4168
No. of parameters	225
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.87, -0.35

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b) and *SHELXTL* (Sheldrick, 2008).

thium disulfides that have been characterized structurally by X-ray diffraction (Fig. 3). For those which do not reside on an inversion center (Kumar *et al.*, 1990; Sączewski *et al.*, 2006) or have conformations obviously perturbed by intermolecular interactions involving the pendant groups on nitrogen (Srinivasan *et al.*, 2012), the average of the absolute value of τ is 88.4°, and the range is 78.0–99.0°. Similarly, the average value of θ is 86.1°, with a range of 79.0–90.0°.

5. Synthesis and crystallization

The synthesis procedure employed was that described by Kapanda *et al.*, 2009. Pale-yellow block-shaped crystals of tetraisobutylthiuram disulfide (m.p. 343 K) were obtained by slow evaporation of a CH₂Cl₂ solution. ¹H NMR (δ , ppm in DMSO-*d*₆): 3.83 [*d*, *J* = 12 Hz, 8H, -CH₂CH(CH₃)₂], 2.39 [*br m*, 4H, -CH₂CH(CH₃)₂], 0.98 [*d*, *J* = 8 Hz, 12H, -CH₂CH(CH₃)₂], 0.87 [*d*, *J* = 8 Hz, 12H, -CH₂CH(CH₃)₂].

6. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms were added in calculated positions and refined with isotropic displacement parameters that were approximately 1.2 times (for -CH- and -CH₂) or 1.5 times (for -CH₃) those of the carbon atoms to which they were attached. The C-H distances assumed were 1.00, 0.99, and 0.98 Å for the -CH-, -CH₂, and -CH₃ types of hydrogen atoms, respectively.

Funding information

This work has been funded in part by support from the NSF (OIA 1539035 and DMR 1460637). The Louisiana Board of Regents is thanked for enhancement grant LEQSF-(2002–03)–ENH–TR–67 with which the Tulane X-ray diffractometer was purchased, and Tulane University is acknowledged for its ongoing support with operational costs for the diffraction facility.

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supporting information

Acta Cryst. (2017). E73, 1764-1769 [https://doi.org/10.1107/S2056989017015158]

Crystal structure of tetraisobutylthiuram disulfide

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Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINTE* (Bruker, 2016); data reduction: *SAINTE* (Bruker, 2016); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

N,N,N',N'-Tetrakis(2-methylpropyl)disulfane-1,2-dicarbothioamide

Crystal data

$C_{18}H_{36}N_2S_4$	$Z = 2$
$M_r = 408.73$	$F(000) = 444$
Triclinic, $P\bar{1}$	$D_x = 1.187 \text{ Mg m}^{-3}$
$a = 7.2449 (11) \text{ \AA}$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$b = 9.6102 (14) \text{ \AA}$	Cell parameters from 4848 reflections
$c = 17.196 (3) \text{ \AA}$	$\theta = 2.2\text{--}25.2^\circ$
$\alpha = 98.580 (2)^\circ$	$\mu = 0.42 \text{ mm}^{-1}$
$\beta = 94.540 (2)^\circ$	$T = 100 \text{ K}$
$\gamma = 103.409 (2)^\circ$	Block, pale yellow
$V = 1143.5 (3) \text{ \AA}^3$	$0.17 \times 0.12 \times 0.06 \text{ mm}$

Data collection

Bruker APEXII CCD diffractometer	17180 measured reflections
Radiation source: fine-focus sealed tube	4168 independent reflections
Graphite monochromator	3161 reflections with $I > 2\sigma(I)$
Detector resolution: 8.3333 pixels mm^{-1}	$R_{\text{int}} = 0.057$
φ and ω scans	$\theta_{\text{max}} = 25.4^\circ$, $\theta_{\text{min}} = 2.2^\circ$
Absorption correction: multi-scan (<i>SADABS</i> ; Bruker, 2016)	$h = -8 \rightarrow 8$
$T_{\text{min}} = 0.745$, $T_{\text{max}} = 0.977$	$k = -11 \rightarrow 11$
	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.052$	H-atom parameters constrained
$wR(F^2) = 0.146$	$w = 1/[\sigma^2(F_o^2) + (0.0883P)^2]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
4168 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
225 parameters	$\Delta\rho_{\text{max}} = 0.87 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.35 \text{ e \AA}^{-3}$

Special details

Experimental. The diffraction data were obtained from 3 sets of 400 frames, each of width 0.5° in ω , collected at $\varphi = 0.00, 90.00$ and 180.00° and 2 sets of 800 frames, each of width 0.45° in φ , collected at $\omega = -30.00$ and 210.00° . The scan time was 60 sec/frame.

