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Trimethoprimium 3,5-dinitrosalicylate

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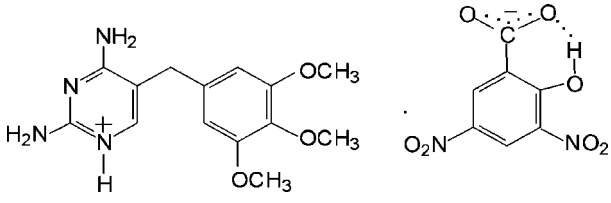
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.015 Å; R factor = 0.064; wR factor = 0.152; data-to-parameter ratio = 6.6.

In the title compound [systematic name: 2,4-diamino-5-(3,4,5-trimethoxybenzyl)pyrimidinium 2-hydroxy-3,5-dinitrobenzoate], $C_{14}H_{19}N_4O_3^+\cdot C_7H_3N_2O_7^-$, the trimethoprimium (TMP) cation is protonated at one of the pyrimidine N atoms. The protonated N atom and the 2-amino group of the TMP cation interact with the carboxylate group of the 3,5-dinitrosalicylate anion through a pair of N—H···O hydrogen bonds. A typical intramolecular O—H···O hydrogen bond is observed in the anion.

Related literature

For related literature, see: Bernstein *et al.* (1995); Hemamalini *et al.* (2005); Hitching *et al.* (1988); Koetzle & Williams (1976); Kuyper (1990); Panneerselvam *et al.* (2002).



Experimental

Crystal data

$C_{14}H_{19}N_4O_3^+\cdot C_7H_3N_2O_7^-$
M_r = 518.45
Orthorhombic, $Pca2_1$
a = 20.928 (3) Å
b = 4.898 (2) Å
c = 22.869 (2) Å
V = 2344.2 (10) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 1.02 mm^{-1}
T = 293 K
0.16 × 0.12 × 0.06 mm

Data collection

Siemens AED single-crystal diffractometer
Absorption correction: none
2244 measured reflections
2244 independent reflections
883 reflections with $I > 2\sigma(I)$
1 standard reflection every 100 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.152
S = 0.92
2244 reflections
338 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O4	0.86	1.90	2.743 (12)	167
N2—H2A···O10^{i}	0.86	2.26	3.101 (12)	166
N2—H2B···O5	0.86	2.10	2.946 (12)	169
N4—H4A···O1^{ii}	0.86	2.23	3.050 (11)	160
N4—H4B···O8^{iii}	0.86	2.59	3.202 (13)	129
O6—H6A···O5	0.82	1.90	2.462 (14)	124
C15—H15A···O3	0.96	2.58	3.093 (16)	114

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

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2509).

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supplementary materials

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Trimethoprimium 3,5-dinitrosalicylate

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Comment

As part of our ongoing studies (Hemamalini *et al.*, 2005) of hydrogen bonding patterns in the molecular salts of protonated trimethoprim [2,4-diamino-5-(3,4,5-trimethoxybenzyl-pyrimidine or TMP], we now report the synthesis and structure of the title compound, (I). [systematic name: 2,4-diamino-5-(3,4,5-trimethoxybenzyl) pyrimidin-1-ium 2-hydroxy-3,5-dinitrobenzoate]. Neutral TMP is a well known antifolate drug and its structure was determined by Koetzle & Williams (1976).

The asymmetric unit of (I) contains a protonated TMP cation and a 3,5-dinitrosalicylate (DNSA) anion (Fig. 1). The trimethoprim molecule is protonated at atom N1 of the pyrimidine moiety, which is evident from the increase in the internal angle at the protonated N1 [C2—N1—C6 = 121.7 (10)°] compared with that at unprotonated atom N3 [C2—N3—C4 = 117.9 (9)°]. The dihedral angle between the pyrimidine and benzene ring planes in (I) is 72.48 (5)°, which falls within the known range of equivalent torsion angles [69.96 (8)–89.5 (2)°] in other TMP structures (Panneerselvam *et al.*, 2002). The conformation of the TMP cation is described by the two torsion angles C4—C5—C7—C8 and C5—C7—C8—C9, which are −176.0 (9)° and 69.9 (13)°, respectively in (I). This TMP conformation plays a very important role in DHFR selectivity (Hitching *et al.*, 1988).

