

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1028). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Symmetrically Substituted Thiourea Derivatives

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Abstract

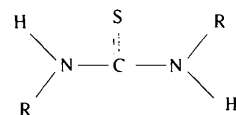
The crystal structures of three symmetrically substituted thiourea derivatives, 1,3-diethylthiourea (DETU), C₅H₁₂N₂S, 1,3-diisopropylthiourea (DIPTU), C₇H₁₆N₂S, and 1,3-diphenylthiourea (DPTU), C₁₃H₁₂N₂S, are reported. N—H...S hydrogen bonds link the molecules into two-dimensional networks in DETU and DIPTU

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and into one-dimensional chains in DPTU. DETU and DIPTU have the same mode of packing in the crystal lattice.

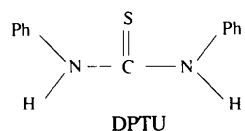
Comment

In the past, many crystal structure analyses of metal complexes of thiourea, but only a few with substituted thioureas, have been reported. There is no structural report exclusively on substituted thiourea derivatives. This may be due to the difficulty in obtaining crystals suitable for X-ray diffraction studies. The preparation of these compounds involves a novel cost-effective synthetic procedure (Ramadas & Janarthanan, 1995) and they have applications as rubber accelerators and as intermediates in 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 the details of the N—H...S hydrogen-bond formation of these ligands in the solid state. In this paper, we report the crystal structure determinations of three symmetrically substituted thiourea derivatives, namely 1,3-diethylthiourea (DETU), 1,3-diisopropylthiourea (DIPTU) and 1,3-diphenylthiourea (DPTU). The *ORTEP* (Johnson, 1965) plots of these molecules together with their numbering schemes are shown in Fig. 1.



DETU: R = CH₂CH₃

DIPTU: R = CH(CH₃)₂



DPTU

The molecule of DETU shows thermal disorder, with the ethyl C atoms having high thermal vibrations. One of the ethyl groups in particular (atoms C2 and C3) shows major disorder. The best model finally adopted was one with an occupancy of one site, but with relatively large displacement parameters and an unusual C2—C3 bond distance [1.366 (6) Å]. Such disorder has been observed previously in one of the DETU ligands in the structure of tetrakis(*N,N'*-DETU)cobalt(II) diperchlorate (Fawcett, Fehskens, Potenza, Schugar & Lalancette, 1979). The S=C1 bond length is between the mean value observed in DETU–metal complexes (1.734 Å) and the unweighted mean value (1.681 Å) given for C=S in thioureas (Allen *et al.*, 1987). The increase in the C=S bond length is reflected in the shortening of

