

C(2)—N—C(9)	118.9 (2)	C(4)—C(10)—C(5)	124.1 (2)
N—C(2)—C(3)	121.5 (2)	C(4)—C(10)—C(9)	116.8 (2)
N—C(2)—C(12)	118.8 (2)	C(5)—C(10)—C(9)	119.0 (2)
C(3)—C(2)—C(12)	119.7 (2)	C(2)—C(12)—C(17)	121.3 (2)
C(2)—C(3)—C(4)	120.6 (2)	C(12)—C(13)—C(14)	120.3 (2)
C(3)—C(4)—C(10)	119.5 (2)	C(13)—C(14)—C(15)	120.6 (3)
C(3)—C(4)—C(11)	116.9 (2)	C(14)—C(15)—C(16)	119.4 (3)
C(10)—C(4)—C(11)	123.5 (2)	C(15)—C(16)—C(17)	120.6 (3)
C(6)—C(5)—C(10)	120.5 (2)	C(16)—C(17)—C(12)	120.2 (3)
C(5)—C(6)—C(7)	120.6 (3)	C(17)—C(12)—C(13)	118.8 (2)
C(6)—C(7)—C(8)	120.5 (3)	O(1)—C(11)—O(2)	125.0 (2)
C(7)—C(8)—C(9)	120.6 (2)	O(1)—C(11)—C(4)	114.3 (2)
N—C(9)—C(8)	118.7 (2)	O(2)—C(11)—C(4)	120.7 (3)
N—C(9)—C(10)	122.6 (2)	C(11)—O(1)—H(1)	107 (2)
C(8)—C(9)—C(10)	118.7 (2)		

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O(1)—H(1)...N ⁱ	0.96 (4)	1.79 (4)	2.725 (3)	165 (4)

Symmetry code: (i) $x - \frac{1}{2}, \frac{1}{2} - y, -z$.

The scan widths used were $(1.20 + 0.35\text{tan}\theta)^\circ$ in ω , with a background/scan time ratio of 0.5. No correction was required for decay or absorption but the data were corrected for Lorentz and polarization effects. The Laue symmetry and systematic absences allowed unique determination of the space group as $P2_12_12_1$; refinement proceeded well and it was adopted. The direct-methods program *DIREDF* (Parthasarathi, Beurskens & Slot, 1983) produced an *E* map from which the initial positions of the C, N and O atoms were identified. Difference Fourier methods were used to locate the initial H-atom positions. Full-matrix least-squares refinement was performed using *TEXSAN* (Molecular Structure Corporation, 1989). In the later stages of refinement, ring H atoms were assigned fixed geometry (C—H 0.96 Å) and isotropic displacement parameters of magnitude 1.2 times those of the attached C atoms. The carboxy H atom was refined isotropically. Also in the late stages, a secondary extinction parameter (Zachariasen, 1963, 1968) was included; the maximum effect of extinction was 2.9% of F_o for 011. The maximum peak on the final difference map was located at (0.21, 0.26, 0.08), near the midpoint of the C(4)—C(10) bond; the minimum peak was located at (0.28, 0.23, 1.020), approximately equidistant from atoms C(2), C(3) and N.

Data collection: *MSC/AFCDiffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFCDiffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: BK1182). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 411–414

Unsymmetrically Substituted Thioureas. 1,1-Dimethyl-3-*o*-tolylthiourea and 1,1-Diethyl-3-*o*-tolylthiourea

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Abstract

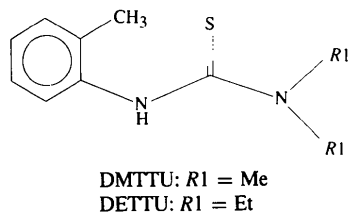
The two unsymmetrically substituted thiourea derivatives, 1,1-dimethyl-3-*o*-tolylthiourea, C₁₀H₁₄N₂S, and 1,1-diethyl-3-*o*-tolylthiourea, C₁₂H₁₈N₂S, both crystallize in the orthorhombic space group $P2_12_12_1$ and have the same type of crystal packing. In both structures, N—H...S hydrogen bonds link the molecules into chains along the *b* axis.