The carboxylate group of the DNSA anion in (I) accepts two N—H···O hydrogen bonds (Table 1) from the cation, forming a fork-like interaction. This can be designated by graph-set notation $R_2^2(8)$ (Bernstein *et al.*, 1995). This common motif has been observed in other DHFR-TMP complexes (Kuyper, 1990) A typical intramolecular hydrogen bond occurs in the anion with graph-set notation S(6) (Fig. 2). The TMP cations self assemble *via* further N—H···O interactions, with the O atom being part of a methoxy or a nitro group. The combination of hydrogen bonds forms a three dimensional network as shown in Fig 3.

Experimental

Hot methanol solutions of trimethoprim (74 mg, obtained as a gift from Shilpa Antibiotics Ltd) and 3,5-dinitrosalicylic acid (57 mg, Merck) were mixed in a 1:1 molar ratio and warmed for half an hour over a water bath. On slow evaporation, yellow prisms of (I) were obtained.

Refinement

All the hydrogen atoms were placed in idealized locations (C—H = 0.96 Å, O—H = 0.82 Å, N—H = 0.86 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(carrier) or 1.5U_{eq}(methyl carrier).

Figures

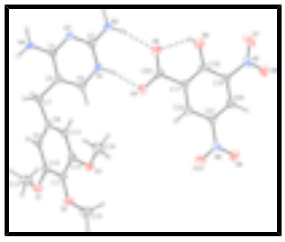

Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids for the non-hydrogen atoms.

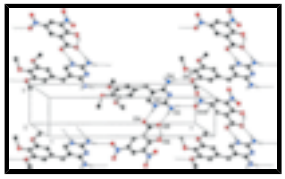

Fig. 2. Hydrogen bonding interactions of the title compound (I), (hydrogen atoms are omitted for clarity). Symmetry codes: (i) *x* + 1/2,-*y*,*z*; (ii) *x* + 1/2,-*y* + 2,*z*.

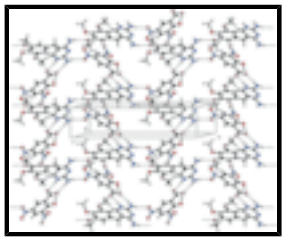

Fig. 3. Packing of the title compound (I).

2,4-diamino-5-(3,4,5-trimethoxybenzyl)pyrimidinium 2-hydroxy-3,5-dinitrobenzoate

Crystal data

$C_{14}H_{19}N_4O_3^+ \cdot C_7H_3N_2O_7^-$	F_{000} = 1080
M_r = 518.45	D_x = 1.469 Mg m^{-3}
Orthorhombic, *Pca*2$_1$	Cu *K*α radiation λ = 1.54178 Å
Hall symbol: P 2c -2ac	Cell parameters from 26 reflections
a = 20.928 (3) Å	θ = 4.7–70.2º
b = 4.898 (2) Å	μ = 1.02 mm^{-1}
c = 22.869 (2) Å	*T* = 293 K
V = 2344.2 (10) Å^3	Prism, light yellow
Z = 4	0.16 × 0.12 × 0.06 mm

Data collection

Siemens AED single-crystal diffractometer	R_{int} =
Radiation source: fine- focus sealed tube	θ_{max} = 70.2º
Monochromator: graphite	θ_{min} = 4.7º
T = 293 K	*h* = −25→0
ω–2θ scans	*k* = −5→0
Absorption correction: none	*l* = 0→27
2244 measured reflections	1 standard reflections

2244 independent reflections
883 reflections with $I > 2\sigma(I)$
every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.152$
$S = 0.92$
2244 reflections
338 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}
Extinction correction: ?
Extinction coefficient: ?

