

4-Amino-3-methyl-6-phenyl-1,2,4-triazin-5(4*H*)-one (metamitron) and 4-amino-6-methyl-3-phenyl-1,2,4-triazin-5(4*H*)-one (isometamitron)

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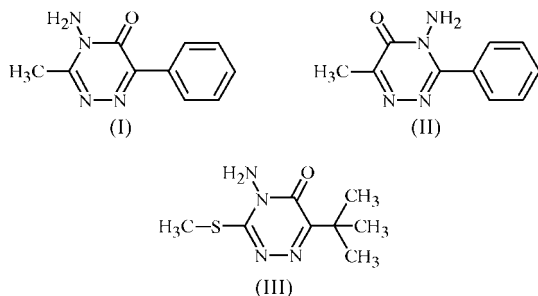
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The title structures, both C₁₀H₁₀N₄O, are substitutional isomers. The N–N bond lengths are longer and the C=N bond lengths are shorter by *ca* 0.025 Å than the respective average values in the C=N–N=C group of asymmetric triazines; the assessed respective bond orders are 1.3 and 1.7. There are N–H···O and N–H···N hydrogen bonds in both structures, with 4-amino-3-methyl-6-phenyl-1,2,4-triazin-5(4*H*)-one containing a rare bifurcated N–H···N,N hydrogen bond. The structures differ in their molecular stacking and the hydrogen-bonding patterns.

Comment

4-Amino-3-methyl-6-phenyl-1,2,4-triazin-5(4*H*)-one (metamitron), (I), and 4-amino-6-*tert*-butyl-3-methylsulfanyl-1,2,4-triazin-5(4*H*)-one (metribuzin), (III), belong to a family of widely used pesticides. Their molecular structures contain an asymmetric triazine heterocyclic ring and the structure of (III) has been reported (Aliev *et al.*, 1989).



Our electrochemical investigations of these triazines (Ludvík *et al.*, 1998*a,b*) indicated a limited electronic delocalization across the N–N bond of the C=N–N=C unit. A logical interpretation of our previous results is that in the formally conjugated C=N–N=C azine system a limited

mutual electronic interaction between the two C=N bonds arises with lowering of the aromaticity of the heterocycle (Zuman & Ludvík, 2000).

In order to extend information on limited delocalization in heterocycles of this type, 4-amino-6-methyl-3-phenyl-1,2,4-triazin-5(4*H*)-one (isometamitron), (II), was synthesized, and the structures of (I) and (II) have been determined (Figs. 1–4). Firstly, we were interested in the N–N ring bond lengths in (I) and (II); in (III) [Cambridge Structural Database (CSD; Version 5.27, update to September 2006; Allen, 2002), refcode VEYSEL (Aliev *et al.*, 1989)], the N–N bond length is 1.358 (7) Å. Secondly, the question arose as to whether and how a phenyl substituent in the 3- and 6-positions in (I) and (II), respectively, could interact with the heterocyclic C=N bonds. The 1,6- and 2,3-C=N bond lengths in (I) and (II), respectively, are similar (Table 3). This means that the influence of the phenyl and methyl substituents on the C=N–N=C group is negligible.

A search of the CSD for asymmetric triazines (determined with *R* < 0.05 and without disorder or errors) is depicted in Fig. 5. This scattergram shows the distribution of N–N *versus* C–N distances in the C=N–N=C unit. The scattergram also shows a general trend in its densest part; the longer the N–N bond length then the shorter the adjacent C–N distances. Structures (I) and (II) are situated at the lower right-hand extremum of the dense region in Fig. 5. The C=N distances in (I) and (II) are shortened by *ca* 0.025 Å from the average value at the expense of elongation (by *ca* 0.025 Å) of

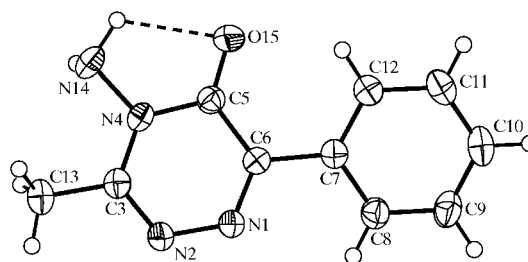


Figure 1

The molecular structure of (I) at 150 K, showing the atom labelling. Displacement ellipsoids are shown at the 50% probability level. The intramolecular N–H···O interaction is shown as a dashed line.

