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Methyl 2-(3,5-dichlorophenyl)-5-dimethylamino-3-methyl-1,1-dioxo-1,2,3,4-tetrahydro-1λ^6,2,4,6-thiatriazine-3-carboxylate

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Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.003 Å
R factor = 0.043
wR factor = 0.113
Data-to-parameter ratio = 18.7

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

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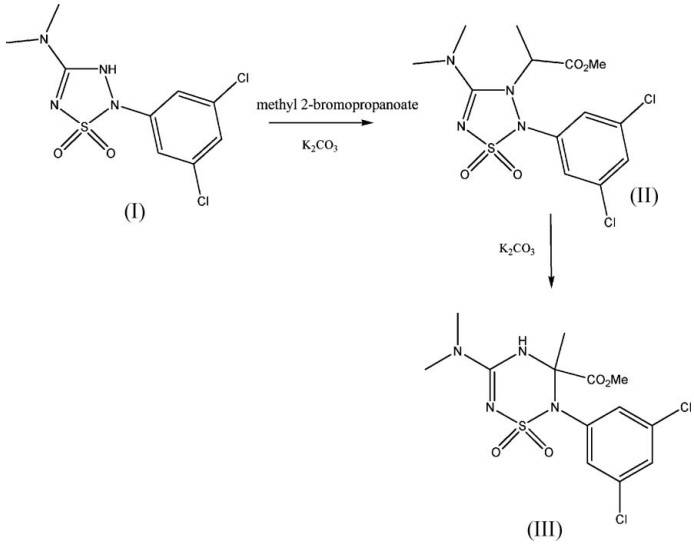
The title compound, $C_{13}H_{16}Cl_2N_4O_4S$, was formed by base-assisted *N*-alkylation of [2-(3,5-dichlorophenyl)-1,1-dioxo-2,3-dihydro-1*H*-1λ^6-1,2,3,5-thiatriazol-4-yl]dimethylamine with methyl 2-bromopropanoate, followed by a novel base-promoted ring-expansion reaction, to form a relatively rare 1,1-dioxo-1,2,4,6-thiatriazine. The thiatriazine heterocycle adopts an envelope conformation. In the crystal structure, adjacent molecules are linked by an N—H···O hydrogen bond to form chains parallel to the *a* direction.

Comment

As part of a programme aimed at the discovery of new low-molecular weight heterocyclic compounds with potential biological activity, we have been investigating the synthesis and properties of 4-amino-1,2,3,5-thiatriazole dioxides (Fallon *et al.*, 2005). In the course of these investigations, we treated the thiatriazole, (I), with methyl-2-bromopropanoate in the presence of K_2CO_3, expecting to form the simple *N*-alkylated product, (II). Suprisingly, the major product from this reaction was not (II) but a ring-expanded compound. The lack of contiguous NMR-responsive nuclei in the product meant that an X-ray structural study was critical in confirming the exact connectivity of the atoms that constitute its heterocyclic ring. In particular, it was important to determine if the product was a 1,2,3,6-, 1,2,4,5- or 1,2,4,6-thiatriazine. Crystals suitable for X-ray analysis were formed by slow evaporation of an ethanol solution. X-ray analysis confirmed that the product was the title 1,2,4,6-thiatriazine dioxide, (III), a relatively rare 1,1-dioxo-1,2,4,6-thiatriazine.



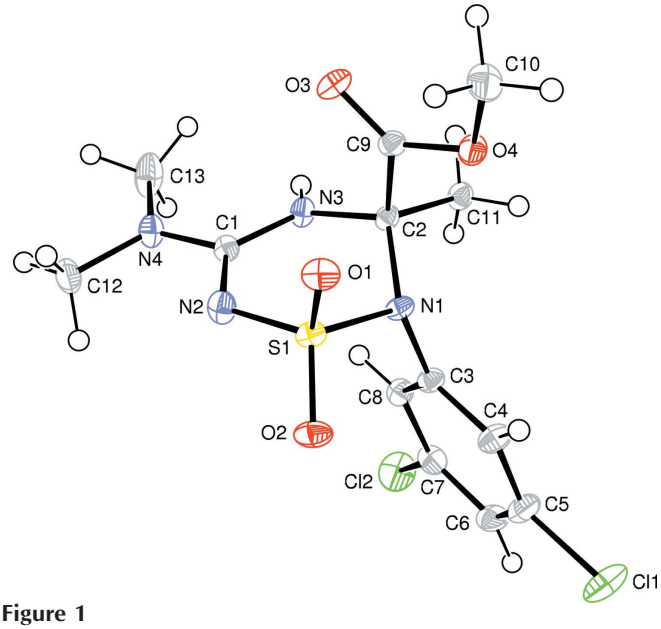


Figure 1
A view of the molecular structure of (III), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