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All e.s.d.'s are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The observed criterion of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating –*R*-factor-obs *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.4839 (3)	0.9192 (16)	−0.0266 (3)	0.057 (3)
O2	0.4526 (3)	0.6666 (16)	−0.1250 (4)	0.058 (3)
O3	0.5418 (3)	0.474 (2)	−0.1986 (4)	0.067 (3)
N1	0.7512 (4)	0.4715 (19)	0.0459 (4)	0.046 (3)
N2	0.8415 (4)	0.420 (2)	0.1010 (4)	0.059 (4)
N3	0.8398 (4)	0.7382 (18)	0.0286 (4)	0.043 (3)
N4	0.8399 (4)	1.0501 (19)	−0.0461 (4)	0.046 (3)
C2	0.8108 (4)	0.546 (3)	0.0580 (5)	0.045 (4)
C4	0.8083 (5)	0.854 (2)	−0.0162 (5)	0.037 (3)
C5	0.7455 (4)	0.7855 (19)	−0.0311 (5)	0.040 (4)
C6	0.7175 (5)	0.590 (2)	0.0023 (5)	0.039 (4)
C7	0.7130 (5)	0.917 (2)	−0.0841 (5)	0.046 (4)
C8	0.6439 (5)	0.834 (2)	−0.0912 (5)	0.045 (4)
C9	0.5960 (5)	0.919 (2)	−0.0531 (5)	0.049 (4)
C10	0.5337 (5)	0.849 (2)	−0.0627 (5)	0.041 (4)

C11	0.5154 (5)	0.708 (2)	−0.1126 (5)	0.041 (3)
C12	0.5628 (5)	0.616 (2)	−0.1511 (5)	0.048 (4)
C13	0.6270 (4)	0.683 (2)	−0.1406 (5)	0.045 (4)
C14	0.4999 (7)	1.075 (4)	0.0227 (6)	0.109 (8)
C15	0.4282 (6)	0.397 (3)	−0.1137 (7)	0.084 (6)
C16	0.5889 (7)	0.331 (3)	−0.2285 (6)	0.084 (6)
O4	0.6798 (4)	0.0705 (17)	0.0983 (3)	0.060 (3)
O5	0.7609 (4)	0.0101 (16)	0.1597 (4)	0.066 (3)
O6	0.7550 (4)	−0.337 (2)	0.2374 (5)	0.077 (4)
O7	0.7225 (5)	−0.608 (2)	0.3338 (4)	0.099 (4)
O8	0.6653 (4)	−0.961 (2)	0.3140 (4)	0.081 (4)
O9	0.4875 (4)	−0.821 (2)	0.1826 (4)	0.094 (4)
O10	0.4860 (4)	−0.473 (2)	0.1288 (4)	0.077 (4)
N5	0.6863 (5)	−0.730 (2)	0.3025 (5)	0.058 (4)
N6	0.5133 (5)	−0.621 (2)	0.1634 (4)	0.056 (3)
C17	0.6689 (4)	−0.266 (2)	0.1725 (4)	0.035 (3)
C18	0.6985 (5)	−0.400 (2)	0.2211 (5)	0.047 (4)
C19	0.6609 (5)	−0.602 (2)	0.2491 (4)	0.040 (4)
C20	0.6015 (5)	−0.662 (2)	0.2316 (4)	0.044 (4)
C21	0.5760 (5)	−0.542 (2)	0.1837 (5)	0.041 (3)
C22	0.6100 (5)	−0.337 (2)	0.1543 (5)	0.047 (4)
C23	0.7064 (5)	−0.043 (2)	0.1412 (6)	0.048 (4)
H1	0.73350	0.34510	0.06640	0.0560*
H2A	0.88020	0.46450	0.10930	0.0710*
H2B	0.82280	0.29290	0.12060	0.0710*
H4A	0.87810	1.09470	−0.03600	0.0550*
H4B	0.82180	1.13030	−0.07510	0.0550*
H6	0.67550	0.53700	−0.00490	0.0470*
H7A	0.71530	1.11400	−0.08020	0.0550*
H7B	0.73630	0.86670	−0.11910	0.0550*
H9	0.60650	1.02530	−0.02070	0.0580*
H13	0.65840	0.62720	−0.16680	0.0540*
H14A	0.53340	0.98490	0.04390	0.1630*
H14B	0.46310	1.09380	0.04730	0.1630*
H14C	0.51420	1.25200	0.01050	0.1630*
H15A	0.45520	0.26450	−0.13210	0.1250*
H15B	0.38570	0.38250	−0.12910	0.1250*
H15C	0.42740	0.36540	−0.07230	0.1250*
H16A	0.61990	0.45630	−0.24380	0.1260*
H16B	0.56980	0.23040	−0.26000	0.1260*
H16C	0.60960	0.20610	−0.20220	0.1260*
H6A	0.76040	−0.17190	0.23330	0.1160*
H20	0.57740	−0.78830	0.25250	0.0530*
H22	0.59190	−0.25010	0.12220	0.0570*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}

