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Methyl 4-*tert*-butoxycarbonyl-*N*-cyanopiperazine-1-carboximidothioate

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Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.004 Å
R factor = 0.034
wR factor = 0.097
Data-to-parameter ratio = 16.6

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

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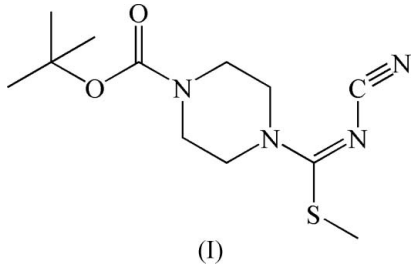
The title compound, $C_{12}H_{20}N_4O_2S$, has been synthesized for use as an intermediate for antihypertensive agents, potential antimalarials and molecular rectification materials. The intermolecular S···N non-bonded separation within a column in the crystal structure is 3.308 (2) Å, indicating a strong intermolecular interaction between the cyano groups and the S atoms. Attractive C—H···O hydrogen bonds are responsible for zigzag molecular chains propagating in the *a*-axis direction; these types of intermolecular interactions combine to form an extended three-dimensional network in the lattice.

Comment

The title compound, (I), may prove to be an intermediate for antihypertensive agents, potential antimalarials (Meyer *et al.*, 1989; Johnson & Werbel, 1983) and molecular rectification materials.



(I)

The molecular structure and atom-labeling scheme are shown in Fig. 1. Selected geometric parameters are given in Table 1. The six-membered ring adopts a chair conformation. It is noteworthy that the presence of a push–pull imine unit, with the methylthio group as electron donor and the cyano group as an electron acceptor, most probably leads to diverse attractive close interactions in the crystal structure. The