Comment

Crystal structure analyses of the title compounds form part of our studies of substituted thiourea derivatives. Unsymmetrically substituted thioureas exhibit agrochemical properties (Sarkis & Faisal, 1985). Our interest is focused on the molecular conformations and N—H...S hydrogen bonding in substituted thiourea derivatives in the solid state. The structure determinations of the title compounds, 1,1-dimethyl-3-*o*-tolylthiourea

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(DMTTU) and 1,1-diethyl-3-*o*-tolylthiourea (DETTU), were carried out at room temperature (293 K) for DMTTU and at 173 K for DETTU.



Displacement ellipsoid plots of the title molecules, with the numbering schemes, are shown in Fig. 1. The C1=S bond lengths observed in both structures are greater than the mean value (1.681 Å) given by Allen *et al.* (1987). The two C_{sp²}-N distances, C1-N1 and C1-N2, show different magnitudes, whereas similar differences are not found in symmetrically substituted thiourea derivatives (Ramnathan *et al.*, 1995). The average values of aromatic C-C bond lengths are 1.383 (6) and 1.386 (4) Å in DMTTU and DETTU, respectively. The angles around atom C1 show appreciable differences compared to other unsymmetrical thioureas (Ramnathan & Sivakumar, unpublished results);

the N1-C1-N2 angles [115.6(3) and 115.6(1)°, respectively] observed in these two structures are more acute than those observed in symmetrical thioureas (Ramnathan *et al.*, 1995). The dihedral angles between the planes of the thiourea moiety and the tolyl ring are 121.4(1) (DMTTU) and 116.7(1)° (DETTU).

The lone N-H group in these structures is involved in N-H···S hydrogen bonding and links the molecules along the *b* axis. The details are: N1···Sⁱ 3.423(3) Å and N1-H1···Sⁱ 140(3)° for DMTTU; N1···Sⁱⁱ 3.363(2) Å and N1-H1···Sⁱⁱ 147(2)° for DETTU [symmetry codes: (i) $-x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $-x, y + \frac{1}{2}, \frac{3}{2} - z$]. The N-H···S angles observed here are less than those observed in symmetrical thioureas (Ramnathan *et al.*, 1995).

The present study shows that the unsymmetrical substitution in the thiourea moiety leads to noncentrosymmetric crystal structures, whereas the symmetrically substituted thioureas crystallize in centrosymmetric space groups. The N-H···S hydrogen bonds are 'three centre' in symmetrical thioureas (which form linear chains), whereas in the present structures they are 'two centre' (Taylor, Kennard & Versichel, 1984). This is due to the presence of only one N-H group in these molecules.

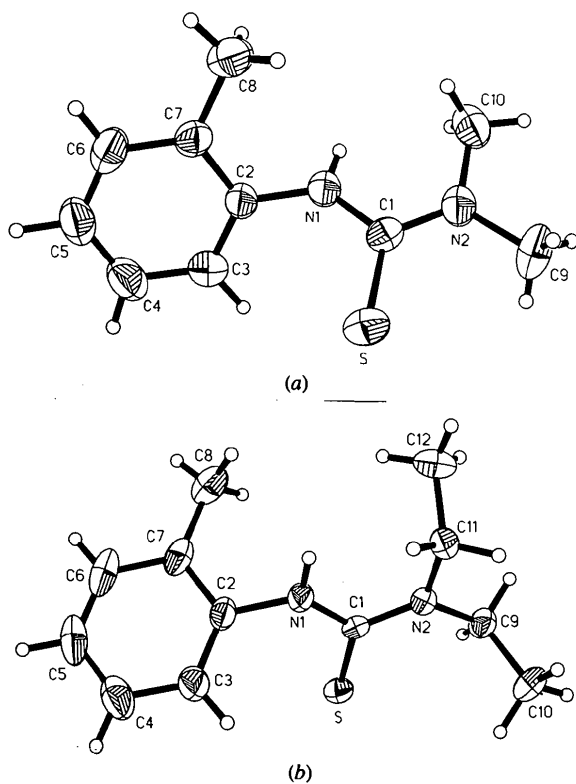


Fig. 1. Displacement ellipsoid plots (50% probability) of (a) DMTTU and (b) DETTU, with the atom-numbering schemes.