O1	0.035 (4)	0.076 (6)	0.060 (5)	0.002 (4)	0.000 (4)	0.000 (5)
O2	0.040 (4)	0.055 (5)	0.079 (6)	−0.004 (4)	−0.017 (4)	0.006 (5)
O3	0.049 (4)	0.093 (7)	0.058 (6)	0.000 (5)	−0.014 (4)	−0.010 (6)
N1	0.044 (5)	0.037 (5)	0.058 (6)	−0.002 (5)	0.008 (4)	0.007 (5)
N2	0.040 (4)	0.074 (7)	0.064 (7)	−0.009 (5)	−0.009 (5)	0.024 (7)
N3	0.033 (4)	0.042 (6)	0.054 (6)	−0.005 (5)	0.005 (4)	0.002 (5)
N4	0.028 (4)	0.060 (7)	0.050 (6)	−0.003 (5)	0.002 (4)	0.009 (6)
C2	0.018 (5)	0.075 (9)	0.043 (6)	0.009 (6)	0.007 (5)	0.004 (7)
C4	0.029 (5)	0.040 (7)	0.041 (6)	0.008 (5)	−0.004 (5)	−0.003 (6)
C5	0.030 (5)	0.027 (6)	0.062 (8)	0.000 (5)	0.011 (5)	−0.005 (6)
C6	0.032 (5)	0.033 (7)	0.052 (7)	0.004 (5)	−0.005 (5)	0.003 (6)
C7	0.046 (6)	0.044 (7)	0.049 (7)	0.003 (6)	−0.012 (5)	0.008 (6)
C8	0.042 (6)	0.038 (7)	0.054 (7)	−0.010 (5)	0.015 (5)	0.011 (6)
C9	0.038 (6)	0.060 (8)	0.048 (7)	0.008 (6)	0.004 (5)	0.015 (7)
C10	0.041 (6)	0.037 (6)	0.046 (7)	0.003 (5)	0.002 (5)	0.008 (6)
C11	0.038 (5)	0.032 (6)	0.054 (7)	−0.003 (5)	−0.016 (6)	0.004 (6)
C12	0.054 (6)	0.052 (7)	0.039 (6)	−0.001 (6)	−0.010 (6)	0.005 (7)
C13	0.033 (5)	0.060 (8)	0.042 (7)	−0.005 (6)	−0.008 (5)	0.017 (6)
C14	0.077 (10)	0.186 (19)	0.064 (9)	0.046 (12)	0.004 (8)	−0.006 (12)
C15	0.063 (7)	0.059 (9)	0.129 (14)	−0.017 (7)	−0.024 (9)	0.032 (10)
C16	0.092 (11)	0.065 (10)	0.095 (11)	−0.016 (9)	−0.037 (9)	−0.018 (9)
O4	0.071 (5)	0.061 (6)	0.048 (5)	−0.008 (5)	0.005 (4)	0.016 (5)
O5	0.053 (5)	0.064 (6)	0.082 (7)	−0.003 (5)	0.018 (5)	0.003 (6)
O6	0.058 (6)	0.085 (7)	0.089 (7)	−0.005 (5)	−0.007 (5)	0.017 (7)
O7	0.151 (9)	0.083 (7)	0.063 (7)	−0.012 (7)	−0.050 (7)	0.009 (6)
O8	0.091 (7)	0.067 (7)	0.085 (7)	−0.009 (6)	0.002 (5)	0.023 (6)
O9	0.079 (6)	0.099 (7)	0.103 (8)	−0.035 (6)	−0.013 (6)	0.044 (7)
O10	0.072 (6)	0.080 (7)	0.078 (7)	−0.017 (6)	−0.028 (5)	0.009 (6)
N5	0.077 (7)	0.055 (7)	0.043 (6)	0.008 (6)	−0.006 (6)	0.008 (6)
N6	0.053 (5)	0.067 (7)	0.047 (6)	−0.006 (6)	0.000 (5)	0.011 (6)
C17	0.038 (5)	0.037 (7)	0.030 (6)	0.013 (5)	0.005 (5)	−0.005 (5)
C18	0.034 (6)	0.050 (8)	0.058 (8)	0.002 (6)	−0.003 (5)	−0.007 (7)
C19	0.045 (6)	0.047 (7)	0.029 (6)	−0.004 (6)	−0.006 (5)	0.012 (6)
C20	0.046 (6)	0.049 (7)	0.038 (6)	0.005 (6)	0.002 (5)	−0.001 (6)
C21	0.042 (5)	0.038 (7)	0.042 (6)	−0.004 (5)	−0.010 (5)	−0.006 (6)
C22	0.058 (7)	0.041 (7)	0.042 (7)	0.009 (6)	0.009 (6)	−0.003 (6)
C23	0.039 (6)	0.031 (7)	0.073 (9)	−0.015 (5)	0.019 (6)	−0.015 (7)

