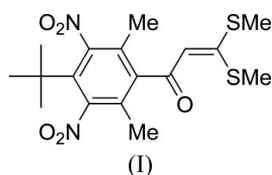


3-(4-*tert*-Butyl-2,6-dimethyl-3,5-dinitrobenzoyl)-
1,1-bis(methylsulfanyl)prop-2-en-1-oneJiang-Peng Liao,^{a,b} Ti Zhang,^{a,b}
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huangzt@public.bta.net.cnThe bond lengths and molecular conformation of the title
compound, C₁₇H₂₂N₂O₅S₂, can be correlated with electronic
conjugation and steric effects.Received 7 September 2006
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Comment

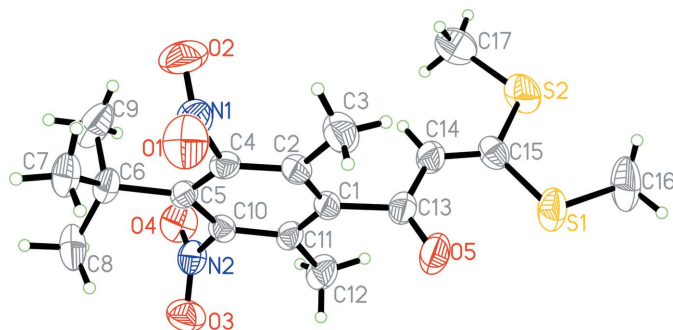
As precursors for the synthesis of heterocyclic ketene amins
(HKAs) (Huang & Wang, 1994, 2002), aroyl-substituted
ketene dimethylmercaptals have been widely used to synthe-
size a variety of heterocycles. The title compound, (I) (Fig. 1),
was obtained from the one-pot reaction of 1-(4-*tert*-butyl-2,6-
dimethyl-3,5-dinitrophenyl)ethanone, carbon disulfide and
methyl iodide.The geometrical parameters for (I) are normal. The length
of the C13—C14 bond is shorter than that of a normal C—C
single bond, owing to the conjugation involving the adjacent
C13=O5 and C14=C15 bonds (Table 1). The lengths of the
C15—S1 and C15—S2 bonds are shorter than that of a normal
C—S single bond for the same reason. The C13/C14/C15/O5/
S1/S2 assembly is almost planar [r.m.s. deviation from the
mean plane of 0.0071 (16) Å] and close to perpendicular to the
benzene ring mean plane [dihedral angle = 89.37 (6)°]. Both
nitro groups are almost perpendicular to the benzene ring
plane, probably for steric reasons to avoid unfavourable
interactions with the C3 and C12 methyl groups and the C6
tert-butyl group.

Experimental

1-(4-*tert*-Butyl-2,6-dimethyl-3,5-dinitrophenyl)ethanone (58.86 g,
0.2 mol) was added dropwise to a suspension of sodium hydride (12 g,
80%, 0.4 mol) in toluene (200 ml) and dimethylformamide (50 ml).
Carbon disulfide (15.23 g, 0.2 mol) was then added dropwise to the
reaction mixture slowly. After stirring for 2 h, methyl iodide (56.78 g,
0.4 mol) was added dropwise while the reaction flask was cooled in an
ice bath. When thin-layer chromatography indicated the reaction was
complete, the mixture was poured into ice-water and the organic
phase was separated from the aqueous phase. The aqueous phase was
extracted with ethyl acetate (3 × 50 ml). The combined organic
phases were dried over anhydrous sodium sulfate. After partial
removal of the solvents, the title compound was crystallized from the
solution: yellow needles of (I) were collected by filtration and washed
with petroleum ether (Huang & Liu, 1989). (yield 51.81 g, 65%; m.p.

Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ (C—C) = 0.004 Å
R factor = 0.044
wR factor = 0.115
Data-to-parameter ratio = 14.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

**Figure 1**

The molecular structure of (I), showing 50% displacement ellipsoids (arbitrary spheres for the H atoms).

495–496 K). $^1\text{H NMR}$ (CDCl_3): δ 6.04 (s, 1H, =CH), 2.52 (s, 3H, SCH_3), 2.47 (s, 3H, SCH_3), 2.12 (s, 6H, 2CH_3), 1.44 (s, 9H, $\text{C}(\text{CH}_3)_3$); ESI-MS: m/z 39 ($M^+ + 1$); Analysis calculated for $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_5\text{S}_2$: C 51.24, H 5.56, N 7.03%; found: C 50.87, H 5.59, N 7.03%.

Crystal data

$\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_5\text{S}_2$ $V = 971.5$ (4) \AA^3
 $M_r = 398.49$ $Z = 2$
 Triclinic, $P\bar{1}$ $D_x = 1.362$ Mg m^{-3}
 $a = 8.657$ (2) \AA Mo $K\alpha$ radiation
 $b = 10.193$ (3) \AA $\mu = 0.30$ mm^{-1}
 $c = 12.561$ (3) \AA $T = 294$ (2) K
 $\alpha = 67.272$ (4) $^\circ$ Prism, yellow
 $\beta = 71.840$ (4) $^\circ$ $0.24 \times 0.20 \times 0.16$ mm
 $\gamma = 82.758$ (4) $^\circ$

Data collection

Bruker SMART CCD 4980 measured reflections
 diffractometer 3403 independent reflections
 ω scans 2092 reflections with $I > 2\sigma(I)$
 Absorption correction: multi-scan $R_{\text{int}} = 0.025$
 (*SADABS*; Bruker, 2002) $\theta_{\text{max}} = 25.0^\circ$
 $T_{\text{min}} = 0.767$, $T_{\text{max}} = 1.000$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.115$
 $S = 1.07$
 3403 reflections
 242 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.003$
 $\Delta\rho_{\text{max}} = 0.25$ e \AA^{-3}
 $\Delta\rho_{\text{min}} = -0.26$ e \AA^{-3}

Table 1

Selected bond lengths (\AA).

C15—S1	1.740 (3)	C13—C14	1.436 (3)
C15—S2	1.753 (3)	C14—C15	1.348 (4)

The H atoms were located in difference maps, repositioned in idealized positions ($\text{C—H} = 0.93\text{--}0.96$ \AA) and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); 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, 2002); software used to prepare material for publication: *SHELXTL*.

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References

- Bruker (2002). *SMART*, *SAINT*, *SADABS* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Huang, Z.-T. & Liu, Z.-R. (1989). *Synth. Commun.* **19**, 943–958.
 Huang, Z.-T. & Wang, M.-X. (1994). *Heterocycles*, **37**, 1233–1262.
 Huang, Z.-T. & Wang, M.-X. (2002). *Prog. Nat. Sci.* **12**, 249–257.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.