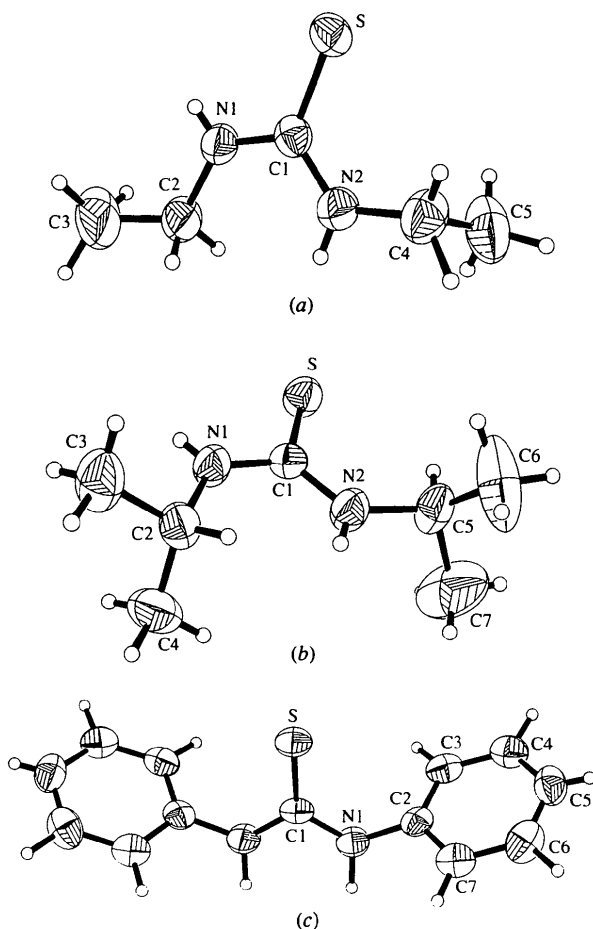


Fig. 1. Displacement ellipsoid plots of (a) DETU, (b) DIPTU and (c) DPTU, with the numbering schemes. Probability levels are 30, 50 and 50%, respectively.

the $N-C_{sp^2}$ distances ($N1-C1$ and $N2-C1$) compared with the mean value of 1.346 \AA in the above reference. The two ethyl groups have different orientations with respect to the thiourea moiety, with torsion angles $C1-N1-C2-C3$ and $C1-N2-C4-C5$ of $153.4(7)$ and $-106.7(5)^\circ$, respectively. The centrosymmetrically related molecules are connected by $N-H \cdots S$ hydrogen bonds [$N1 \cdots S^i$ $3.458(3) \text{ \AA}$ and $N1-H \cdots S^i$ $170(1)^\circ$; symmetry code: (i) $-x, -y, -z$] and hence the molecules exist as dimers. The glide-related dimers are linked by another $N-H \cdots S$ hydrogen bond between atoms $N2$ and S [$N2 \cdots S^{ii}$ $3.506(3) \text{ \AA}$ and $N2-H \cdots S^{ii}$ $163(1)^\circ$; symmetry code: (ii) $x, \frac{1}{2}-y, \frac{1}{2}+z$] (Fig. 2). These two hydrogen bonds link the molecules to form zigzag chains along the b and c axes, so that the crystal lattice consists of two-dimensionally knitted layers of DETU molecules.

The $C1=S$ bond length in DIPTU is in agreement with the DETU value, but the $C1-N1$ and $C1-N2$ distances are longer than those observed in DETU and closer to the $C-N$ value given by Allen *et al.* (1987).

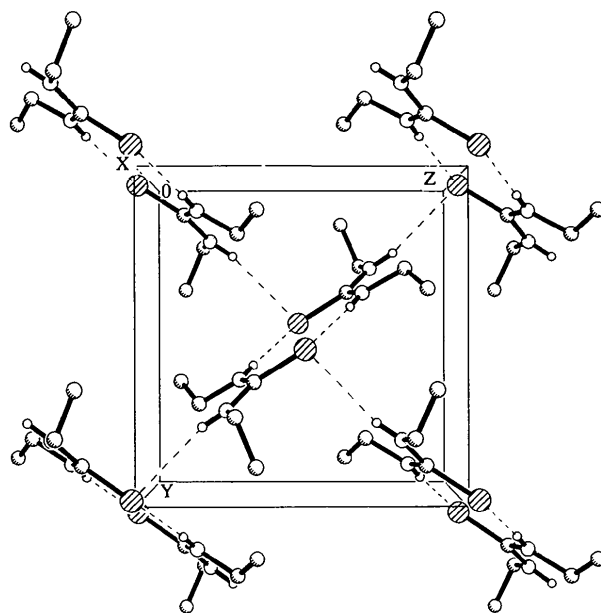


Fig. 2. Packing of the DETU molecules in the unit cell illustrating the dimer formation by the $N-H \cdots S$ hydrogen bonds (shown as dashed lines).