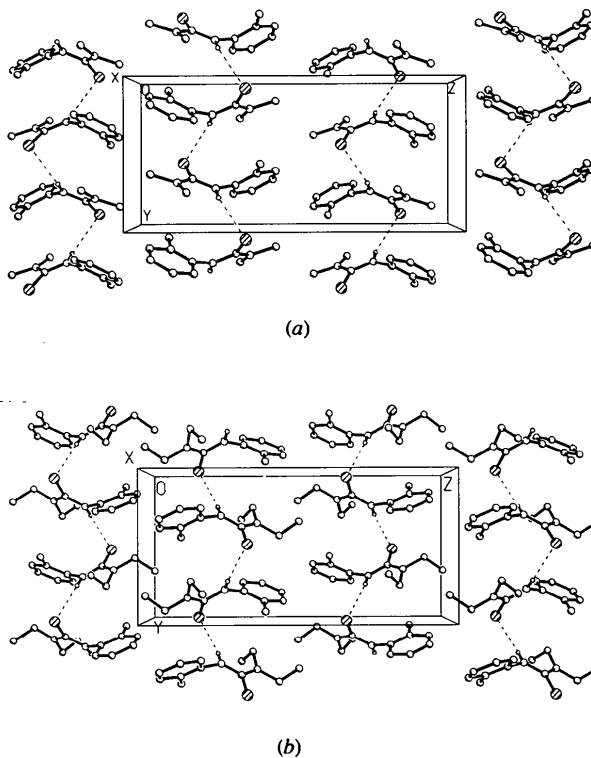


Fig. 2. Packing of (a) DMTTU and (b) DETTU molecules in their unit cells. In both structures, the molecules are linked by N-H···S hydrogen bonds (shown as dashed lines) along the *b* axis.

Experimental

The preparation of these compounds is described elsewhere (Ramadas, Srinivasan & Janarthanan, 1993). Single crystals suitable for X-ray study were obtained from ethanol solution on slow evaporation.

DMTTU

Crystal data

$C_{10}H_{14}N_2S$

$M_r = 194.29$

Orthorhombic

$P2_12_12_1$

$a = 7.580$ (1) Å

$b = 7.912$ (1) Å

$c = 17.423$ (3) Å

$V = 1044.9$ (3) Å³

$Z = 4$

$D_x = 1.235$ Mg m⁻³

Data collection

Siemens P4 diffractometer

$\theta/2\theta$ scans

Absorption correction:

none

1923 measured reflections

1758 independent reflections

1199 observed reflections

$[I > 2\sigma(I)]$

$R_{int} = 0.0249$

Refinement

Refinement on F^2

$R(F) = 0.0402$

$wR(F^2) = 0.0919$

$S = 0.887$

1758 reflections

174 parameters

All H-atom parameters

refined

$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25

reflections

$\theta = 8-15^\circ$

$\mu = 0.266$ mm⁻¹

$T = 293$ (2) K

Needle

$0.56 \times 0.35 \times 0.18$ mm

Colourless

$\theta_{max} = 27.48^\circ$

$h = -1 \rightarrow 9$

$k = -1 \rightarrow 10$

$l = -1 \rightarrow 22$

3 standard reflections

monitored every 97

reflections

intensity decay: <2%

$\Delta\rho_{max} = 0.18$ e Å⁻³

$\Delta\rho_{min} = -0.22$ e Å⁻³

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Absolute configuration:

Flack (1983) parameter

= -0.06 (14)

Table 2. Selected geometric parameters (Å, °) for DMTTU

S—C1	1.693 (3)	C2—C7	1.392 (4)
N1—C1	1.356 (4)	C3—C4	1.382 (5)
N1—C2	1.429 (4)	C4—C5	1.380 (6)
N2—C1	1.337 (4)	C5—C6	1.371 (5)
N2—C10	1.463 (5)	C6—C7	1.391 (5)
N2—C9	1.465 (5)	C7—C8	1.505 (5)
C2—C3	1.380 (5)		
C1—N1—C2	126.8 (3)	C7—C2—N1	118.1 (3)
C1—N2—C10	122.6 (3)	C2—C3—C4	119.9 (3)
C1—N2—C9	121.8 (3)	C5—C4—C3	119.7 (3)
C10—N2—C9	115.2 (3)	C6—C5—C4	120.0 (3)
N2—C1—N1	115.6 (3)	C5—C6—C7	121.6 (3)
N2—C1—S	122.9 (2)	C6—C7—C2	117.6 (3)
N1—C1—S	121.5 (3)	C6—C7—C8	120.8 (3)
C3—C2—C7	121.1 (3)	C2—C7—C8	121.6 (3)
C3—C2—N1	120.7 (3)		

