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3,5-Dimethyl-6-(4-nitroanilino)-2,3,4,5-tetrahydro-1,3,5-triazine-2,4-dione, (II), 3,5-dimethyl-6-(*N*-methyl-4-nitroanilino)-2,3,4,5-tetrahydro-1,3,5-triazine-2,4-dione, (III), and 1,3,5-trimethyl-6-(4-nitrophenylimino)-1,3,5-triazinane-2,4-dione, (IV)

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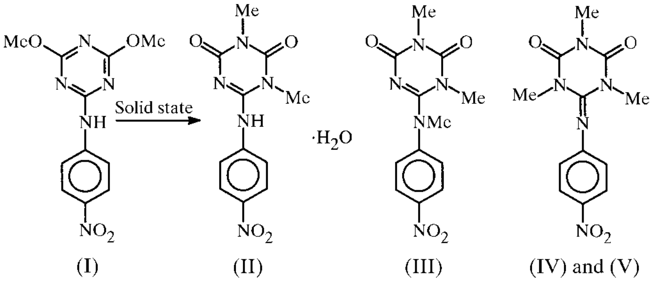
Methyl rearrangement in the solid state of 2,4-dimethoxy-6-(4-nitroanilino)-1,3,5-triazine reveals three different products: (II), $C_{11}H_{11}N_5O_4{\cdot}H_2O$, (III), $C_{12}H_{13}N_5O_4$, and (IV), $C_{12}H_{13}N_5O_4$. (II) crystallizes with a molecule of water and (IV) crystallizes in two polymorphic forms. The conformation of the molecules is expressed by the torsion about the bond joining the triazine and the aniline moieties. The two moieties are almost coplanar in (II) due to an intramolecular hydrogen bond between a triazine-N atom and a phenyl-H atom. The methyl groups of the triazine exert severe steric repulsion in the other two compounds, affecting not only the conformation but also the exocyclic bond angles.

Comment

Methoxy-*s*-triazines and their thio-analogues tend to undergo methyl rearrangement either in the liquid or solid state (Paolini *et al.*, 1968; Tosato, 1982, 1984; Kaftory & Handelsman-Benory, 1994; Handelsman-Benory *et al.*, 1995, 2000; Greenberg *et al.*, 1999). In the course of a study on the alkyl rearrangement of four derivatives of 6-anilino-2,4-dialkoxy-1,3,5-triazines, it was found that while three of the compounds undergo rearrangement in the liquid state, the fourth, (I), undergoes methyl rearrangement in the solid state (see scheme). The crystal structures and the thermal behaviour of these compounds are described elsewhere (Taycher *et al.*, 2000). Based on the crystal structure of 2,4-dimethoxy-6-(4-nitroanilino)-1,3,5-triazine, it was concluded that the rearrangement is not topochemically controlled. As a result of the rearrangement, a mixture of products is produced, of which three were analyzed by ^{1}H NMR and by single-crystal structure determination. One of the products, (II), crystallizes with a molecule of water, which is hydrogen-bonded to the amino-H atom. A second product, (IV), crystallizes in two polymorphic forms. The crystal structures of all four compounds, (II)–(V), are shown in Figs. 1–4.



A comparison of bond lengths and angles of the *s*-triazine moiety is given in Table 1. Some differences of bond angles should be noted. The endocyclic bond angles at the C atoms (C1, C2, C3) in the two polymorphs [(IV) and (V)] are significantly smaller than the endocyclic bond angles at the N atoms (N1, N2, N3); 114.8 (2)–116.9 (2)° compared with 123.1 (2)–124.7 (2)°. In compounds (II) and (III), however, only the N1—C3—N3 bond angle is significantly smaller [115.6 (3), 115.5 (2)°]. Similar differences between the endocyclic bond angles are found in all *s*-triazine moieties whenever the carbonyl-C atom is bonded to two N—CH_3 groups (Greenberg *et al.*, 2000; Thalladi *et al.*, 1998; Handelsman-Benory *et al.*, 1995).