There is only one previously reported crystal structure involving DIPTU in a complex, namely hexakis(diisopropylthiourea)nickel(II) diperchlorate (Bentley & Waters, 1974). The geometric parameters cannot, however, be compared here since they were poor, the structure refinement resulting in a high R value (0.106). The isopropyl side chains adopt a *trans-cis* configuration with respect to each other. In the case of diisopropylurea (DIPUR), the configuration is found to be *cis-cis* (Toniole *et al.*, 1988). As observed in DETU, the molecules across the inversion centres are connected by $N-H \cdots S$ hydrogen bonds [$N1 \cdots S^i$ $3.447(1) \text{ \AA}$ and $N1-H1 \cdots S^i$ $167(2)^\circ$] and exist as dimers. Again, the glide-related dimers are connected by a hydrogen bond between $N2$ and S [$N2 \cdots S^{ii}$ $3.629(2) \text{ \AA}$ and $N2-H2 \cdots S^{ii}$ $160(2)^\circ$], but this is very weak compared to that in DETU. As described for DETU, DIPTU also has molecules linked into zigzag chains along the b and c axes, forming two-dimensional layers.

The molecule of DPTU has mirror symmetry with the $C=S$ bond in the mirror plane at $y = \frac{1}{4}$. It shows some difference in its structural features compared with the other two derivatives. First of all, the substituent groups (phenyl rings) adopt a *cis-cis* configuration, as opposed to the *trans-cis* configurations in DETU and DIPTU. However, in the two reported metal complexes of DPTU, the phenyl rings are found to be in *trans-cis* configurations (Bonamartini, Mangia & Pelizzi, 1973; Mangia & Pelizzi, 1973). The $C1=S$ and $N1-C1$ bond lengths agree well with the mean values of Allen *et al.* (1987) for thioureas, but are far shorter than those found in both DETU and DIPTU. In addition, the $N1-$

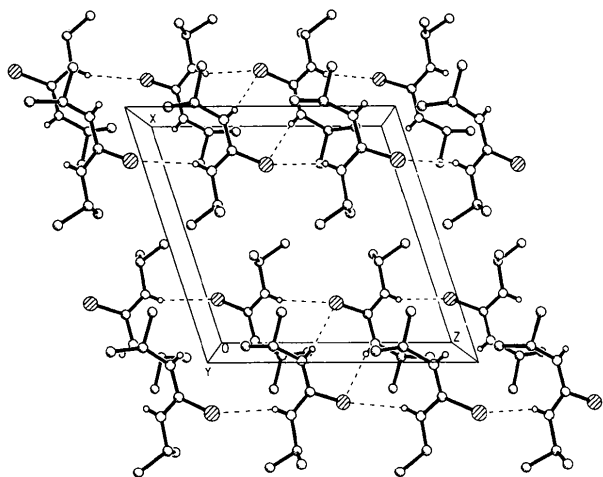


Fig. 3. Two layers of DIPTU molecules, each consisting of DIPTU molecules knitted together in the *bc* plane by N—H...S hydrogen bonds.

C2 distance is less than those observed (1.442 Å) in the metal complexes of DPTU and the N—C—N bond angle is far less than those observed in both DETU and DIPTU. The dihedral angle between the planes of the two phenyl rings is 36.9(1)° and that between the thiourea plane and the phenyl planes is 104.8(1)°. The S atom is involved in two mirror-symmetrical N—H...S hydrogen bonds (Fig. 4); N1...S^{iii,iv} 3.510(4) Å and N1—H1...S^{iii,iv} 154(4)° [symmetry codes: (iii) $x - \frac{1}{2}, y, \frac{1}{2} - z$; (iv) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z$]. These hydrogen bonds link the DPTU molecules along the *a* axis as zigzag chains. An analysis of urea analogues of DPTU reveals that 1,3-diphenylurea (DPUR) and substituted phenyl derivatives of DPUR prefer only the *cis-cis* configuration and not the *trans-cis* (Stankovic & Andreotti, 1978; Dannecker, Kopf & Rust, 1979; Leonhard, Plute, Haltiwanger & DuBois, 1979; Etter,

Zofia, Mohammed & Panunto, 1990). However, in the case of substituted thioureas, only the *trans-cis* configuration is favoured (Sivakumar & Akilan, 1995).

In conclusion, the present study shows that a *trans-cis* configuration of the substituents leads to the formation of two-dimensional layers of thiourea derivatives, whereas a *cis-cis* configuration leads to one-dimensional chains via N—H...S hydrogen bonds. The N—H...S hydrogen bond formed by the *cis*-oriented NH group is always stronger than that formed by the *trans*-NH group in the *trans-cis* molecules of thiourea derivatives.