DETTU

Crystal data

$C_{12}H_{18}N_2S$

$M_r = 222.34$

Orthorhombic

$P2_12_12_1$

$a = 8.436$ (1) Å

$b = 8.488$ (1) Å

$c = 17.419$ (3) Å

$V = 1247.3$ (3) Å³

$Z = 4$

$D_x = 1.184$ Mg m⁻³

Data collection

Siemens P4 diffractometer

$\theta/2\theta$ scans

Absorption correction:

none

2226 measured reflections

2039 independent reflections

1892 observed reflections

$[I > 2\sigma(I)]$

$R_{int} = 0.0278$

Refinement

Refinement on F^2

$R(F) = 0.0291$

$wR(F^2) = 0.0792$

$S = 1.048$

2039 reflections

208 parameters

All H-atom parameters

refined

$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25

reflections

$\theta = 8-15^\circ$

$\mu = 0.231$ mm⁻¹

$T = 193$ (2) K

Needle

$0.58 \times 0.46 \times 0.24$ mm

Colourless

$\theta_{max} = 27.50^\circ$

$h = -4 \rightarrow 10$

$k = -11 \rightarrow 10$

$l = -5 \rightarrow 22$

3 standard reflections

monitored every 97

reflections

intensity decay: <2%

$\Delta\rho_{max} = 0.17$ e Å⁻³

$\Delta\rho_{min} = -0.17$ e Å⁻³

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Absolute configuration:

Flack (1983) parameter

= -0.11 (8)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for DMTTU

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	x	y	z	U_{eq}
S	0.18441 (12)	0.43449 (11)	0.64877 (4)	0.0489 (2)
N1	0.0007 (4)	0.2672 (3)	0.75490 (14)	0.0415 (7)
N2	-0.1420 (3)	0.3098 (3)	0.64144 (15)	0.0441 (7)
C1	0.0046 (4)	0.3320 (4)	0.6828 (2)	0.0369 (7)
C2	0.1323 (4)	0.2868 (4)	0.8129 (2)	0.0384 (7)
C3	0.3001 (5)	0.2230 (5)	0.8025 (2)	0.0489 (8)
C4	0.4244 (5)	0.2394 (5)	0.8601 (2)	0.0577 (10)
C5	0.3804 (5)	0.3207 (5)	0.9275 (2)	0.0573 (10)
C6	0.2127 (6)	0.3816 (4)	0.9378 (2)	0.0517 (10)
C7	0.0845 (4)	0.3663 (4)	0.8811 (2)	0.0407 (8)
C8	-0.0994 (5)	0.4324 (6)	0.8938 (2)	0.0545 (9)
C9	-0.1541 (8)	0.3651 (7)	0.5614 (2)	0.0662 (13)
C10	-0.3071 (6)	0.2490 (6)	0.6750 (2)	0.0551 (9)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for DETTU

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	x	y	z	U_{eq}
S	0.17870 (5)	0.01745 (5)	0.66497 (2)	0.03234 (12)
N1	0.0119 (2)	0.2102 (2)	0.75544 (8)	0.0326 (3)
N2	-0.0989 (2)	0.1615 (2)	0.63799 (7)	0.0289 (3)
C1	0.0218 (2)	0.1353 (2)	0.68674 (8)	0.0270 (3)

