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N,N′-Bis(*tert*-butoxycarbonyl)thiourea

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Key indicators

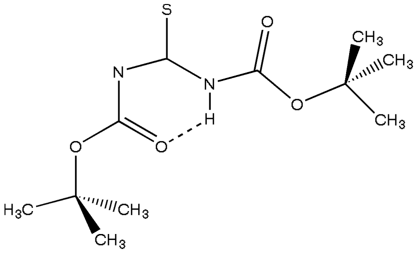
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.004 Å
R factor = 0.045
wR factor = 0.057
Data-to-parameter ratio = 13.4

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

The title compound, $C_{11}H_{20}O_4N_2S$, has a planar skeleton and its crystal structure is stabilized by extensive intermolecular (N—H···S) and intramolecular (N—H···O and C—H···O) hydrogen-bonding interactions.

Comment

The positively charged residue of arginine (Arg), *i.e.* the guanidinium residue, having a pK_a of 12.5, is perceived to bind anions such as phosphate and carboxylate in simulated physiological conditions. This demonstrates the ability of guanidinium to hydrolyse phosphodiesters in DNA and RNA (Aït-Haddou *et al.*, 2002; Wilcox, 1996), or to selectively signal specific amino acids through co-operative chelation with metals (Aït-Haddou *et al.*, 2001; Severin *et al.*, 1998). Guanidines can be prepared by the reaction of an amine with various guanylating agents.



(I)

Recently, *N,N′*-bis(*tert*-butoxycarbonyl)thiourea, (I) (Kim & Qian, 1993), was not only proved to be an efficient guanylating agent for the general primary and unhindered secondary amines in high yields, but also to show similar activity towards hindered or unreactive amines in the presence of catalysts such as mercury salts or Mukaiyama's reagent (Yong *et al.*, 1997; Expósito *et al.*, 2001). With this background, we report the structure (I).

The basic skeleton of (I) has a planar conformation (Fig. 1 and Table 1). The presence of an intramolecular hydrogen bond N1—H···O4 (Table 2) results in the compression of the N1—C6—N2 angle from 120° to 113.2 (2)°, resulting in an S1—C6—N2 bond angle of 119.5 (2)°. The widening of the S1—C6—N1 angle from the normal 120° to 127.3 (2)° is due to the presence of an interaction between atoms S1 and O2 [3.05 (2) Å]. This also leads to a large deviation [167.5 (2)°] of the O1/C5/O2 least-squares plane from the hydrogen-bonded six-membered ring, O4—C11—N2—C6—N1—H1N; the deviation of the latter plane from O3/C11/C4 is 175.8 (2)°.

This planar conformation is further stabilized by intermolecular N—H···S bonds (Fig. 2 and Table 2). It is interesting to note that, due to the staggered arrangement of the *tert*-butyl methyl groups with respect to the carboxylate groups, one of the O—C—C angles of each substituent is much

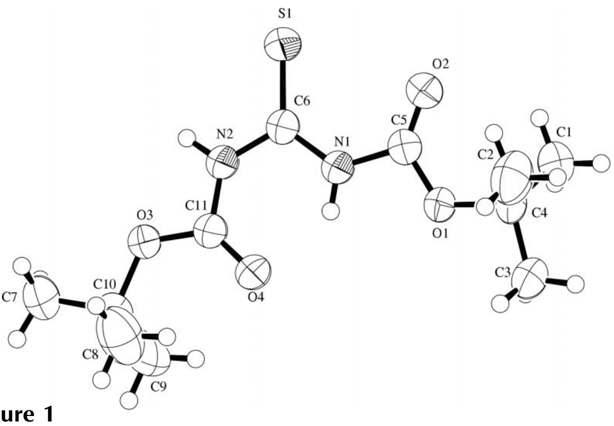


Figure 1
An *ORTEP*II (Johnson, 1976) drawing of the molecule (50% probability ellipsoids), showing the crystallographic labelling scheme.

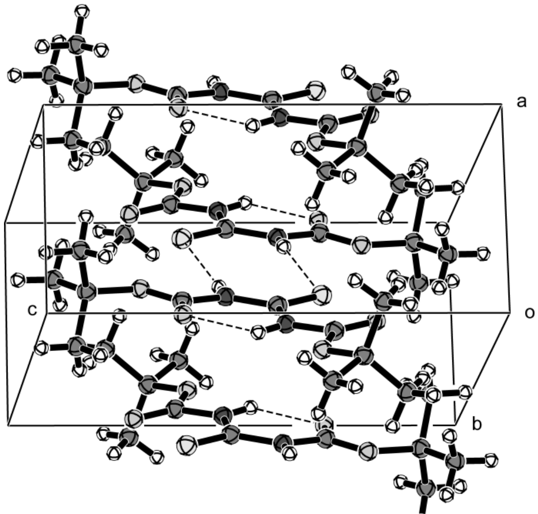


Figure 2
Packing diagram of (I) in the unit cell. Hydrogen bonds are shown as dashed lines.

smaller than the other two. Thus, the O1—C4—C3 angle is only 101.8 (2)° and, similarly, the O3—C10—C7 angle is 102.0 (2)°. Furthermore, the C···O distances fall in the range 2.962 (3)–3.117 (4) Å and are indicative of weak C—H···O intramolecular contacts involving the carbonyl O atoms (Table 2).