Experimental

The DETU, DIPTU and DPTU samples were recrystallized from benzene, ethanol and a methanol-hexane mixture, respectively.

DETU

Crystal data

C₅H₁₂N₂S

$M_r = 132.23$

Monoclinic

$P2_1/c$

$a = 9.005(1) \text{ \AA}$

$b = 9.416(1) \text{ \AA}$

$c = 9.269(1) \text{ \AA}$

$\beta = 90.58(1)^\circ$

$V = 785.89(15) \text{ \AA}^3$

$Z = 4$

$D_x = 1.118 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 9-24^\circ$

$\mu = 0.324 \text{ mm}^{-1}$

$T = 293(2) \text{ K}$

Thick plate

$0.56 \times 0.48 \times 0.30 \text{ mm}$

Colourless

Data collection

Siemens P4 diffractometer

$\theta/2\theta$ scans

Absorption correction:

none

2313 measured reflections

1746 independent reflections

1065 observed reflections

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

$R_{\text{int}} = 0.0550$

$\theta_{\text{max}} = 27.49^\circ$

$h = -1 \rightarrow 10$

$k = -1 \rightarrow 12$

$l = -12 \rightarrow 12$

3 standard reflections

monitored every 100

reflections

intensity decay: <3%

Refinement

Refinement on F^2

$R(F) = 0.0723$

$wR(F^2) = 0.2364$

$S = 1.021$

1746 reflections

81 parameters

Only H-atom U 's refined

$w = 1/[\sigma^2(F_o^2) + (0.1529P)^2]$

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

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

$\Delta\rho_{\text{max}} = 0.458 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.331 \text{ e \AA}^{-3}$

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992),

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

DIPTU

Crystal data

C₇H₁₆N₂S

$M_r = 160.28$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

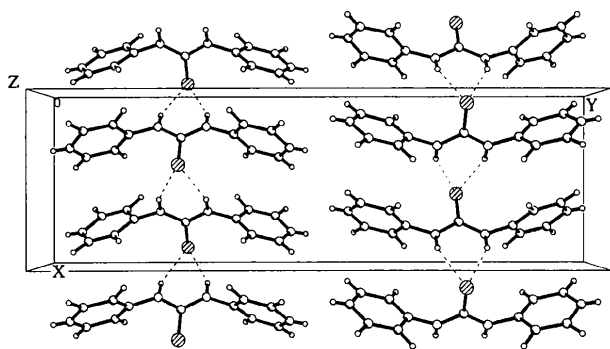


Fig. 4. The molecular packing of DPTU showing the chains of molecules connected by N—H...S hydrogen bonds parallel to the *a* axis.

Monoclinic
 $P2_1/c$
 $a = 10.463$ (2) Å
 $b = 9.276$ (2) Å
 $c = 10.596$ (3) Å
 $\beta = 107.83$ (2)°
 $V = 979.0$ (4) Å³
 $Z = 4$
 $D_x = 1.087$ Mg m⁻³

Data collection

Siemens P4 diffractometer
 $\theta/2\theta$ scans
Absorption correction:
none
2906 measured reflections
2231 independent reflections
1852 observed reflections
 $[I > 2\sigma(I)]$
 $R_{\text{int}} = 0.0570$

Refinement

Refinement on F^2
 $R(F) = 0.0395$
 $wR(F^2) = 0.1153$
 $S = 1.058$
2231 reflections
155 parameters
All H-atom parameters
refined
 $w = 1/[\sigma^2(F_o^2) + (0.0671P)^2 + 0.0511P]$
where $P = (F_o^2 + 2F_c^2)/3$

DPTU**Crystal data**

$C_{13}H_{12}N_2S$
 $M_r = 228.31$
Orthorhombic
 $Pnma$
 $a = 7.951$ (2) Å
 $b = 25.576$ (9) Å
 $c = 5.689$ (2) Å
 $V = 1156.9$ (6) Å³
 $Z = 4$
 $D_x = 1.311$ Mg m⁻³