Selected intermolecular hydrogen-bond geometries are given in Tables 2–5. Weak C—H···O and C—H···N hydrogen bonds have only a little effect on the conformation of the molecules, but they determine the packing of molecules in the unit cell of each of the compounds. The intramolecular hydrogen bond in (II), N2···H5 [2.32 (4) Å], forces the triazine and the aniline moieties to be almost coplanar [the C2—N4—C4—C5 torsion angle is 21.5 (8)°]. The molecules pack in layers where the water molecules, through hydrogen bonds,

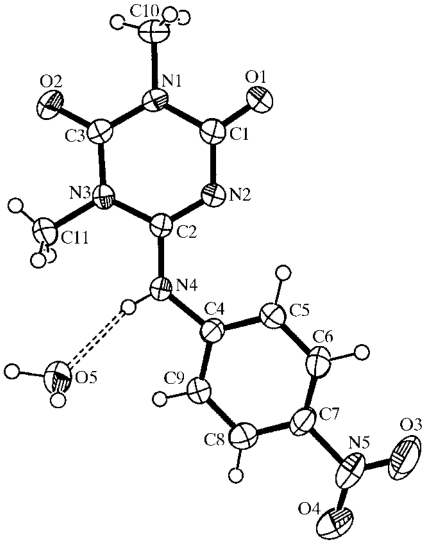


Figure 1
*ORTEP*3 (Farrugia, 1998) drawing of (II) showing the atomic numbering. Ellipsoids of atomic displacement for non-H atoms are drawn at the 50% probability level. H atoms are drawn as small circles of arbitrary radii.

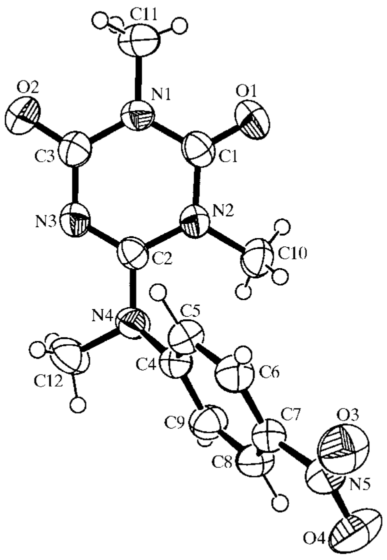


Figure 2
*ORTEP*3 (Farrugia, 1998) drawing of (III) showing the atomic numbering. Ellipsoids are drawn as in Fig. 1.

form the glue between neighbouring molecules in the layer.

A severe steric effect determines the conformation of the torsion angles N2—C2—N4—C4 and C2—N4—C4—C5 and the external ring bond angles at C2. The only difference between compounds (II) and (III) is the substituent on N4, an H atom and a methyl group, respectively. The presence of the smaller H atom is not followed by a rotation of the aniline moiety about C2—N4, thus the torsion angle is only −1.8 (8)°, with the torsion angle about the N4—C4 bond at 21.5 (8)°. This conformation is also stabilized by the hydrogen bond discussed above. Replacing the H atom by a CH_3 group causes an increase of the rotation of the aniline moiety, thus the torsion angle about the C2—N4 bond increases to −131.2 (2)°, and the torsion about the N4—C4 bond increases to 36.0 (3)°. As a result, the two moieties are perpendicular to each other and the close proximity of the two methyl groups C11 and C12 is avoided.

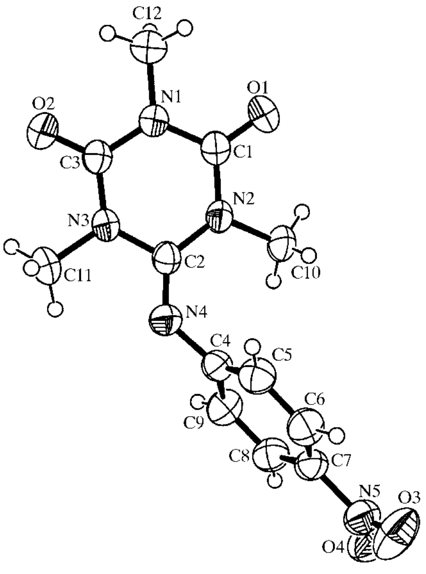


Figure 3
*ORTEP*3 (Farrugia, 1998) drawing of (IV) showing the atomic numbering. Ellipsoids are drawn as in Fig. 1.