Experimental

Compound (I) was prepared according to the method of Expósito *et al.* (2001). To a stirred solution of thiourea (571 mg, 7.50 mmol) in anhydrous THF (150 ml) under argon in an ice bath was added sodium hydride (1.35 g, 33,8 mmol, 60% in mineral oil). After 5 min, di-*tert*-butyl dicarbonate (3.60 g, 16.5 mmol) was added, and the mixture was stirred at room temperature for 2 h. Then the reaction was quenched with $NaHCO_3$ aqueous solution (15 ml). The reaction mixture was poured into 250 ml water and extracted with EtOAc (3 × 70 ml). The organic phase was dried with anhydrous Na_2SO_4 and concentrated *in vacuo* to give (I) as a white solid with a stimulating smell (1.72 g, 83%). Crystals suitable for X-ray data collection were obtained by slow evaporation of an EtOAc solution of the compound held at room temperature.

Crystal data

$C_{11}H_{20}N_2O_4S$
$M_r = 276.35$
Triclinic, $P\overline{1}$
$a = 6.171$ (2) Å
$b = 11.334$ (3) Å
$c = 11.653$ (3) Å
$\alpha = 81.25$ (1)°
$\beta = 87.31$ (1)°
$\gamma = 74.27$ (1)°
$V = 775.4$ (4) Å^3
$Z = 2$
$D_x = 1.184$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 31 reflections
$\theta = 1.1$–27.5°
$\mu = 0.22$ mm^{-1}
$T = 298$ K
Block, colourless
0.39 × 0.15 × 0.08 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{\min} = 0.960$, $T_{\max} = 0.984$
4811 measured reflections
3344 independent reflections
2188 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.020$
$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 7$
$k = -13 \rightarrow 14$
$l = -14 \rightarrow 14$

Refinement

Refinement on F
$R = 0.045$
$wR = 0.057$
$S = 1.57$
2188 reflections
163 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o) + 0.0005(F_o)^2]$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C6	1.637 (2)	N2—C6	1.380 (3)
O1—C4	1.487 (3)	N2—C11	1.383 (3)
O1—C5	1.337 (3)	C1—C4	1.508 (3)
O2—C5	1.179 (3)	C2—C4	1.500 (4)
O3—C10	1.477 (3)	C3—C4	1.508 (4)
O3—C11	1.323 (3)	C7—C10	1.514 (4)
O4—C11	1.203 (3)	C8—C10	1.505 (4)
N1—C5	1.402 (3)	C9—C10	1.495 (4)
N1—C6	1.364 (3)		
C4—O1—C5	121.1 (2)	S1—C6—N1	127.3 (2)
C10—O3—C11	121.9 (2)	S1—C6—N2	119.5 (2)
C5—N1—C6	127.5 (2)	N1—C6—N2	113.2 (2)
C6—N2—C11	129.4 (2)	O3—C10—C7	102.0 (2)
O1—C4—C1	110.6 (2)	O3—C10—C8	109.4 (2)
O1—C4—C2	108.7 (2)	O3—C10—C9	109.6 (2)
O1—C4—C3	101.8 (2)	C7—C10—C8	111.6 (2)
C1—C4—C2	113.1 (2)	C7—C10—C9	110.4 (2)
C1—C4—C3	110.2 (2)	C8—C10—C9	113.2 (3)
C2—C4—C3	111.8 (2)	O3—C11—O4	127.0 (2)
O1—C5—O2	128.2 (2)	O3—C11—N2	107.9 (2)
O1—C5—N1	105.3 (2)	O4—C11—N2	125.0 (2)
O2—C5—N1	126.5 (2)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···O4	0.87	1.96	2.658 (3)	137
N2—H2*N*···S1$^{\rm i}$	0.87	2.56	3.395 (2)	162
C1—H1*A*···O2	0.95	2.37	2.980 (4)	122
C2—H2*C*···O2	0.95	2.54	3.117 (4)	119
C8—H8*B*···O4	0.95	2.51	3.093 (5)	120
C9—H9*B*···O4	0.95	2.35	2.962 (3)	122

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

All H atoms were placed in geometrically calculated positions and refined as riding on their parent atoms.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN* (Molecular Structure corporation, 1992); molecular graphics: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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