Data collection

Siemens P4 diffractometer
 $\theta/2\theta$ scans
Absorption correction:
none
1902 measured reflections
1352 independent reflections
737 observed reflections
 $[I > 2\sigma(I)]$
 $R_{\text{int}} = 0.1352$

Refinement

Refinement on F^2
 $R(F) = 0.0676$
 $wR(F^2) = 0.2088$

Cell parameters from 25
reflections
 $\theta = 9-25^\circ$
 $\mu = 0.270$ mm⁻¹
 $T = 293$ (2) K
Prism
 $0.58 \times 0.44 \times 0.24$ mm
Colourless

$\theta_{\text{max}} = 27.50^\circ$
 $h = -1 \rightarrow 13$
 $k = -1 \rightarrow 12$
 $l = -13 \rightarrow 13$
3 standard reflections
monitored every 100
reflections
intensity decay: <3%

$(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.249$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.230$ e Å⁻³
Atomic scattering factors
from *International Tables*
for *Crystallography* (1992,
Vol. C, Tables 4.2.6.8 and
6.1.1.4)

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
Cell parameters from 25
reflections
 $\theta = 8-24^\circ$
 $\mu = 0.252$ mm⁻¹
 $T = 293$ (2) K
Thin flake
 $0.52 \times 0.44 \times 0.10$ mm
Colourless

$\theta_{\text{max}} = 27.50^\circ$
 $h = -1 \rightarrow 10$
 $k = -1 \rightarrow 33$
 $l = -1 \rightarrow 7$
3 standard reflections
monitored every 100
reflections
intensity decay: <5%

$(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.311$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.331$ e Å⁻³

$S = 0.933$
1351 reflections
100 parameters
All H-atom parameters
refined
 $w = 1/[\sigma^2(F_o^2) + (0.1226P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

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 (Å²) for DETU, DIPTU and DPTU

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

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
DETU				
S	-0.24092 (9)	0.03845 (10)	-0.01078 (9)	0.0772 (4)
N1	-0.0491 (3)	0.1283 (3)	0.1842 (3)	0.0810 (9)
N2	-0.2820 (3)	0.2089 (3)	0.2138 (3)	0.0805 (8)
C1	-0.1874 (3)	0.1323 (3)	0.1384 (3)	0.0645 (8)
C2	0.0145 (5)	0.1993 (5)	0.3083 (6)	0.111 (2)
C3	0.1367 (10)	0.1369 (10)	0.3695 (10)	0.247 (6)
C4	-0.4385 (4)	0.2207 (5)	0.1849 (5)	0.1027 (13)
C5	-0.4759 (5)	0.3534 (5)	0.1260 (6)	0.144 (2)
DIPTU				
S	0.20492 (4)	0.07118 (5)	0.05004 (4)	0.0485 (2)
N1	0.02277 (13)	0.1589 (2)	0.15831 (13)	0.0460 (3)
N2	0.23725 (13)	0.2322 (2)	0.26638 (14)	0.0504 (3)
C1	0.15254 (14)	0.1604 (2)	0.16667 (13)	0.0398 (3)
C2	-0.0408 (2)	0.2221 (2)	0.2507 (2)	0.0477 (4)
C3	-0.1841 (2)	0.2637 (3)	0.1742 (3)	0.0698 (6)
C4	-0.0332 (3)	0.1205 (3)	0.3633 (2)	0.0711 (6)
C5	0.3806 (2)	0.2530 (2)	0.2866 (2)	0.0570 (4)
C6	0.4099 (4)	0.4094 (4)	0.2788 (8)	0.128 (2)
C7	0.4585 (4)	0.1896 (8)	0.4173 (4)	0.123 (2)
DPTU				
S	0.4141 (2)	1/4	0.6124 (2)	0.0448 (5)
C1	0.2557 (6)	1/4	0.4168 (8)	0.0347 (11)
N1	0.1881 (4)	0.29421 (12)	0.3286 (6)	0.0466 (8)
C2	0.2357 (4)	0.34551 (13)	0.3963 (7)	0.0391 (8)
C3	0.1842 (5)	0.3660 (2)	0.6105 (7)	0.0496 (10)
C4	0.2228 (6)	0.4168 (2)	0.6653 (8)	0.0557 (11)
C5	0.3169 (6)	0.4471 (2)	0.5129 (9)	0.0554 (12)
C6	0.3665 (5)	0.4269 (2)	0.3001 (9)	0.0573 (12)
C7	0.3252 (5)	0.3762 (2)	0.2402 (8)	0.0483 (10)

