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(4-Bromophenyl)(5-dimethylamino-1,1-dioxo-2-phenyl-1,2-dihydro-1λ^6,2,4,6-thiatriazin-3-yl)-methanone

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Key indicators

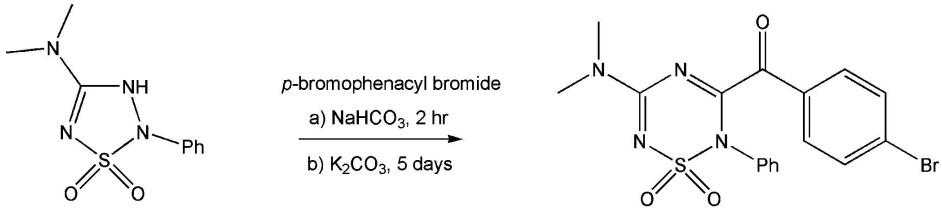
Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.003 Å
R factor = 0.034
wR factor = 0.087
Data-to-parameter ratio = 17.2

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

The title compound, $C_{17}H_{15}BrN_4O_3S$, was formed by base-assisted *N*-alkylation of (1,1-dioxo-2-phenyl-2,3-dihydro-1*H*-1λ^6,2,3,5-thiatriazol-4-yl)dimethylamine with *p*-bromophenacyl bromide, followed by ring expansion and aerial oxidation to form an unusual 5-acyl-substituted 3-amino-1,1-dioxo-1,2,4,6-thiatriazine. The thiatriazine ring adopts an envelope conformation, with the S atom displaced by 0.308 (2) Å from the plane of the other five atoms.

Comment

We have been investigating methods for the preparation of a diverse range of sulfur-containing heterocycles with potential biological activity (Fallon, Jahangiri *et al.*, 2005; Fallon, Francis *et al.*, 2005). We recently reported the structure of a 1,1-dioxo-1,2,4,6-thiatriazine obtained from the 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 (Duggan *et al.*, 2005). We report here the structure of the product obtained from a similar reaction, this time between the thiazole, (I), and *p*-bromophenacyl bromide, using a stepwise addition of $NaHCO_3$ and K_2CO_3. As in the previous example, the lack of contiguous NMR-responsive nuclei in the product meant that an X-ray structural study was necessary to confirm the identity of the product. Crystals suitable for X-ray analysis were formed by crystallization from dichloromethane/ethyl acetate (1:1). X-ray analysis confirmed that the product was the title 1,2,4,6-thiatriazine dioxide, (II).



(I) (II)

The molecular structure of (II) is shown in Fig. 1. The thiatriazine heterocycle adopts an envelope conformation, with atom S1 0.308 (2) Å out of the N2/C2/N3/C1/N1 plane. The N2/S1/N1 plane subtends an angle of 17.5 (1)° with the above plane. This confirms the non-aromatic character of this unsaturated heterocycle and is consistent with that observed in a related 3-methoxy-1,1-dioxo-1,2,4,6-thiatriazine (Hamprecht *et al.*, 1985). The short C2—N4 bond length of 1.328 (3) Å and the coplanarity of the guanidinium-type unit defined by C17/N4/C16/C2/N2/N3 indicate significant conju-

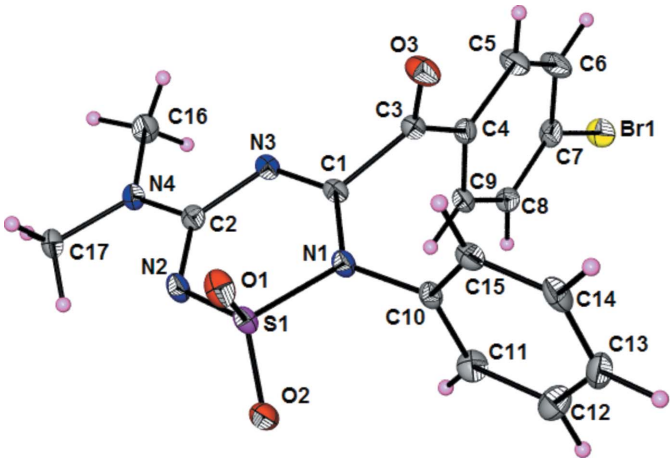


Figure 1
View of the molecular structure of (II) (50% probability displacement ellipsoids) showing the atom numbering scheme.