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.11097 (10)	0.22088 (8)	0.72835 (4)	0.0265 (2)
S2	0.35046 (10)	0.62092 (8)	0.68215 (4)	0.0268 (2)
S3	0.37169 (10)	0.47724 (7)	0.84025 (4)	0.0250 (2)
S4	0.13548 (10)	0.54581 (8)	0.82084 (4)	0.0253 (2)
N1	0.4760 (3)	0.2440 (2)	0.77920 (12)	0.0177 (5)
N2	0.0291 (3)	0.6939 (2)	0.71490 (12)	0.0184 (5)
C1	0.3217 (4)	0.2980 (3)	0.77839 (15)	0.0195 (6)
C2	0.1689 (4)	0.6296 (3)	0.73258 (16)	0.0208 (6)
C3	0.6574 (4)	0.3090 (3)	0.83096 (15)	0.0195 (6)
H3A	0.6641	0.4125	0.8506	0.023*
H3B	0.7650	0.3052	0.7993	0.023*
C4	0.6811 (4)	0.2335 (3)	0.90154 (15)	0.0253 (6)
H4	0.6567	0.1270	0.8813	0.030*
C5	0.8874 (4)	0.2875 (4)	0.94048 (18)	0.0375 (8)
H5A	0.9155	0.3924	0.9597	0.056*
H5B	0.9740	0.2674	0.9017	0.056*
H5C	0.9052	0.2375	0.9851	0.056*
C6	0.5418 (5)	0.2552 (4)	0.96030 (17)	0.0384 (8)
H6A	0.5722	0.3576	0.9854	0.058*
H6B	0.5511	0.1948	1.0009	0.058*
H6C	0.4115	0.2273	0.9328	0.058*
C7	0.4768 (4)	0.1089 (3)	0.72601 (15)	0.0215 (6)
H7A	0.3433	0.0528	0.7085	0.026*
H7B	0.5411	0.0491	0.7556	0.026*
C8	0.5774 (4)	0.1370 (3)	0.65392 (16)	0.0295 (7)
H8	0.7063	0.2031	0.6734	0.035*
C9	0.6088 (4)	-0.0045 (3)	0.61130 (17)	0.0303 (7)
H9A	0.6814	-0.0465	0.6480	0.045*
H9B	0.6803	0.0145	0.5664	0.045*
H9C	0.4849	-0.0727	0.5920	0.045*
C10	0.4765 (5)	0.2120 (4)	0.59941 (19)	0.0437 (9)
H10A	0.5528	0.2336	0.5562	0.066*
H10B	0.4598	0.3026	0.6291	0.066*
H10C	0.3510	0.1484	0.5775	0.066*
C11	-0.1242 (4)	0.7070 (3)	0.76450 (15)	0.0191 (6)
H11A	-0.1361	0.6320	0.7988	0.023*