Geometric parameters (Å, °)

O1—C10	1.373 (13)	C7—C8	1.511 (15)
O1—C14	1.402 (17)	C8—C13	1.396 (15)
O2—C11	1.360 (12)	C8—C9	1.392 (15)
O2—C15	1.439 (16)	C9—C10	1.366 (15)
O3—C12	1.363 (14)	C10—C11	1.388 (16)
O3—C16	1.389 (17)	C11—C12	1.401 (15)
O4—C23	1.258 (15)	C12—C13	1.404 (14)
O5—C23	1.244 (14)	C6—H6	0.9312
O6—C18	1.278 (14)	C7—H7B	0.9691

O7—N5	1.201 (15)	C7—H7A	0.9702
O8—N5	1.242 (14)	C9—H9	0.9319
O9—N6	1.202 (14)	C13—H13	0.9303
O10—N6	1.216 (13)	C14—H14C	0.9586
O6—H6A	0.8219	C14—H14A	0.9599
N1—C6	1.352 (14)	C14—H14B	0.9582
N1—C2	1.329 (13)	C15—H15C	0.9595
N2—C2	1.327 (15)	C15—H15A	0.9579
N3—C4	1.344 (14)	C15—H15B	0.9593
N3—C2	1.306 (15)	C16—H16A	0.9592
N4—C4	1.352 (14)	C16—H16B	0.9600
N1—H1	0.8604	C16—H16C	0.9611
N2—H2B	0.8612	C17—C22	1.347 (14)
N2—H2A	0.8599	C17—C23	1.524 (14)
N4—H4A	0.8603	C17—C18	1.432 (14)
N4—H4B	0.8589	C18—C19	1.417 (14)
N5—C19	1.472 (15)	C19—C20	1.339 (15)
N6—C21	1.445 (15)	C20—C21	1.353 (15)
C4—C5	1.399 (14)	C21—C22	1.402 (15)
C5—C6	1.358 (14)	C20—H20	0.9303
C5—C7	1.532 (15)	C22—H22	0.9293
C10—O1—C14	116.0 (9)	C8—C7—H7A	108.96
C11—O2—C15	116.3 (9)	C5—C7—H7A	108.87
C12—O3—C16	114.9 (9)	C5—C7—H7B	108.86
C18—O6—H6A	109.37	H7A—C7—H7B	107.69
C2—N1—C6	121.7 (10)	C10—C9—H9	119.55
C2—N3—C4	117.9 (9)	C8—C9—H9	119.67
C6—N1—H1	119.08	C8—C13—H13	119.86
C2—N1—H1	119.23	C12—C13—H13	119.82
C2—N2—H2A	120.11	O1—C14—H14C	109.44
H2A—N2—H2B	119.76	O1—C14—H14B	109.42
C2—N2—H2B	120.13	H14A—C14—H14C	109.56
C4—N4—H4A	119.95	O1—C14—H14A	109.29
H4A—N4—H4B	120.07	H14A—C14—H14B	109.55
C4—N4—H4B	119.99	H14B—C14—H14C	109.57
O7—N5—C19	120.7 (10)	H15A—C15—H15B	109.60
O7—N5—O8	123.4 (11)	O2—C15—H15A	109.48
O8—N5—C19	115.8 (10)	O2—C15—H15B	109.33
O9—N6—O10	120.8 (10)	O2—C15—H15C	109.35
O10—N6—C21	118.4 (9)	H15B—C15—H15C	109.52
O9—N6—C21	120.6 (9)	H15A—C15—H15C	109.54
N1—C2—N2	118.8 (11)	H16B—C16—H16C	109.30
N2—C2—N3	119.4 (9)	O3—C16—H16B	109.43
N1—C2—N3	121.8 (10)	O3—C16—H16C	109.44
N3—C4—C5	123.1 (10)	H16A—C16—H16B	109.65
N3—C4—N4	116.5 (9)	H16A—C16—H16C	109.31
N4—C4—C5	120.5 (10)	O3—C16—H16A	109.69
C6—C5—C7	123.4 (9)	C18—C17—C22	121.2 (9)
C4—C5—C6	116.0 (10)	C18—C17—C23	118.1 (8)