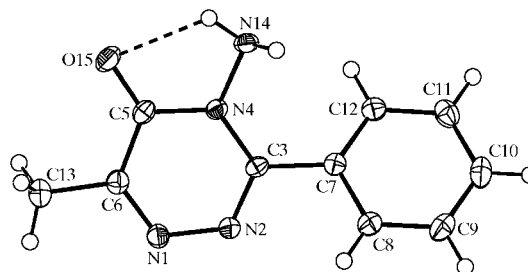


Figure 2

The molecular structure of (II) at 150 K, showing the atom labelling. Displacement ellipsoids are shown at the 50% probability level. The intramolecular N–H···O interaction is shown as a dashed line.

the N–N bond. Therefore, in (I) and (II), the single- and double-bond characters of the respective N–N and C=N bonds are enhanced compared with related compounds. The bond order of the C=N bonds in (I) and (II) is calculated as 1.7 (Fig. 6) (polynomial fit with *Origin 6.1*; OriginLab, 2000) from the data (in Table 4), and the bond order for N–N is 1.3.

The carbonyl group influences adjacent distances in the asymmetric triazine rings in (I) and (II). The short C=O bond length especially affects the adjacent C–C bonds, which acquire a large proportion of single-bond character [C5–C6 in (I) and (II) and C2–C3 in (III)]. This is accentuated in (III), where the C=O bond length is even shorter. The –NH₂ groups are not planar in either (I) or (II), as is relatively common in N–NH₂ groups in the CSD. However, one of the H atoms of the NH₂ group in both (I) and (II) lies close to the plane of the asymmetric (planar) triazine (Figs. 1 and 2).

Although (I) and (II) are similar in shape and are positional isomers they differ in packing as well as in their hydrogen-bonding patterns. The differences between the unit-cell volumes/formula unit show that molecules are more densely packed in (II). In both (I) and (II), there is a similar intramolecular N–H···O hydrogen bond (Figs. 1 and 2), forming an *S*(5) graph set (Bernstein *et al.*, 1995). There are other common features: (i) both H atoms of the primary amine group are involved in interactions and (ii) the same H atoms involved in the intramolecular N–H···O hydrogen bonds

also participate in intermolecular N–H···O or N–H···N hydrogen bonds in (I) and (II), respectively.

A difference between (I) (Table 1 and Fig. 3) and (II) (Table 2 and Fig. 4) is that, in (I), there is a bifurcated N–H142···N,N hydrogen bond, while H142 is not involved in other interactions. Few similar examples are present in the CSD [among structures without errors or disorder and with $R < 0.05$, only AQESUK (Hammerl *et al.*, 2003) and VEYGEL (Aliev *et al.*, 1989), where the H atoms involved in the bifurcated hydrogen bond to a pair of the bonded N atoms, do not also participate in other hydrogen bonds; in VEYGEL, the primary amine group is almost perpendicular to the plane of the asymmetric triazine ring].

In addition to the *S*(5) motif, the hydrogen-bond graph sets in (I) are $R_1^2(3)$ for atoms H142, N1ⁱⁱ and N2ⁱⁱ [symmetry code: (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; Table 1], and $R_2^2(4)$ for atoms H141 and O15. The latter motif with H141 is also a part of a larger cyclic system, $R_2^2(10)$. In addition to *S*(5), the hydrogen-bond graph set in (II) is based on $R_4^4(10)$ (Fig. 4).

The packing of the molecules in (I) and (II) is different. In (I), all the molecules are not parallel stacked (Fig. 3). The closest distance [3.5092 (6) Å for molecules linked by the operation $(-x + 1, -y + 1, -z + 1)$] is between the centroids of the asymmetric triazine rings, while the phenyl ring centroids are at 5.0207 (8) Å [for molecules related by operations $(x - \frac{1}{2}, y, -z + \frac{3}{2})$ and $(x + \frac{1}{2}, y, -z + \frac{3}{2})$]. The N–H···O and N–