C2	0.1203 (2)	0.1948 (2)	0.81824 (9)	0.0329 (4)
C3	0.2730 (2)	0.2522 (3)	0.81227 (11)	0.0438 (5)
C4	0.3746 (3)	0.2436 (3)	0.87460 (14)	0.0559 (6)
C5	0.3206 (3)	0.1802 (3)	0.94295 (12)	0.0542 (6)
C6	0.1690 (3)	0.1259 (2)	0.94869 (10)	0.0497 (5)
C7	0.0633 (3)	0.1303 (2)	0.88655 (9)	0.0383 (4)
C8	-0.1016 (3)	0.0665 (3)	0.89237 (13)	0.0505 (5)
C9	-0.1112 (2)	0.0771 (2)	0.56451 (10)	0.0344 (4)
C10	-0.0462 (3)	0.1711 (3)	0.49793 (11)	0.0436 (5)
C11	-0.2299 (2)	0.2700 (2)	0.65445 (10)	0.0352 (4)
C12	-0.3668 (3)	0.1924 (4)	0.6958 (2)	0.0578 (6)

Table 4. Selected geometric parameters (Å, °) for DETTU

S—C1	1.702 (2)	C3—C4	1.385 (3)
N1—C1	1.358 (2)	C4—C5	1.384 (4)
N1—C2	1.432 (2)	C5—C6	1.363 (4)
N2—C1	1.344 (2)	C6—C7	1.403 (3)
N2—C11	1.467 (2)	C7—C8	1.496 (3)
N2—C9	1.470 (2)	C9—C10	1.511 (3)
C2—C3	1.381 (3)	C11—C12	1.512 (3)
C2—C7	1.395 (2)		
C1—N1—C2	126.24 (14)	C2—C3—C4	120.0 (2)
C1—N2—C11	123.43 (13)	C5—C4—C3	119.4 (2)
C1—N2—C9	121.51 (14)	C6—C5—C4	120.2 (2)
C11—N2—C9	115.02 (13)	C5—C6—C7	122.1 (2)
N2—C1—N1	115.63 (14)	C2—C7—C6	116.7 (2)
N2—C1—S	123.07 (12)	C2—C7—C8	121.3 (2)
N1—C1—S	121.30 (12)	C6—C7—C8	121.9 (2)
C3—C2—C7	121.6 (2)	N2—C9—C10	112.69 (15)
C3—C2—N1	120.4 (2)	N2—C11—C12	113.3 (2)
C7—C2—N1	117.9 (2)		

The two title structures were solved by direct methods and refined by a full-matrix least-squares technique. All H atoms in both structures were located from difference maps and refined isotropically.

For both compounds, data collection: XSCANS (Siemens, 1994); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structures: SHELXS86 (Sheldrick, 1990a); program(s) used to refine structures: SHELXL93 (Sheldrick, 1993); molecular graphics: SHELXTL/PC (Sheldrick, 1990b); software used to prepare material for publication: SHELXL93. Geometric calculations: PARST (Nardelli, 1983).

One of the authors (KS) thanks the Universiti Sains Malaysia for a Visiting Post Doctoral Research Fellowship.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1206). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 414–416

$\alpha\beta\beta\alpha$ -3,4-Dimethyl-2,5-bis(3,4,5-trimethoxyphenyl)tetrahydrofuran

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Abstract

The crystal structure determination of the title compound, C₂₄H₃₂O₇, a second isomer of the natural 2,5-bisaryltetrahydrofuran lignans, reveals that the molecule adopts an $\alpha\beta\beta\alpha$ configuration. The tetrahydrofuran ring is in an intermediate conformation between half-chair and envelope.

Comment

There are ten possible stereoisomers for natural 2,5-bisaryltetrahydrofuran lignans, (I), consisting of four diastereomeric pairs and two *meso* forms (Biftu & Stevenson, 1987). Although these isomers are found in nature, only the crystal structure of (–)-grandisin, an $\alpha\beta\alpha\beta$ isomer, has been reported (Saad, Soepadmo, Fang, McLaughlin & Fanwick, 1991). We have now determined the crystal structure of one of the *meso* isomers, (II), a compound isolated from the roots of *Polyalthia bullata* (Annonaceae), a medicinal plant of Malaysia used for various ailments (Burkhill, 1966). The chemical structure was verified by its melting point, NMR and mass spectral data, which are similar to those of a compound isolated earlier from *Aristolochia birotis* (Conserva, Da Silva & Filho, 1990) and also to those of the synthetic compound (Biftu, Hazra & Stevenson, 1979).

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