H11B	-0.2462	0.6864	0.7296	0.023*
C12	-0.0943 (4)	0.8561 (3)	0.81718 (16)	0.0266 (7)
H12	-0.1195	0.9262	0.7826	0.032*
C13	0.1058 (4)	0.9157 (3)	0.86038 (18)	0.0337 (7)
H13A	0.1164	1.0126	0.8906	0.051*
H13B	0.1988	0.9220	0.8218	0.051*
H13C	0.1316	0.8510	0.8966	0.051*
C14	-0.2443 (5)	0.8413 (3)	0.87450 (18)	0.0353 (7)
H14A	-0.2247	0.7710	0.9081	0.053*
H14B	-0.3719	0.8077	0.8446	0.053*
H14C	-0.2329	0.9358	0.9077	0.053*
C15	0.0346 (4)	0.7671 (3)	0.64587 (15)	0.0209 (6)
H15A	0.1683	0.8198	0.6436	0.025*
H15B	-0.0420	0.8400	0.6531	0.025*
C16	-0.0405 (4)	0.6652 (3)	0.56672 (15)	0.0232 (6)
H16	0.0321	0.5883	0.5614	0.028*
C17	-0.2504 (4)	0.5917 (4)	0.56081 (18)	0.0360 (8)
H17A	-0.3243	0.6653	0.5659	0.054*
H17B	-0.2725	0.5343	0.6033	0.054*
H17C	-0.2908	0.5276	0.5094	0.054*
C18	0.0007 (5)	0.7523 (3)	0.50071 (17)	0.0385 (8)
H18A	-0.0641	0.8315	0.5064	0.058*
H18B	-0.0459	0.6888	0.4494	0.058*
H18C	0.1388	0.7927	0.5036	0.058*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0192 (4)	0.0294 (4)	0.0315 (4)	0.0091 (3)	0.0001 (3)	0.0041 (3)
S2	0.0186 (4)	0.0343 (4)	0.0328 (4)	0.0133 (3)	0.0059 (3)	0.0101 (3)
S3	0.0285 (4)	0.0215 (4)	0.0278 (4)	0.0155 (3)	-0.0030 (3)	0.0013 (3)
S4	0.0285 (4)	0.0274 (4)	0.0283 (4)	0.0188 (3)	0.0074 (3)	0.0100 (3)
N1	0.0191 (12)	0.0171 (11)	0.0176 (11)	0.0076 (9)	-0.0006 (9)	0.0013 (9)
N2	0.0163 (11)	0.0180 (11)	0.0235 (12)	0.0087 (9)	0.0031 (9)	0.0045 (9)
C1	0.0240 (15)	0.0182 (13)	0.0206 (14)	0.0106 (11)	0.0053 (11)	0.0070 (11)
C2	0.0195 (14)	0.0196 (14)	0.0237 (14)	0.0061 (11)	0.0002 (11)	0.0037 (11)
C3	0.0184 (14)	0.0165 (13)	0.0243 (14)	0.0066 (11)	-0.0010 (11)	0.0039 (11)
C4	0.0280 (16)	0.0263 (15)	0.0239 (15)	0.0103 (12)	-0.0007 (12)	0.0075 (12)
C5	0.0311 (18)	0.053 (2)	0.0319 (17)	0.0170 (15)	-0.0057 (13)	0.0111 (15)
C6	0.0363 (18)	0.054 (2)	0.0283 (17)	0.0109 (16)	0.0034 (14)	0.0167 (15)
C7	0.0260 (15)	0.0158 (13)	0.0255 (15)	0.0111 (11)	0.0052 (12)	0.0020 (11)
C8	0.0365 (18)	0.0273 (16)	0.0288 (16)	0.0152 (14)	0.0092 (13)	0.0033 (13)
C9	0.0390 (18)	0.0301 (16)	0.0289 (16)	0.0204 (14)	0.0079 (13)	0.0068 (13)
C10	0.059 (2)	0.048 (2)	0.0371 (19)	0.0299 (18)	0.0191 (17)	0.0126 (16)
C11	0.0152 (13)	0.0184 (13)	0.0267 (14)	0.0088 (11)	0.0041 (11)	0.0047 (11)
C12	0.0342 (17)	0.0212 (14)	0.0301 (16)	0.0143 (13)	0.0071 (13)	0.0088 (12)
C13	0.0413 (19)	0.0250 (16)	0.0339 (17)	0.0071 (14)	0.0042 (14)	0.0040 (13)
C14	0.0410 (19)	0.0326 (17)	0.0377 (18)	0.0196 (15)	0.0118 (15)	0.0033 (14)

C15	0.0216 (14)	0.0179 (13)	0.0258 (15)	0.0101 (11)	0.0001 (11)	0.0050 (11)
C16	0.0206 (14)	0.0256 (14)	0.0257 (15)	0.0102 (12)	0.0020 (11)	0.0048 (12)
C17	0.0275 (17)	0.0418 (19)	0.0328 (17)	0.0045 (14)	0.0003 (13)	-0.0043 (14)
C18	0.0384 (19)	0.045 (2)	0.0327 (18)	0.0081 (15)	0.0006 (14)	0.0130 (15)

Geometric parameters (Å, °)

S1—C1	1.642 (3)	C9—H9B	0.9800
S2—C2	1.643 (3)	C9—H9C	0.9800
S3—C1	1.826 (3)	C10—H10A	0.9800
S3—S4	1.9931 (10)	C10—H10B	0.9800
S4—C2	1.828 (3)	C10—H10C	0.9800
N1—C1	1.337 (3)	C11—C12	1.536 (4)
N1—C7	1.474 (3)	C11—H11A	0.9900
N1—C3	1.476 (3)	C11—H11B	0.9900
N2—C2	1.341 (3)	C12—C13	1.516 (4)
N2—C15	1.466 (3)	C12—C14	1.521 (4)
N2—C11	1.469 (3)	C12—H12	1.0000
C3—C4	1.522 (4)	C13—H13A	0.9800
C3—H3A	0.9900	C13—H13B	0.9800
C3—H3B	0.9900	C13—H13C	0.9800
C4—C6	1.510 (4)	C14—H14A	0.9800
C4—C5	1.527 (4)	C14—H14B	0.9800
C4—H4	1.0000	C14—H14C	0.9800
C5—H5A	0.9800	C15—C16	1.532 (4)
C5—H5B	0.9800	C15—H15A	0.9900
C5—H5C	0.9800	C15—H15B	0.9900
C6—H6A	0.9800	C16—C17	1.510 (4)
C6—H6B	0.9800	C16—C18	1.516 (4)
C6—H6C	0.9800	C16—H16	1.0000
C7—C8	1.514 (4)	C17—H17A	0.9800
C7—H7A	0.9900	C17—H17B	0.9800
C7—H7B	0.9900	C17—H17C	0.9800
C8—C10	1.506 (4)	C18—H18A	0.9800
C8—C9	1.520 (4)	C18—H18B	0.9800
C8—H8	1.0000	C18—H18C	0.9800
C9—H9A	0.9800		
C1—S3—S4	104.71 (9)	H9B—C9—H9C	109.5
C2—S4—S3	104.22 (9)	C8—C10—H10A	109.5
C1—N1—C7	121.1 (2)	C8—C10—H10B	109.5
C1—N1—C3	125.3 (2)	H10A—C10—H10B	109.5
C7—N1—C3	113.6 (2)	C8—C10—H10C	109.5
C2—N2—C15	119.3 (2)	H10A—C10—H10C	109.5
C2—N2—C11	123.9 (2)	H10B—C10—H10C	109.5
C15—N2—C11	116.6 (2)	N2—C11—C12	114.6 (2)
N1—C1—S1	126.7 (2)	N2—C11—H11A	108.6
N1—C1—S3	111.45 (18)	C12—C11—H11A	108.6