C4—C5—C7	120.6 (9)	C22—C17—C23	120.8 (9)
N1—C6—C5	119.5 (9)	O6—C18—C19	123.4 (10)
C5—C7—C8	113.4 (9)	C17—C18—C19	115.5 (9)
C7—C8—C13	118.2 (9)	O6—C18—C17	121.1 (10)
C7—C8—C9	122.8 (10)	N5—C19—C18	118.1 (9)
C9—C8—C13	118.9 (9)	C18—C19—C20	122.3 (9)
C8—C9—C10	120.8 (10)	N5—C19—C20	119.3 (9)
O1—C10—C11	114.2 (9)	C19—C20—C21	120.9 (9)
C9—C10—C11	121.4 (10)	N6—C21—C22	119.9 (10)
O1—C10—C9	124.4 (10)	C20—C21—C22	119.9 (10)
O2—C11—C12	120.4 (10)	N6—C21—C20	120.1 (9)
C10—C11—C12	118.8 (10)	C17—C22—C21	120.1 (10)
O2—C11—C10	120.8 (10)	O4—C23—C17	117.1 (9)
C11—C12—C13	119.7 (10)	O5—C23—C17	117.5 (10)
O3—C12—C11	115.9 (9)	O4—C23—O5	125.4 (10)
O3—C12—C13	124.4 (10)	C19—C20—H20	119.73
C8—C13—C12	120.3 (9)	C21—C20—H20	119.41
C5—C6—H6	120.30	C17—C22—H22	119.93
N1—C6—H6	120.20	C21—C22—H22	119.99
C8—C7—H7B	108.93		
C14—O1—C10—C9	0.5 (16)	C9—C8—C13—C12	−0.7 (15)
C14—O1—C10—C11	−176.6 (11)	C8—C9—C10—C11	−4.6 (16)
C15—O2—C11—C12	78.5 (14)	C8—C9—C10—O1	178.5 (10)
C15—O2—C11—C10	−103.5 (12)	O1—C10—C11—C12	−177.2 (9)
C16—O3—C12—C13	17.4 (16)	C9—C10—C11—C12	5.6 (15)
C16—O3—C12—C11	−165.6 (10)	O1—C10—C11—O2	4.8 (14)
C6—N1—C2—N3	0.3 (18)	C9—C10—C11—O2	−172.4 (10)
C6—N1—C2—N2	−179.4 (10)	O2—C11—C12—C13	173.9 (9)
C2—N1—C6—C5	1.7 (16)	C10—C11—C12—C13	−4.1 (15)
C2—N3—C4—C5	2.5 (16)	O2—C11—C12—O3	−3.3 (15)
C2—N3—C4—N4	−179.3 (10)	C10—C11—C12—O3	178.7 (9)
C4—N3—C2—N2	177.3 (10)	C11—C12—C13—C8	1.8 (15)
C4—N3—C2—N1	−2.3 (17)	O3—C12—C13—C8	178.7 (10)
O8—N5—C19—C18	−155.6 (10)	C23—C17—C18—O6	−0.8 (15)
O8—N5—C19—C20	30.1 (14)	C23—C17—C18—C19	178.9 (9)
O7—N5—C19—C20	−146.2 (11)	C18—C17—C22—C21	1.2 (15)
O7—N5—C19—C18	28.1 (15)	C23—C17—C22—C21	−179.8 (10)
O10—N6—C21—C22	−14.5 (15)	C18—C17—C23—O4	179.4 (10)
O10—N6—C21—C20	164.4 (10)	C22—C17—C18—O6	178.3 (10)
O9—N6—C21—C22	169.3 (10)	C22—C17—C18—C19	−2.0 (14)
O9—N6—C21—C20	−11.9 (16)	C22—C17—C23—O5	−179.0 (10)
N3—C4—C5—C7	−177.7 (9)	C22—C17—C23—O4	0.3 (15)
N4—C4—C5—C6	−178.7 (10)	C18—C17—C23—O5	0.1 (15)
N4—C4—C5—C7	4.2 (15)	O6—C18—C19—C20	179.2 (11)
N3—C4—C5—C6	−0.6 (15)	O6—C18—C19—N5	5.0 (16)
C4—C5—C6—N1	−1.4 (15)	C17—C18—C19—N5	−174.7 (9)
C6—C5—C7—C8	7.2 (14)	C17—C18—C19—C20	−0.5 (15)
C4—C5—C7—C8	−176.0 (9)	N5—C19—C20—C21	178.1 (9)
C7—C5—C6—N1	175.5 (9)	C18—C19—C20—C21	4.0 (16)

