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1,3-Dibenzylthiourea and 1,3-Dicyclohexylthiourea

Akilan Ramnathan,[a] Kandasamy Sivakumar,[a]† Kulandaivelu Subramanian,[a] Dravida Meerarani,[b] Krishnamoorthy Ramadas[b] and Hoong-Kun Fun[c]

[a]*Department of Physics, Anna University, Madras-600 025, India,* [b]*Centre for Agrochemical Research, SPIC Science Foundation, 110, Mount Road, Madras-600 032, India, and* [c]*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia*

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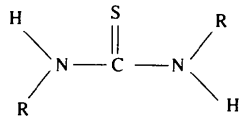
Abstract

Crystal structures of two symmetrically substituted thiourea derivatives, 1,3-dibenzylthiourea, $C_{15}H_{16}N_2S$ (DBTU), and 1,3-dicyclohexylthiourea, $C_{13}H_{24}N_2S$ (DCHTU), are reported. One of the cyclohexane rings in DCHTU is disordered adopting two orientations separated by an angle of 44.6 (2)°. In both structures centrosymmetrically related molecules are linked by N—H···S hydrogen bonds to form dimers and weak N—H···S bonds connecting glide-related molecules are also observed in both DBTU and DCHTU.

Comment

There have been many structural studies of metal complexes of thiourea but relatively few of substituted thioureas, possibly as a result of the difficulty in obtaining suitable crystals for X-ray diffraction studies. These thioureas find applications as rubber accelerators and as intermediates for dye preparation; they are also used for the synthesis of unsymmetrical thioureas (Ramadas, Srinivasan & Janarthanan, 1993), which are very useful agrochemical intermediates. We are interested in the molecular conformations and N—H···S hydrogen bonding of substituted thiourea derivatives in the solid state. In this paper we report the crystal structures of two symmetrically substituted thiourea derivatives, namely 1,3-dibenzylthiourea (DBTU) and 1,3-dicyclohexylthiourea (DCHTU). The preparation of these compounds involves a novel and cost-effective synthetic procedure described elsewhere (Ramadas & Janarthanan, 1995). A previous report on the cell dimensions and space group of DBTU (Gilli, Michelon & Toniolo, 1968) is consistent with the results given here. The displacement ellipsoid plots of the molecules with numbering scheme are shown in Fig. 1.



DBTU: R = $CH_2C_6H_5$

DCHTU: R = C_6H_{11}

DBTU: The C1═S distance, 1.700 (1) Å, is longer than the unweighted mean value, 1.681 Å, given for C═S in thioureas by Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987), but is in agreement with the values observed in other symmetrically substituted thioureas (Akilan, Sivakumar, Subramanian, Janarthanan, Ramadas & Fun, 1995*a*). The bond lengths in the two symmetric segments of the molecule show some differences (Table 2); N1—C2 and C2—C3 [1.462 (2) and 1.511 (2) Å, respectively] are slightly longer than their counterparts N2—C9 and C9—C10 [1.456 (2) and 1.507 (2) Å, respectively]. The orientations of the two benzyl groups with respect to the thiourea moiety are different and relevant torsion angles are given in Table 2; the dihedral angle between the planes of the benzyl

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† Visiting Post Doctoral Research Fellow, School of Physics, University Sains Malaysia, Malaysia.

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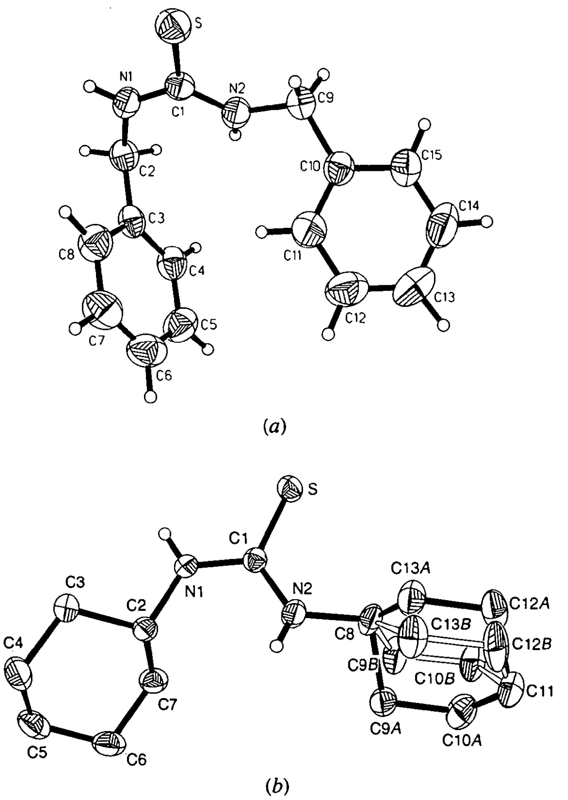