One of the two degrees of freedom available in (II) and (III) to overcome steric repulsion is lost in (IV) due to the replacement of the single with a double bond (C2=N4). Partial relief of the steric repulsion is achieved by rotation of the phenyl ring about the N4—C4 bond [71.1 (2) and −64.7 (2)° in polymorphs (IV) and (V), respectively], and also by a small rotation about the double bond [8.5 (2) and −18.3 (2)° in (IV) and (V), respectively] which indicates that there is some π-delocalization along the chain joining the triazine to the phenyl. Moreover, the N2—C2—N4 bond angle opens up to 128.5 (2)° and the N3—C2—N4 bond angle closes to 116.6 (2)° in both polymorphs. Similar differences between the exocyclic bond angles are found to a lesser extent (124.8 and 118.2°) in *N*-methylthio-*N*′-(2,6-dimethylphenyl)-2,6-dimethyl-1,4-quinonediimine (Klerks *et al.*, 1981) and to a higher extent (134.1 and 113.9°) when the N—CH_3 is replaced by N—C—$(CH_3)_2$ (Al-Talib *et al.*, 1985).

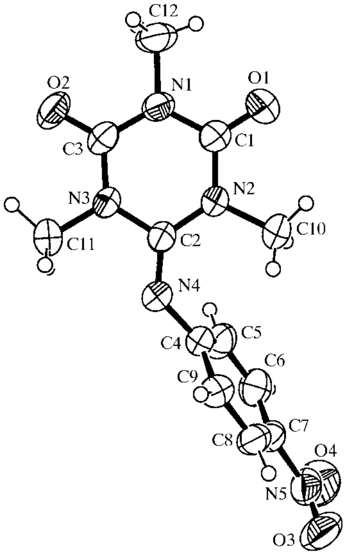


Figure 4
*ORTEP*3 (Farrugia, 1998) drawing of (V) showing the atomic numbering. Ellipsoids are drawn as in Fig. 1.

Experimental

The title compounds were obtained by heating 2,4-dimethoxy-6-(4-nitroanilino)-1,3,5-triazine to 493 K. Crystals of (II) and (IV) were obtained from MeOH solution, crystals of (III) from $CHCl_3$ solution and crystals of (V) from MeOH/EtOH solution.

Compound (II)

Crystal data

$C_{11}H_{11}N_5O_4{\cdot}H_2O$
$M_r = 295.26$
Orthorhombic, $P2_12_12_1$
$a = 18.170$ (4) Å
$b = 10.530$ (3) Å
$c = 6.972$ (2) Å
$V = 1334.0$ (6) Å^3
$Z = 4$
$D_x = 1.470$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 3.2$–19.7°
$\mu = 0.118$ mm^{-1}
$T = 293$ (2) K
Prism, pale yellow
0.80 × 0.50 × 0.40 mm

Data collection

Philips PW1100 diffractometer
$\omega/2\theta$ scans
1339 measured reflections
1339 independent reflections
1152 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 25.00°$
$h = 0 \rightarrow 21$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 8$
3 standard reflections
every 120 min reflections
intensity decay: 2.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.130$
$S = 1.194$
1339 reflections
205 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0499P)^2 + 0.9787P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.030$
$\Delta\rho_{\max} = 0.203$ e Å^{-3}
$\Delta\rho_{\min} = -0.197$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.024 (3)

Table 1
Comparison of bond lengths and bond angles (Å, °) of the *s*-triazine moiety.