C5—C7—C8—C13	−115.1 (11)	C19—C20—C21—C22	−4.9 (16)
C5—C7—C8—C9	69.9 (13)	C19—C20—C21—N6	176.3 (9)
C7—C8—C13—C12	−175.9 (9)	N6—C21—C22—C17	−178.9 (10)
C13—C8—C9—C10	2.1 (15)	C20—C21—C22—C17	2.3 (16)
C7—C8—C9—C10	177.0 (10)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O4	0.86	1.90	2.743 (12)	167
N2—H2A···O10^{i}	0.86	2.26	3.101 (12)	166
N2—H2B···O5	0.86	2.10	2.946 (12)	169
N4—H4A···O1^{ii}	0.86	2.23	3.050 (11)	160
N4—H4B···O8^{iii}	0.86	2.59	3.202 (13)	129
O6—H6A···O5	0.82	1.90	2.462 (14)	124
C15—H15A···O3	0.96	2.58	3.093 (16)	114

Symmetry codes: (i) *x*+1/2, −*y*, *z*; (ii) *x*+1/2, −*y*+2, *z*; (iii) −*x*+3/2, *y*+2, *z*−1/2.

Fig. 1

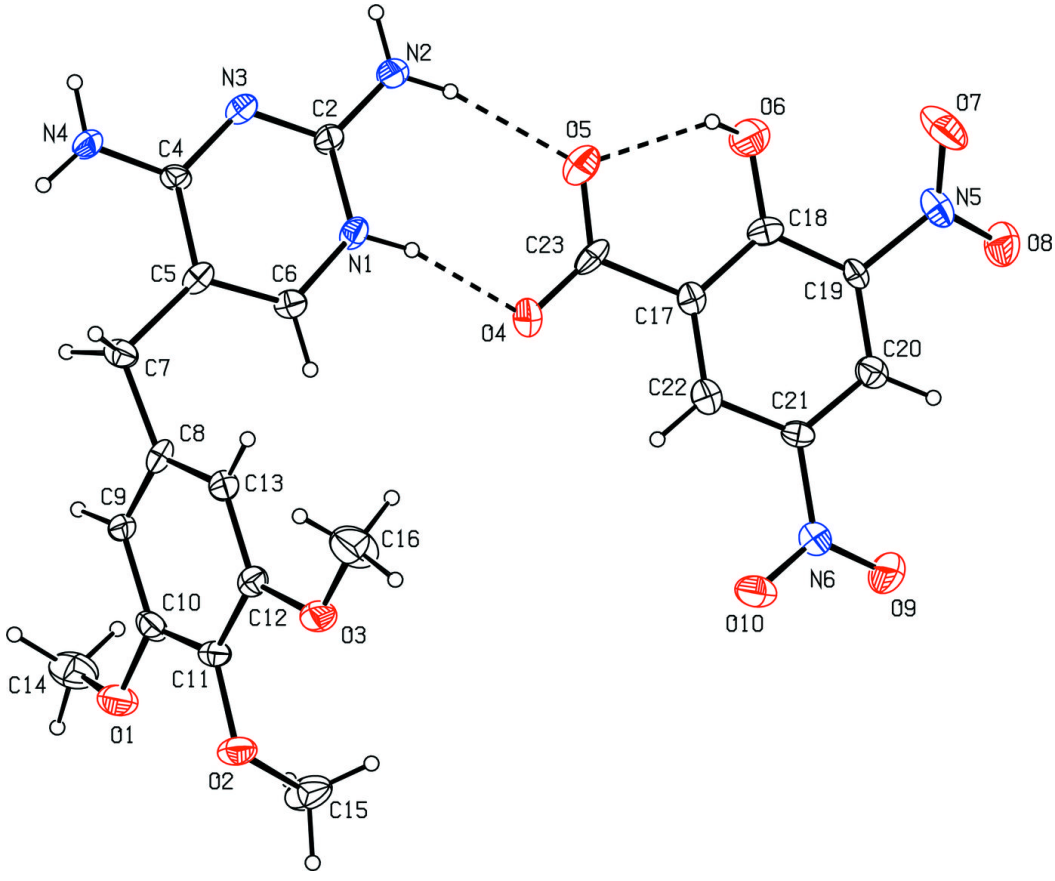
N2
N3
C2
O6
O7
N4
C4
O5
N5
C18
O8
C23
C5
C6
N1
C19
C17
O4
C20
C7
C22
C21
C8
C13
C9
C16
N6
C10
C12
O3
O10
O9
C14
C11
O1
O2
C15

Fig. 2

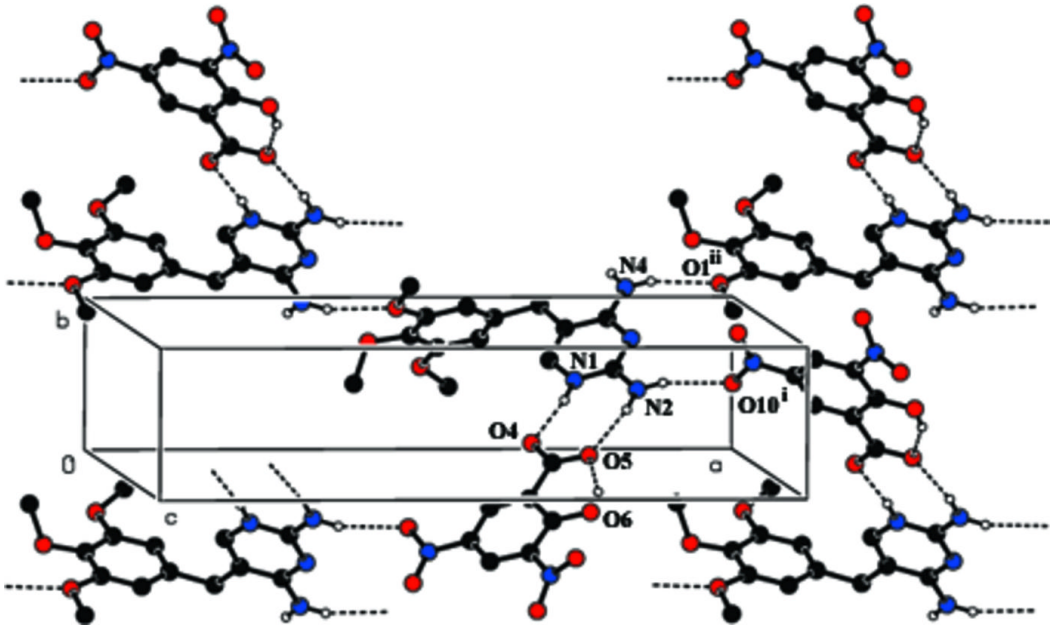

Fig. 3