(*a*)

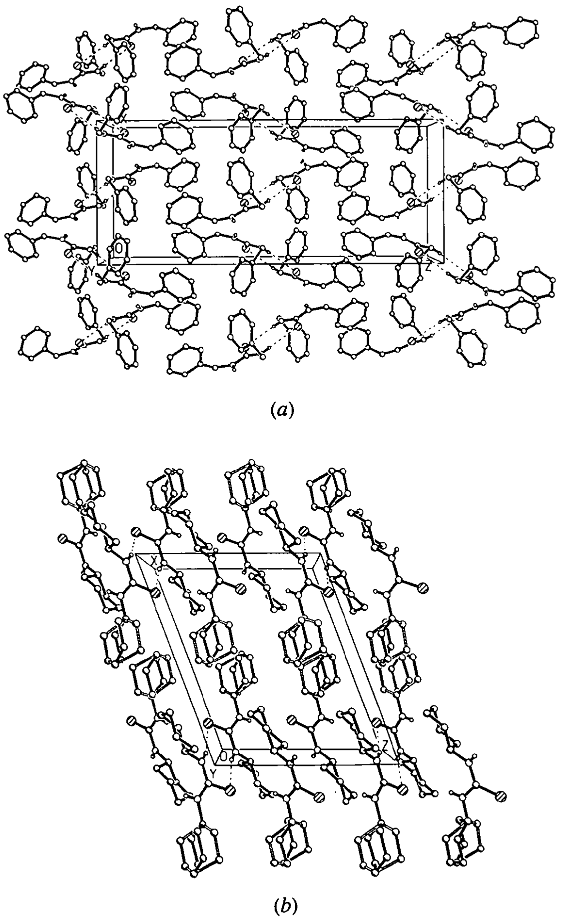
(*b*)

Fig. 1. 50% Probability displacement ellipsoid plots of (*a*) DBTU and (*b*) DCHTU with the numbering schemes. The atoms belonging to the two groups in the disordered cyclohexane ring of DCHTU are connected by solid and open bonds, respectively.

rings is 49.36 (6)°; one is almost perpendicular to the thiourea plane [ring C3–C8 93.02 (5)°], while the corresponding angle for the second ring is 63.56 (4)°. The molecules are linked by N—H···S hydrogen bonds, leading to the formation of dimeric pairs around centres of symmetry [N1···S^{i} 3.498 (1) Å and N1—H1N···S^{i} 154 (2)°; (i) $-x$, $-y$, $-z$]. There is no structural report either on a complex of DBTU or on its urea analogue.

DCHTU: One of the cyclohexane rings (C8–C13, II) shows disorder; it adopts two different orientations related by a rotation of 44.6 (2)° about the N2—C8 bond. The C1=S bond length and the bond distances around N1 and N2 are in agreement with the corresponding values observed in DBTU. The average C_{sp^3}—C_{sp^3} bond length, 1.517 (3) Å, observed in the ordered cyclohexane ring I (C2–C7) is less than the mean of 1.535 Å reported for such distances by Allen *et al.* (1987). The bond lengths observed in the cyclohexane ring II deviate from normal values, as is typical for such disordered rings (see *Experimental*). Both cyclohexane rings adopt chair conformations. As in the case of DBTU, in this structure the molecules are also linked around inversion centres by N1—H···S hydrogen bonds to form dimeric pairs [N1···S^{i} 3.653 (1) Å and N1—H1N···S^{i} 162 (3)°; (i) $-x$, $1-y$, $-z$]. This hydrogen bond is weak compared with that in DBTU or in other symmetrical thiourea derivatives; the N···S distance is 3.458 Å in diethylthiourea (DETU) and 3.447 Å in di-isopropylthiourea [DIPTU (Akilan *et al.*, 1995*a*)]. In DCHTU the two substituted cyclohexyl groups take up a *cis–trans* configuration with respect to the central thiourea moiety, whereas in its urea analogue, dicyclohexylurea (DCHUR), the configuration is *cis–cis* (Toniolo, Valle, Bonora, Crisma, Moretto, Izdebski, Pelka, Pawlak & Schneider, 1988).