	(II)	(III)	(IV)	(V)
O1—C1	1.223 (5)	1.213 (3)	1.221 (2)	1.209 (3)
O2—C3	1.212 (5)	1.209 (3)	1.221 (2)	1.215 (2)
N1—C3	1.365 (5)	1.364 (3)	1.384 (3)	1.373 (3)
N1—C1	1.404 (5)	1.399 (3)	1.393 (3)	1.377 (3)
N2—C2	1.300 (5)	1.304 (3)	1.401 (2)	1.381 (3)
N2—C1	1.351 (5)	1.362 (3)	1.395 (3)	1.381 (3)
N3—C2	1.377 (5)	1.375 (3)	1.409 (3)	1.396 (3)
N3—C3	1.391 (5)	1.395 (3)	1.388 (3)	1.371 (3)
N4—C2	1.355 (5)	1.364 (3)	1.274 (3)	1.265 (3)
N4—C4	1.416 (5)	1.435 (3)	1.406 (3)	1.396 (3)
C3—N1—C1	122.9 (3)	123.1 (2)	124.02 (17)	123.22 (18)
C2—N2—C1	119.5 (4)	119.5 (2)	123.14 (16)	123.78 (18)
C2—N3—C3	119.6 (3)	120.0 (2)	124.68 (16)	124.47 (18)
N2—C1—N1	118.4 (4)	118.4 (2)	116.51 (17)	116.87 (19)
N2—C2—N3	123.8 (3)	123.2 (2)	114.84 (16)	114.79 (18)
N1—C3—N3	115.6 (3)	115.5 (2)	115.50 (16)	116.37 (17)
C2—N4—C4	128.2 (4)	118.8 (2)	130.02 (18)	130.05 (19)
N2—C2—N4	120.4 (4)	119.5 (2)	128.54 (18)	128.53 (19)
N4—C2—N3	115.8 (4)	117.2 (2)	116.58 (17)	116.64 (18)

Table 2
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N4—H1N4···O5	0.81 (5)	2.16 (5)	2.933 (5)	162 (5)
O5—H2O5···O2^{i}	0.92 (11)	1.96 (11)	2.867 (5)	166 (10)
O5—H1O5···O1^{ii}	0.83 (6)	2.18 (6)	2.895 (6)	145 (5)
O9—H9···O5	0.93 (5)	2.55 (5)	3.175 (6)	125 (4)
C5—H5···N2	0.93 (5)	2.32 (4)	2.874 (5)	117 (4)
C6—H6···O4^{iii}	0.93 (5)	2.45 (5)	3.333 (6)	158 (4)
C8—H8···O1^{iv}	0.93 (5)	2.52 (5)	3.438 (6)	169 (4)

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

Compound (III)

Crystal data

$C_{12}H_{13}N_5O_4$
$M_r = 291.27$
Monoclinic, $P2_1/c$
$a = 11.3330$ (12) Å
$b = 16.0250$ (14) Å
$c = 7.1620$ (7) Å
$\beta = 95.587$ (5)°
$V = 1294.5$ (2) Å^3
$Z = 4$
$D_x = 1.495$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 15151 reflections
$\theta = 2.21$–$27.50°$
$\mu = 0.116$ mm^{-1}
$T = 293$ (2) K
Prism, pale yellow
0.40 × 0.18 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
φ scans
16754 measured reflections
2776 independent reflections
1216 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.115$
$\theta_{\max} = 27.58°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 20$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.141$
$S = 0.734$
2776 reflections
243 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0927P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.187$ e Å^{-3}
$\Delta\rho_{\min} = -0.204$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.040 (6)

Table 3
Hydrogen-bonding geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···O2^{i}	1.01 (2)	2.62 (2)	3.204 (3)	117 (2)
C5—H5···N3^{i}	1.01 (2)	2.51 (2)	3.500 (3)	168 (2)
C9—H9···O3^{ii}	1.02 (3)	2.45 (3)	3.374 (3)	151 (2)
C10—H101···O2^{iii}	0.97 (3)	2.58 (3)	3.087 (3)	112 (2)
C12—H123···N3^{iv}	0.98 (4)	2.68 (4)	3.579 (4)	153 (3)

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

Compound (IV)