The molecular structure of (III) is shown in Fig. 1. The thiatriazine heterocycle adopts an envelope conformation, with atom N1 0.636 (2) Å out of the S1/C1/C2/N2/N3 plane. The S1/N1/C2 plane subtends an angle of 46.3 (1)° with the above plane.

A search of the Cambridge Structural Database (Version 5.26, with February and May 2005 updates; Allen, 2002) found no other 1,1-dioxo-1,2,4,6-thiatriazine compounds with the same substitution pattern as (III).

In the crystal structure of (III), adjacent molecules are linked by an N—H···O hydrogen bond to form chains parallel to the *a* direction (Table 1).

The scope of the unusual ring-expansion reaction that produced compound (III) is currently under investigation and will be the subject of a future publication.

Experimental

The thiatriazole dioxide (I) (200 mg, 0.65 mmol), produced by a previously described method (Fallon *et al.*, 2005), was dissolved in dimethylformamide (2 ml) containing anhydrous K_2CO_3 (175 mg, 1.3 mmol). Methyl 2-bromopropanoate (220 mg, 1.3 mmol) was added and the resultant mixture was stirred at room temperature for 6 d. The reaction mixture was diluted with water (10 ml) and diethyl ether (5 ml), stirred briefly and left to stand for 4 h. Clusters of short colourless needles formed at the interface between the aqueous and organic layers. The whole was filtered, and the crystals were washed with diethyl ether and dried (yield 51 mg, 20%). A sample of (III) was recrystallized by slow evaporation of an ethanol solution to give needles suitable for X-ray analysis. Spectroscopic analysis: ^{1}H NMR ($CDCl_3$, 400 MHz, δ, p.p.m.): 7.39 (1H, *s*, *p*-ArH), 7.32 (2H, *s*, *o*-ArH), 5.57 (1H, *s*, NH), 3.85 (3H, *s*, CO_2CH_3), 3.10 (6H, *s*, $N(CH_3)_2$), 1.50 (3H, *s*, CCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz, δ, p.p.m.): 171.3, 153.7, 139.0, 135.0, 129.6, 129.2, 74.7, 53.9, 37.1, 24.9; *m*/*z* (ESI, +ve): 395, 397 (*M*+1); m.p. 486–488 K (decomposition).

Crystal data

$C_{13}H_{16}Cl_2N_4O_4S$	$Z = 2$
$M_r = 395.26$	$D_x = 1.541$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 6.4226$ (1) Å	Cell parameters from 14510 reflections
$b = 9.7869$ (2) Å	$\theta = 3.5$–$28.2°$
$c = 13.9309$ (4) Å	$\mu = 0.53$ mm^{-1}
$\alpha = 81.3584$ (8)°	$T = 123$ (2) K
$\beta = 88.7526$ (9)°	Acicular, colourless
$\gamma = 79.765$ (2)°	0.3 × 0.22 × 0.12 mm
$V = 851.93$ (3) Å^3	

Data collection

Nonius KappaCCD area-detector diffractometer	$R_{int} = 0.029$
Thick-slice ω and φ scans	$\theta_{max} = 28.2°$
14510 measured reflections	$h = -8 \rightarrow 8$
4122 independent reflections	$k = -12 \rightarrow 12$
3598 reflections with $I > 2\sigma(I)$	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 1.1152P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.043$	$(\Delta/\sigma)_{max} = 0.008$
$wR(F^2) = 0.113$	$\Delta\rho_{max} = 0.97$ e Å^{-3}
$S = 1.04$	$\Delta\rho_{min} = -0.71$ e Å^{-3}
4122 reflections	
221 parameters	
H-atom parameters constrained	

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O1^{i}	0.88	2.12	2.964 (2)	162

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

All H atoms were placed in calculated positions, with C—H distances in the range 0.95–0.98 Å and N—H = 0.88 Å. They were included in the refinement in a riding-model approximation, with U_{iso}(H) = 1.2U_{eq} (1.5U_{eq} for methyl H atoms) of the carrier atom.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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