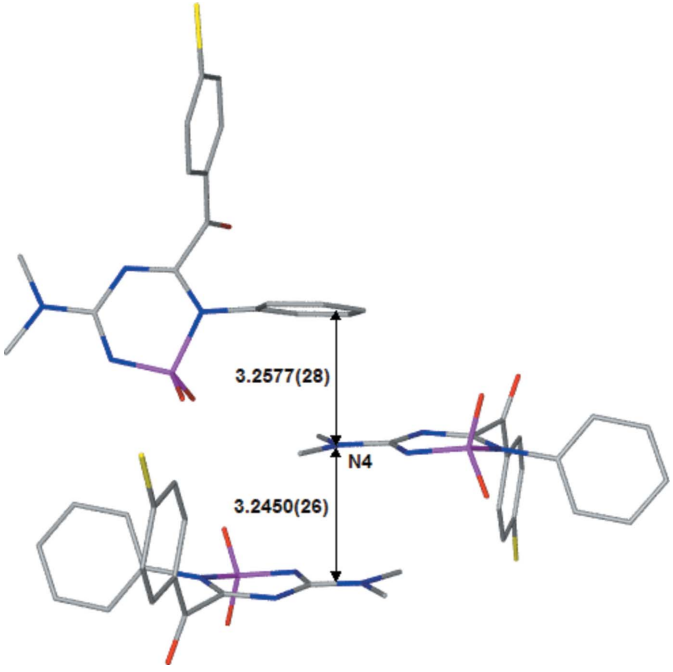


Figure 2
View of the crystal structure of (II) showing π-stacking interactions. H atoms have been omitted.

gation in this region. The shorter S1—N2 bond length of 1.561 (2) Å suggests that this bond is also partially conjugated with the above system. A similar effect is not observed with the S1—N1 bond, presumably because the torsion angle N3—C1—C3—O3 is 95.5 (2)°, thus limiting conjugation. This is also consistent with the unusually long bond length for adjacent Csp^2 atoms of 1.528 (3) Å, seen for the C1—C3 bond.

Interestingly, in the crystal structure of (II), there appears to be intermolecular π stacking occurring between the guanidinium region centred on C2, N4 in another molecule and the non-brominated phenyl ring of a third molecule, as indicated in Fig. 2.

A publication detailing the scope of the uncommon ring-expansion reaction that produced compound (II) is currently in preparation.

Experimental

The title compound was prepared from the phenylthiatriazole dioxide, (I) (100 mg, 0.42 mmol), by an initial 5 min treatment with $NaHCO_3$ (42 mg, 0.50 mmol) in *N*,*N*-dimethylformamide (1 ml) at room temperature, followed by the addition of *p*-bromophenacyl bromide (139 mg, 0.50 mmol) dissolved in *N*,*N*-dimethylformamide (0.5 ml). The mixture was stirred at room temperature for 2 h. K_2CO_3 (71 mg, 0.51 mmol) was then added and stirring was continued for a further 5 d. The reaction mixture was diluted with water (5 ml) and diethyl ether (2 ml), and then extracted with $CHCl_3$ (3×), and the combined organic layers were washed with water (2×), dried ($MgSO_4$), filtered and concentrated to yield the product (102 mg, 56%) as an orange foam. A sample was further purified by radial chromatography using a hexane/ethyl acetate solvent gradient then recrystallized from dichloromethane/ethyl acetate (1:1) to give colourless needles suitable for X-ray analysis. *m*/*z* (APCI, +ve, MeOH:CH_3CN:H_2O 2:1:1) 435, 437 (*M*+1). Analysis, calculated for $C_{17}H_{15}BrN_4O_3S$: C 46.91, H 3.47, N 12.87, S 7.37%; found: C 47.17, H 3.53, N 12.89, S 7.08%. M.p. 427–429 K.

Crystal data

$C_{17}H_{15}BrN_4O_3S$
M_r = 435.3
Monoclinic, $C2/c$
a = 23.4478 (3) Å
b = 10.0971 (2) Å
c = 15.2847 (2) Å
β = 101.518 (1)°
V = 3545.85 (10) Å^3
Z = 8
D_x = 1.631 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 2.46 mm^{-1}
T = 123 (2) K
Block, colourless
0.25 × 0.25 × 0.1 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: empirical (using intensity measurements) (*SORTAV*; Otwinowski & Minor, 1997)
T_{min} = 0.578, T_{max} = 0.791
18424 measured reflections
4071 independent reflections
3411 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 27.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.087
S = 1.05
4071 reflections
237 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.044P)^2 + 4.5742P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.60 e Å^{-3}

H atoms were placed in calculated positions, with C—H distances ranging from 0.95 to 0.98 Å, and included in the refinement in the riding-model approximation with U_{iso}(H) = 1.2U_{eq}(C), or U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms. The highest residual density peak is located 0.93 Å from atom Br1.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO*–SMN (Otwinowski & Minor, 1997); data reduction: *X-SEED* (Barbour, 2001); program(s) used to solve structure:

SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* and *POV-RAY* (Persistence of Vision, 2004); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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