S1—C1—S3	121.80 (15)	N2—C11—H11B	108.6
N2—C2—S2	125.8 (2)	C12—C11—H11B	108.6
N2—C2—S4	112.26 (19)	H11A—C11—H11B	107.6
S2—C2—S4	121.90 (16)	C13—C12—C14	111.6 (2)
N1—C3—C4	113.4 (2)	C13—C12—C11	113.9 (2)
N1—C3—H3A	108.9	C14—C12—C11	107.2 (2)
C4—C3—H3A	108.9	C13—C12—H12	108.0
N1—C3—H3B	108.9	C14—C12—H12	108.0
C4—C3—H3B	108.9	C11—C12—H12	108.0
H3A—C3—H3B	107.7	C12—C13—H13A	109.5
C6—C4—C3	112.5 (2)	C12—C13—H13B	109.5
C6—C4—C5	111.4 (2)	H13A—C13—H13B	109.5
C3—C4—C5	108.8 (2)	C12—C13—H13C	109.5
C6—C4—H4	108.0	H13A—C13—H13C	109.5
C3—C4—H4	108.0	H13B—C13—H13C	109.5
C5—C4—H4	108.0	C12—C14—H14A	109.5
C4—C5—H5A	109.5	C12—C14—H14B	109.5
C4—C5—H5B	109.5	H14A—C14—H14B	109.5
H5A—C5—H5B	109.5	C12—C14—H14C	109.5
C4—C5—H5C	109.5	H14A—C14—H14C	109.5
H5A—C5—H5C	109.5	H14B—C14—H14C	109.5
H5B—C5—H5C	109.5	N2—C15—C16	114.4 (2)
C4—C6—H6A	109.5	N2—C15—H15A	108.7
C4—C6—H6B	109.5	C16—C15—H15A	108.7
H6A—C6—H6B	109.5	N2—C15—H15B	108.7
C4—C6—H6C	109.5	C16—C15—H15B	108.7
H6A—C6—H6C	109.5	H15A—C15—H15B	107.6
H6B—C6—H6C	109.5	C17—C16—C18	111.2 (2)
N1—C7—C8	112.5 (2)	C17—C16—C15	112.8 (2)
N1—C7—H7A	109.1	C18—C16—C15	108.2 (2)
C8—C7—H7A	109.1	C17—C16—H16	108.2
N1—C7—H7B	109.1	C18—C16—H16	108.2
C8—C7—H7B	109.1	C15—C16—H16	108.2
H7A—C7—H7B	107.8	C16—C17—H17A	109.5
C10—C8—C7	113.3 (3)	C16—C17—H17B	109.5
C10—C8—C9	112.2 (3)	H17A—C17—H17B	109.5
C7—C8—C9	109.4 (2)	C16—C17—H17C	109.5
C10—C8—H8	107.2	H17A—C17—H17C	109.5
C7—C8—H8	107.2	H17B—C17—H17C	109.5
C9—C8—H8	107.2	C16—C18—H18A	109.5
C8—C9—H9A	109.5	C16—C18—H18B	109.5
C8—C9—H9B	109.5	H18A—C18—H18B	109.5
H9A—C9—H9B	109.5	C16—C18—H18C	109.5
C8—C9—H9C	109.5	H18A—C18—H18C	109.5
H9A—C9—H9C	109.5	H18B—C18—H18C	109.5

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
C3—H3A...S3	0.99	2.34	2.907 (3)	115
C7—H7A...S1	0.99	2.60	3.084 (3)	110
C8—H8...S1 ⁱ	1.00	2.97	3.834 (3)	146
C11—H11A...S4	0.99	2.33	2.896 (3)	115
C11—H11B...S2 ⁱⁱ	0.99	2.87	3.810 (3)	160
C16—H16...S2	1.00	2.91	3.473 (3)	117

Symmetry codes: (i) $x+1, y, z$; (ii) $x-1, y, z$.