Our structural studies on thiourea derivatives reveal that only in the case of diphenylthiourea (DPTU) is the C1—S distance [1.681 (5) Å] significantly shorter than those observed in related structures, including the present investigations of DBTU and DCHTU (Akilan *et al.*, 1995*a*,*b*). This shows that the C=S distance may be influenced by the nature of the substituent group and, in particular, its ability to participate in π conjugation. We also note that among symmetrically substituted thiourea



(*a*)

(*b*)

Fig. 2. Packing of the (*a*) DBTU and (*b*) DCHTU molecules in the unit cell illustrating dimer formation by N—H···S hydrogen bonding (shown as dashed lines).

derivatives the *cis–trans* configuration of the substituted groups leads to the formation of a two-dimensional network of molecules *via* N—H···S hydrogen bonds. In the present two structures, which fall into the same category, the N—H···S hydrogen bonds between glide-related molecules, which are essential for the formation of the two-dimensional network, are found to be weak. The closest contacts between the donor and acceptor atoms are nearly equal to the sum of the van der Waals radii N2···S^{ii} 3.703 (1), H2N···S^{ii} 3.02 (2) Å and N2—H2N···S^{ii} 141 (2)° [(ii) $-x - \frac{1}{2}, y + \frac{1}{2}, z$] for DBTU, and N2···S^{iii} 3.752 (2), H2N···S^{iii} 3.01 (2) Å and N—H2N···S^{iii} 162 (3)° [(iii) $x, \frac{1}{2} - y, \frac{1}{2} + z$] for DCHTU. These longer distances may be attributed to the bulkier benzyl substitution in DBTU and to the disorder in one of the cyclohexane rings in DCHTU.

Experimental

DBTU was recrystallized from an ethanol solution by slow evaporation. DCHTU was recrystallized from a methanol/hexane mixture by slow evaporation.

Compound DBTU

Crystal data

$C_{15}H_{16}N_2S$
$M_r = 256.36$
Orthorhombic
Pbca
$a = 10.888$ (1) Å
$b = 9.381$ (1) Å
$c = 26.597$ (3) Å
$V = 2716.6$ (5) Å^3
$Z = 8$
$D_x = 1.254$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 32 reflections
$\theta = 8$–25°
$\mu = 0.222$ mm^{-1}
$T = 293$ (2) K
Prism
0.40 × 0.36 × 0.32 mm
Colourless

Data collection

Siemens P4 diffractometer
θ–2θ scans
Absorption correction: none
3951 measured reflections
3099 independent reflections
2365 observed reflections [$I > 2\sigma(I)$]
$R_{\text{int}} = 0.0264$

$\theta_{\max} = 27.49°$
$h = -1 \rightarrow 14$
$k = -1 \rightarrow 12$
$l = -34 \rightarrow 1$
3 standard reflections monitored every 100 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0395$
$wR(F^2) = 0.1064$
$S = 1.117$
3098 reflections
227 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0678P)^2 + 0.0672P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for DBTU*

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S	−0.08043 (4)	−0.08622 (4)	0.07694 (2)	0.04761 (14)
N1	−0.09665 (12)	0.15992 (14)	0.02969 (5)	0.0432 (3)
N2	−0.17036 (12)	0.16194 (14)	0.10994 (4)	0.0434 (3)
C1	−0.11789 (12)	0.08919 (14)	0.07235 (5)	0.0369 (3)
C2	−0.09934 (15)	0.3149 (2)	0.02409 (6)	0.0435 (3)
C3	−0.00088 (13)	0.38958 (14)	0.05424 (5)	0.0395 (3)
C4	−0.0292 (2)	0.5075 (2)	0.08334 (6)	0.0476 (4)
C5	0.0610 (2)	0.5764 (2)	0.11092 (7)	0.0572 (4)
C6	0.1805 (2)	0.5284 (2)	0.10933 (7)	0.0591 (4)
C7	0.2100 (2)	0.4123 (2)	0.08024 (8)	0.0609 (5)
C8	0.12013 (15)	0.3423 (2)	0.05301 (7)	0.0522 (4)
C9	−0.1958 (2)	0.1063 (2)	0.15996 (6)	0.0515 (4)
C10	−0.15785 (14)	0.20826 (15)	0.20091 (5)	0.0422 (3)
C11	−0.0543 (2)	0.2925 (2)	0.19716 (7)	0.0574 (4)
C12	−0.0206 (2)	0.3817 (2)	0.23652 (8)	0.0695 (5)
C13	−0.0901 (2)	0.3875 (2)	0.27954 (8)	0.0699 (6)
C14	−0.1929 (2)	0.3039 (2)	0.28340 (7)	0.0721 (6)
C15	−0.2269 (2)	0.2158 (2)	0.24435 (6)	0.0585 (4)