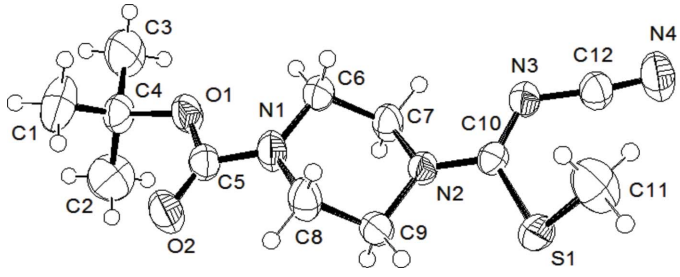


Figure 1
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

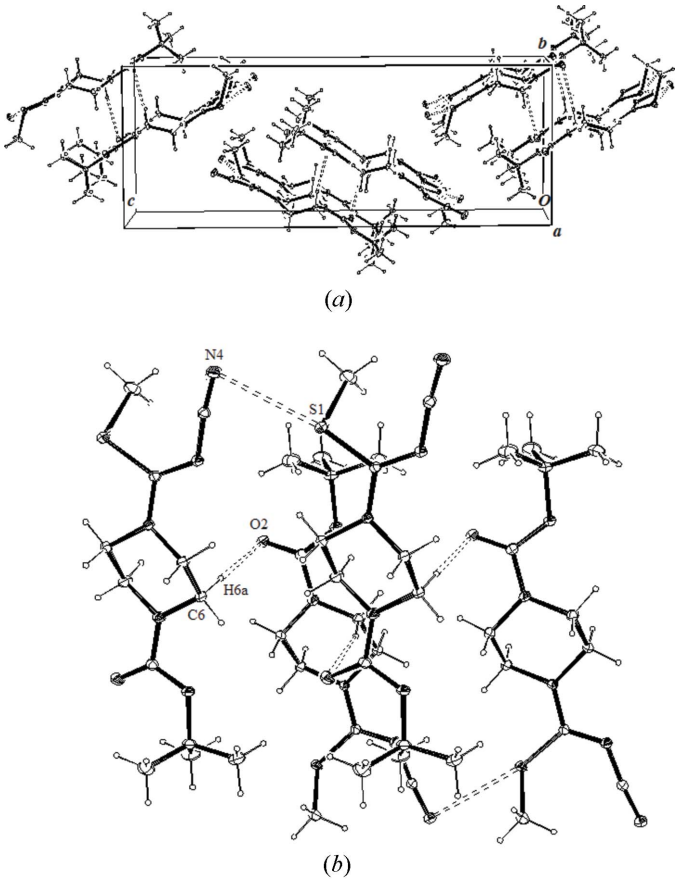


Figure 2
(*a*) The crystal structure of (I), viewed along the *a* axis. Dashed lines indicate hydrogen bonds. (*b*) A single column spread out for clarity. Dashed lines indicate intermolecular S1···N4 interactions and C6—H6*A*···O2 hydrogen bonds.

S1···N4^{ii} [symmetry code: (ii) 1 + *x*, *y*, *z*] non-bonded separation is 3.308 (2) Å, which indicates a strong intermolecular interaction between these two atoms. In addition, there are also weak S···C interactions [non-bonded separation = 3.402 (3) Å], as well as S···N short contacts [3.814 (3) Å].

Further examination of the crystal structure of (I) reveals the existence of possible C—H···O, C—H···S and C—H···π(C≡N) interactions (Table 1) (Kumar *et al.*, 1998; Lu *et al.*, 2004). Intermolecular C6—H6*A*···O2^{i} hydrogen bonds [symmetry code: (i) $-\frac{1}{2}+x, \frac{3}{2}-y, -z$] forms zigzag molecular chains propagating in the *a*-axis direction within each column, as shown in Fig. 2. As a result, all these types of interaction together form an extended three-dimensional network in the crystal structure of (I), resulting in a highly ordered molecular packing array.

Experimental

To 1-Boc-piperazine (20 mmol, 3.72 g) was added dimethyl cyanoimidodithiocarbonate (20 mmol, 2.92 g) in benzene (250 ml, previously dried over CaH_2). The reaction mixture turned cloudy immediately upon combination of the starting materials and the evolution of methyl mercaptan was apparent. The mixture was heated under reflux with stirring for about 6 h. The white precipitate was filtered from the reaction mixture and air dried. Reduction of the volume of the filtrate yielded no additional material. The crude product was recrystallized from acetone to yield 4.83 g (85%) of pale-yellow crystals (m.p. 393–395 K).^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.82 (*t*, 4H), 3.50 (*t*, 4H), 2.79 (*s*, 3H), 1.47 (*s*, 9H); IR (KBr): ν 2946, 2167, 1685, 1551, 1430, 1350, 1287, 848, 715 cm^{-1}.

Crystal data

$C_{12}H_{20}N_4O_2S$
M_r = 284.38
Orthorhombic, $P2_12_12_1$
a = 6.358 (2) Å
b = 9.382 (3) Å
c = 24.646 (8) Å
V = 1470.1 (8) Å^3
Z = 4
D_x = 1.285 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2619 reflections
θ = 2.3–22.1°
μ = 0.23 mm^{-1}
T = 273 (2) K
Spiky fragment, yellow
0.20 × 0.15 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.956, T_{max} = 0.978
7193 measured reflections
2875 independent reflections
2436 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 26.0°
$h = -7 \rightarrow 7$
$k = -11 \rightarrow 10$
$l = -30 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.098
S = 1.09
2875 reflections
173 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0538P)^2 + 0.11P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter: 0.0 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1*B*···O2	0.96	2.39	2.991 (2)	120
C2—H2*C*···O2	0.96	2.43	3.025 (2)	120
C6—H6*A*···O2^{i}	0.97	2.69	3.645 (3)	168
C9—H9*A*···S1	0.97	2.46	2.980 (2)	113
C11—H11*C*···N4≡C12	0.96	2.50	3.361 (2)	149
C11—H11*C*···C12≡N4	0.96	2.34	2.974 (2)	123

Symmetry code: (i) $x-\frac{1}{2}, -y+\frac{3}{2}, -z$.

H atoms were included using a riding model, with C—H = 0.96 or 0.97 Å and $U_{iso} = 1.2U_{eq}$(C).

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *ORTEP3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Sheldrick, 1997*b*).

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