Crystal data

$C_{12}H_{13}N_5O_4$
$M_r = 291.27$
Triclinic, $P\overline{1}$
$a = 8.253$ (6) Å
$b = 8.493$ (3) Å
$c = 10.084$ (2) Å
$\alpha = 78.79°$
$\beta = 88.52°$
$\gamma = 74.95°$
$V = 669.3$ (6) Å^3
$Z = 2$
$D_x = 1.445$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 2.5$–$16.6°$
$\mu = 0.112$ mm^{-1}
$T = 293$ (2) K
Plate, pale yellow
0.9 × 0.45 × 0.1 mm

Data collection

Philips PW1100 diffractometer
$\omega/2\theta$ scans
2494 measured reflections
2349 independent reflections
1806 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.068$
$\theta_{\max} = 25.02°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 10$
$l = 0 \rightarrow 11$
3 standard reflections
frequency: 120 min
intensity decay: 2.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.144$
$S = 0.907$
2349 reflections
242 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0885P)^2 + 0.2017P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.011$
$\Delta\rho_{\max} = 0.237$ e Å^{-3}
$\Delta\rho_{\min} = -0.253$ e Å^{-3}

Table 4
Hydrogen-bonding geometry (Å, °) for (IV).

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···O4^{i}	0.94 (2)	2.72 (3)	3.624 (4)	163 (2)
C12—H121···O3^{ii}	0.98 (3)	2.62 (4)	3.529 (3)	153 (3)
C12—H122···O2^{iii}	0.95 (4)	2.50 (4)	3.426 (4)	163 (3)

Symmetry codes: (i) $1+x, y, z$; (ii) $-x, -y, 1-z$; (iii) $1-x, 1-y, -z$.

Compound (V)

Crystal data

$C_{12}H_{13}N_5O_4$
$M_r = 291.27$
Monoclinic, $P2_1/c$
$a = 11.1270$ (6) Å
$b = 9.1950$ (9) Å
$c = 13.0940$ (11) Å
$\beta = 101.264$ (5)°
$V = 1313.88$ (18) Å^3
$Z = 4$

$D_x = 1.473$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4397 reflections
$\theta = 1.02$–25.35°
$\mu = 0.114$ mm^{-1}
$T = 293$ (2) K
Cube, pale yellow
0.25 × 0.25 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
φ scans
7133 measured reflections
2404 independent reflections
1739 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.035$
$\theta_{\rm max} = 25.36°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 11$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.142$
$S = 1.049$
2404 reflections
243 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0636P)^2 + 0.3001P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.193$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.155$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.016 (4)

Table 5
Hydrogen-bonding geometry (Å, °) for (V).

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···O2$^{\rm i}$	0.93 (3)	2.49 (3)	3.402 (3)	165 (2)
C6—H6···O1$^{\rm ii}$	0.94 (3)	2.72 (3)	3.377 (3)	128 (2)
C8—H8···O1$^{\rm iii}$	0.94 (2)	2.65 (2)	3.539 (3)	157 (2)
C9—H9···O3$^{\rm iv}$	1.00 (3)	2.67 (3)	3.366 (3)	127 (2)
C10—H102···O3$^{\rm v}$	0.91 (4)	2.68 (3)	3.104 (4)	109 (3)

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

No attempt has been made to find the absolute structure of (II). H atoms were treated by a mixture of independent (H atoms of the water molecule) and constrained refinement. Crystals of (III) were unstable and poorly diffracted; therefore, the data were not collected to completeness and the $R_{\rm int}$ value was greater than expected.

For compound (II), data collection: *Philips PW*1110/20 (Philips, 1973); for all other compounds, data collection: *COLLECT* (Nonius, 1998). For compound (II), cell refinement: *Philips PW* 1110/20; for all other compounds, cell refinement: *DENZO* (Otwinowski & Minor, 1997). For compound (II), data reduction: *PROCN* (Hornstra & Stubbe, 1973); for all other compounds, data reduction: *DENZO*. For all compounds, program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *TEXSAN* (Molecular Structure Corporation, 1995); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1458). Services for accessing these data are described at the back of the journal.

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