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

S—C1	1.6996 (14)	C6—C7	1.375 (3)
N1—C1	1.335 (2)	C7—C8	1.383 (3)
N1—C2	1.462 (2)	C9—C10	1.507 (2)
N2—C1	1.339 (2)	C10—C15	1.380 (2)
N2—C9	1.456 (2)	C10—C11	1.381 (2)
C2—C3	1.511 (2)	C11—C12	1.390 (3)
C3—C4	1.385 (2)	C12—C13	1.373 (3)
C3—C8	1.391 (2)	C13—C14	1.370 (3)
C4—C5	1.385 (2)	C14—C15	1.378 (3)
C5—C6	1.377 (3)		
C1—N1—C2	125.28 (13)	C6—C7—C8	120.4 (2)
C1—N2—C9	125.51 (13)	C7—C8—C3	120.4 (2)
N1—C1—N2	117.09 (13)	N2—C9—C10	112.37 (13)
N1—C1—S	120.06 (11)	C15—C10—C11	118.4 (2)
N2—C1—S	122.84 (11)	C15—C10—C9	119.22 (15)
N1—C2—C3	113.14 (13)	C11—C10—C9	122.33 (14)
C4—C3—C8	118.59 (14)	C10—C11—C12	120.4 (2)
C4—C3—C2	120.61 (14)	C13—C12—C11	120.4 (2)
C8—C3—C2	120.79 (14)	C14—C13—C12	119.3 (2)
C3—C4—C5	120.7 (2)	C13—C14—C15	120.4 (2)
C6—C5—C4	120.1 (2)	C14—C15—C10	121.0 (2)
C7—C6—C5	119.8 (2)		
C2—N1—C1—N2	14.8 (2)	N1—C2—C3—C4	−133.23 (14)
C2—N1—C1—S	−166.05 (12)	N1—C2—C3—C8	47.4 (2)
C9—N2—C1—N1	−177.01 (14)	C1—N2—C9—C10	134.24 (15)
C9—N2—C1—S	3.9 (2)	N2—C9—C10—C15	145.4 (2)
C1—N1—C2—C3	64.4 (2)	N2—C9—C10—C11	−36.2 (2)

Compound DCHTU

Crystal data

$C_{13}H_{24}N_2S$
$M_r = 240.40$
Monoclinic
$P2_1/c$
$a = 12.611$ (2) Å
$b = 11.224$ (1) Å
$c = 10.435$ (1) Å
$\beta = 110.70$ (1)°
$V = 1381.7$ (3) Å^3
$Z = 4$
$D_x = 1.156$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 8$–25°
$\mu = 0.213$ mm^{-1}
$T = 293$ (2) K
Thick plate
0.48 × 0.44 × 0.32 mm
Colourless

Data collection

Siemens P4 diffractometer
θ–2θ scans
Absorption correction: none
4046 measured reflections
3166 independent reflections
2133 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0228$

$\theta_{\rm max} = 27.50°$
$h = -16 \rightarrow 15$
$k = -14 \rightarrow 1$
$l = -1 \rightarrow 13$
3 standard reflections monitored every 100 reflections
intensity decay: <4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0367$
$wR(F^2) = 0.0853$
$S = 1.039$
3166 reflections
301 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0475P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.17$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.12$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for DCHTU*