Table 2. Selected geometric parameters (Å, °) for DETU, DIPTU and DPTU

DETU			
S—C1	1.707 (3)	N2—C4	1.437 (5)
N1—C1	1.312 (4)	C2—C3	1.366 (6)
N1—C2	1.444 (5)	C4—C5	1.403 (6)
N2—C1	1.321 (4)		
C1—N1—C2	127.8 (3)	N2—C1—S	122.2 (2)
C1—N2—C4	125.5 (3)	C3—C2—N1	116.3 (4)
N1—C1—N2	117.3 (3)	C5—C4—N2	111.9 (4)
N1—C1—S	120.4 (2)		
DIPTU			
S—C1	1.7109 (15)	C2—C4	1.503 (3)
N1—C1	1.333 (2)	C2—C3	1.520 (3)
N1—C2	1.464 (2)	C5—C6	1.490 (4)
N2—C1	1.331 (2)	C5—C7	1.496 (4)
N2—C5	1.461 (2)		
C1—N1—C2	127.82 (13)	N1—C2—C3	108.74 (14)
C1—N2—C5	125.91 (14)	C4—C2—C3	112.7 (2)
N2—C1—N1	118.35 (13)	N2—C5—C6	109.9 (2)
N2—C1—S	122.19 (11)	N2—C5—C7	109.1 (2)
N1—C1—S	119.46 (11)	C6—C5—C7	111.8 (4)
N1—C2—C4	110.8 (2)		

C1—N1—C2—C4	−84.6 (2)	C1—N2—C5—C6	115.7 (4)
C1—N1—C2—C3	151.0 (2)	C1—N2—C5—C7	−120.4 (3)
DPTU			
S—C1	1.681 (5)	N1—C2	1.419 (5)
C1—N1	1.349 (4)		
N1 ¹ —C1—N1	113.9 (4)	C1—N1—C2	124.6 (3)
N1 ¹ —C1—S	123.0 (2)	C7—C2—N1	119.2 (4)
N1—C1—S	123.0 (2)	C3—C2—N1	120.6 (4)

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

The structures were solved by direct methods and refined by a full-matrix least-squares technique. The H atoms were geometrically fixed in the case of DETU and located from difference maps for both DIPTU and DPTU. The large *R* factors for DETU and DPTU result from the partly disordered structure and/or large displacement factors.

For all 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).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1179). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A 2:1 Solid Solution of 6-Chloro-2,3,6-trideoxy-D-erythro-hex-2-enono-1,5-lactone and its 6-Bromo Analogue

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Abstract

The structure of an unusual 1:2 mixture of isomorphous bromo and chloro derivatives of a 1,5-lactone, 0.34C₆H₇BrO₃.0.66C₆H₇ClO₃, is reported, together with the absolute configuration of the molecules. The lactone ring adopts a conformation between sofa and half-chair. The crystal structure is stabilized by O—H···O hydrogen bonds between the hydroxy and carbonyl groups.

Comment

1,5-Lactones are substructures of many natural products (El-Zayat, Ferrigni, McCloud, McKenzie, Byrn, Casady, Chang & McLaughlin, 1985). Our research group is interested in their synthesis with a view to further expanding them into some of these natural products. We reported previously the synthesis and crystal structure of 2,3-dideoxy-D-erythro-hex-2-enono-1,5-lactone, (1), from tri-*O*-acetyl-D-glucal (Fun, Sivakumar, Ang, Sam & Gan, 1995). We are now interested in preparing halides of (1), since they are important intermediates in

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