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1-*tert*-Butyl-2-(*tert*-butoxysulfanyl)-1-(3,5-dimethylbenzoyl)-2-(4-ethylbenzoyl)hydrazine

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Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.003 Å
R factor = 0.043
wR factor = 0.130
Data-to-parameter ratio = 15.9

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

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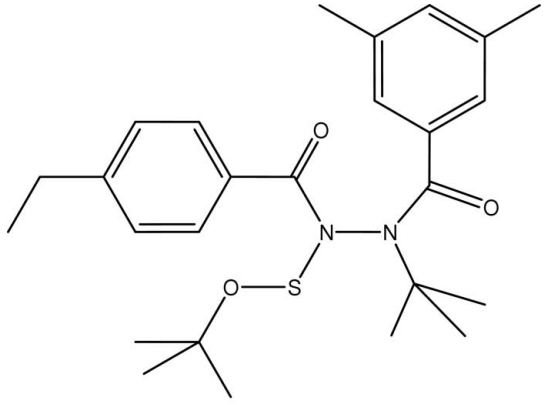
In the title compound, $C_{26}H_{36}N_2O_3S$, the amide bearing the N—S bond has an *s-cis* conformation, whereas that bearing the *N-tert*-butyl group has an *s-trans* conformation, the N—N—C=O torsion angles being −15.1 (2) and −174.3 (2)°, respectively. The steric size of the *N-tert*-butyl group causes the 3,5-dimethylphenyl group to be directed away from it.

Comment

1-*tert*-Butyl-1,2-diacylhydrazines are a new class of insect growth regulators. They have been found to mimic the action of 20-hydroxyecdysone to activate the ecdysone receptor, leading to lethal premature moulting (Wing, 1988, 1995; Wing *et al.*, 1988). Among nonsteroidal ecdysone agonists, 1-*tert*-butyl-2-(4-ethylbenzoyl)-1-(3,5-dimethylbenzoyl)hydrazine (tebufenozide, RH-5992) was the first to be commercialized as a lepidopteran-specific insecticide, with a low toxicity profile towards mammals, birds and fish, as well as towards non-target arthropods such as insect pollinators, predators and parasitoids (Dhadialla & Jansson, 1999). At present, a further three new structural analogues, methoxyfenozide (RH-2485), halofenozide (RH-0345) and chromafenozide (ANS-118), have already been brought to the market (Carlson *et al.*, 2001; Yanagi *et al.*, 2000). Therefore, in a search for new insect growth regulators with improved biological properties and a different activity spectrum, we synthesized the title compound, (I). The crystal structure has been determined in order to investigate the structure–activity relationship.



(I)

The molecular structure of (I) is shown in Fig. 1. The two amide groups adopt the expected planar structure. The amide bearing the N—S bond has an *s-cis* conformation, with an N1—N2—C18—O2 torsion angle of −15.1 (2)°, whereas the amide bearing the *N-tert*-butyl group has an *s-trans* confor-

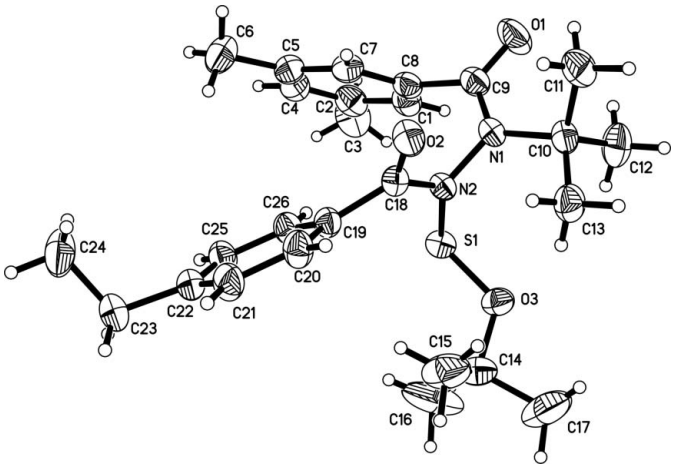


Figure 1
The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

mation, with an N2—N1—C9—O1 torsion angle of −174.3 (2)°. Clearly, the steric size of the *tert*-butyl group bonded to N1 causes the 3,5-dimethylphenyl group to be directed away from it. The N—N bond adopts a *gauche* conformation, with a C9—N1—N2—C18 torsion angle of −96.7 (2)°. A similar *gauche* conformation has been observed for other hydrazine derivatives (Chan *et al.*, 1990; Wolfe, 1972).

Experimental

To a stirred solution of sulfur dichloride (0.08 mol) and dichloromethane (15 ml), a solution of pyridine (0.008 mol) in dichloromethane (5 ml) was added dropwise at 263 K. A solution of 1-*tert*-butyl-1-(3,5-dimethylbenzoyl)-2-(4-ethylbenzoly)hydrazine (0.007 mol) in dichloromethane (5 ml) was then added at 263 K. The mixture was stirred at room temperature for 4 h and then the solution was added dropwise to *tert*-butanol sodium (0.007 mol). After the addition was complete, the reaction mixture was stirred for 6 h at room temperature. The solid was then filtered off and the filtrate was concentrated under vacuum. The residue was purified by column chromatography on silica gel using petroleum ether (b.p. 333–363 K), dichloromethane and ethyl acetate (20:1:1 *v*/*v*/*v*) as eluent. Crystals of (I) were grown from a solution in propan-2-ol by slow evaporation (yield 76%).

Crystal data

$C_{26}H_{36}N_2O_3S$
M_r = 456.63
Monoclinic, $P2_1/c$
a = 11.163 (5) Å
b = 10.422 (4) Å
c = 23.031 (10) Å
β = 93.298 (5)°
V = 2675.2 (19) Å^3
Z = 4
D_x = 1.134 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.15 mm^{-1}
T = 273 (2) K
Tablet, colourless
0.32 × 0.18 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.646, T_{max} = 1.000
13998 measured reflections
4727 independent reflections
3488 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 25.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.130
S = 1.03
4727 reflections
297 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.048P)^2 + 0.7023P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—O3	1.6315 (16)	N1—N2	1.416 (2)
S1—N2	1.6860 (17)	N2—C18	1.412 (2)
N1—C9	1.366 (3)		
N2—S1—O3—C14	104.40 (16)	C1—C8—C9—O1	68.4 (3)
C9—N1—N2—C18	−96.7 (2)	N1—N2—C18—O2	−15.1 (2)
C9—N1—N2—S1	78.5 (2)	O2—C18—C19—C26	133.8 (2)
N2—N1—C9—O1	−174.3 (2)		

All H atoms were placed in calculated positions, with C—H = 0.93, 0.96 or 0.97 Å, and included in the final cycles of refinement using a riding model, with U_{iso}(H) = 1.2U_{eq}(C), or 1.5U_{eq}(C) for methyl groups.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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