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
S	0.16307 (3)	0.40901 (4)	0.00294 (4)	0.04594 (13)
N1	0.00971 (10)	0.32186 (11)	0.09514 (14)	0.0401 (3)
N2	0.18571 (11)	0.23960 (14)	0.1915 (2)	0.0520 (4)
C1	0.11789 (11)	0.31715 (12)	0.10284 (14)	0.0377 (3)
C2	−0.04735 (12)	0.24099 (13)	0.1594 (2)	0.0383 (3)
C3	−0.15884 (13)	0.2972 (2)	0.1546 (2)	0.0468 (4)
C4	−0.2242 (2)	0.2144 (2)	0.2148 (2)	0.0615 (5)
C5	−0.2430 (2)	0.0935 (2)	0.1477 (2)	0.0671 (5)
C6	−0.1315 (2)	0.0383 (2)	0.1547 (2)	0.0633 (5)
C7	−0.0674 (2)	0.11932 (15)	0.0909 (2)	0.0504 (4)
C8	0.30398 (14)	0.2145 (2)	0.2092 (2)	0.0554 (5)
C9*A*	0.3179 (3)	0.0706 (3)	0.2360 (5)	0.0553 (10)
C9*B*	0.3298 (4)	0.1189 (6)	0.1493 (7)	0.0644 (15)
C10*A*	0.4411 (4)	0.0377 (4)	0.2559 (5)	0.0738 (11)
C10*B*	0.4571 (4)	0.0933 (7)	0.1775 (8)	0.071 (2)
C11	0.5245 (2)	0.1048 (3)	0.3483 (3)	0.0902 (9)
C12*A*	0.5033 (4)	0.2410 (5)	0.3248 (8)	0.0808 (14)
C12*B*	0.5069 (5)	0.2050 (11)	0.3960 (7)	0.079 (2)
C13*A*	0.3809 (3)	0.2766 (4)	0.3110 (6)	0.0626 (11)
C13*B*	0.3853 (6)	0.2330 (10)	0.3716 (8)	0.065 (2)

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

S—C1	1.7013 (15)	C8—C9*B*	1.339 (6)
N1—C1	1.339 (2)	C8—C13*A*	1.352 (5)
N1—C2	1.460 (2)	C8—C13*B*	1.655 (7)
N2—C1	1.336 (2)	C9*A*—C10*A*	1.538 (5)
N2—C8	1.464 (2)	C9*B*—C10*B*	1.554 (7)
C2—C7	1.521 (2)	C10*A*—C11	1.374 (6)
C2—C3	1.526 (2)	C10*B*—C11	1.687 (8)
C3—C4	1.518 (2)	C11—C12*A*	1.556 (6)
C4—C5	1.507 (3)	C11—C12*B*	1.280 (10)
C5—C6	1.514 (3)	C12*A*—C13*A*	1.551 (6)
C6—C7	1.517 (2)	C12*B*—C13*B*	1.496 (10)
C8—C9*A*	1.638 (4)		
C1—N1—C2	127.22 (13)	C7—C2—C3	110.94 (13)
C1—N2—C8	125.94 (15)	C4—C3—C2	111.23 (14)
N2—C1—N1	117.15 (13)	C5—C4—C3	112.2 (2)
N2—C1—S	123.23 (11)	C4—C5—C6	110.8 (2)
N1—C1—S	119.61 (11)	C5—C6—C7	111.3 (2)
N1—C2—C7	111.68 (13)	C6—C7—C2	111.0 (2)
N1—C2—C3	109.02 (12)		

The structures were solved by direct methods and refined by the full-matrix least-squares technique. All H atoms in DBTU were located from difference maps and refined isotropically. The disordered cyclohexane ring in DCHTU was resolved into two components by separating C9, C10, C12 and C13 atoms into two groups, *A* and *B*. Their occupancies were initially refined and later fixed at 0.6 and 0.4, respectively. Attempts to apply bond-length restraints to the disordered ring were unsuccessful. Only the free refinement of the disordered C atoms gave good convergence and was therefore used to derive the results in Tables 3 and 4. Some bond lengths in the disordered ring deviate from normal values (*e.g.* C8—C9*A*, 1.638 Å and C8—C9*B*, 1.339 Å). In DCHTU the H atoms of the disordered cyclohexane ring were positioned geometrically while the rest were located from difference maps; all were refined isotropically with a common $U_{\rm iso}$ for the H atoms belonging to each group of disordered C atoms. The program *PARST* (Nardelli, 1983) was used for geometric calculations.

For both compounds, data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990*a*); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*); software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1200). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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