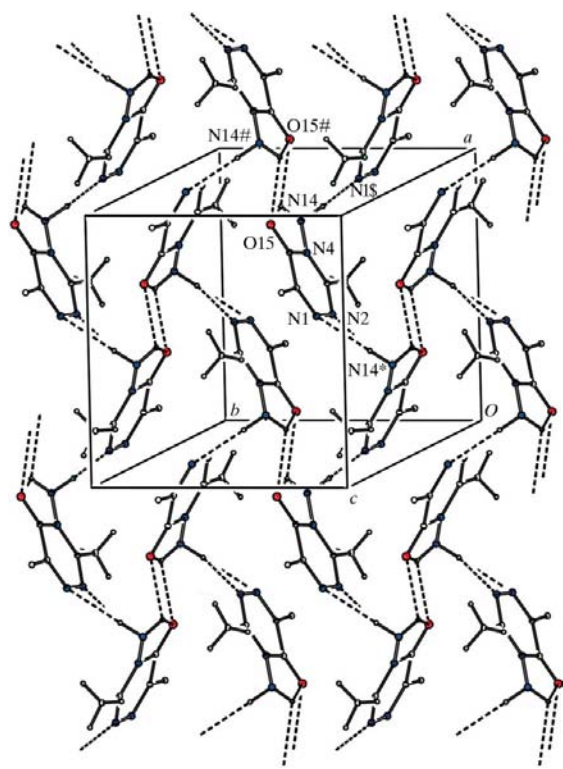


Figure 3

A view of the primary interactions in (I); for clarity, only the *C*_{ipso} atom of the phenyl ring is included. Atoms labelled with a hash (#), an asterisk (*) and an ampersand (&) are at the symmetry positions $(x + \frac{1}{2}, -y + \frac{3}{2}, -z)$, $(-z + 1, -y + 1, -z + 1)$ and $(-x + 2, -y + 1, -z + 1)$, respectively.

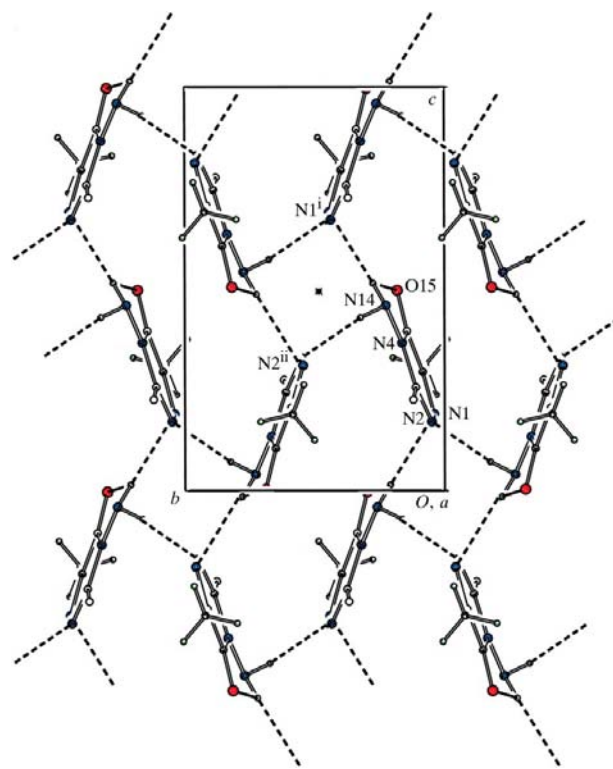


Figure 4

A view of the interactions in (II) and the unit cell along the *a*-axis direction; for clarity, only the *C*_{ipso} atom of the phenyl ring is included. Symmetry codes are given in Table 2. The $R_4^4(10)$ motif is depicted by an asterisk (*) (centre).

H \cdots N hydrogen bonds form a two-dimensional network that is perpendicular to the *c* axis.

In (II), the molecules are stacked along the monoclinic axis (Fig. 4). The distances between the asymmetric triazine ring centroids and the substituted phenyl ring centroids are 3.5249 (6) and 3.7171 (6) Å for molecules linked by the operations $(-x + 1, y - \frac{1}{2}, -z + 1)$ and $(-x + 1, y - \frac{1}{2}, -z + 1)$, respectively. The N—H \cdots O and N—H \cdots N interactions form a three-dimensional network. Values of 3.50 Å between the centroids indicate π – π stacking interactions between the pertinent rings in both structures.

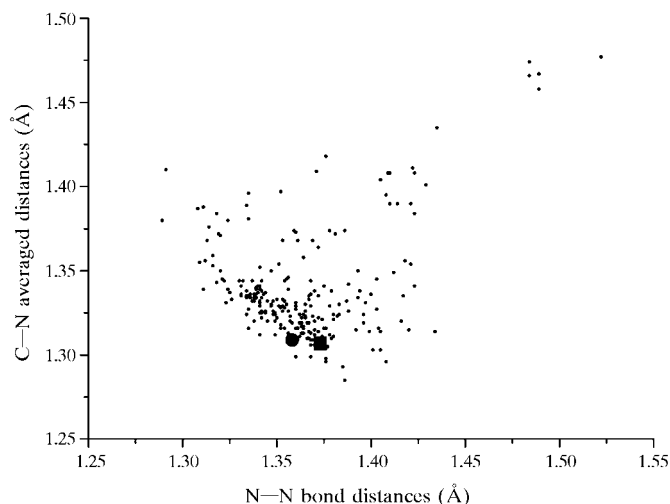


Figure 5

A plot of the N–N distances *versus* the average value of both C–N distances (Å) in the C=N–N=C fragments in asymmetric triazine rings (CSD, with *R* factors < 0.05 and without errors or disorder). Compound (III) and the superimposed (I) and (II) are highlighted by the circle (left) and square (right), respectively.

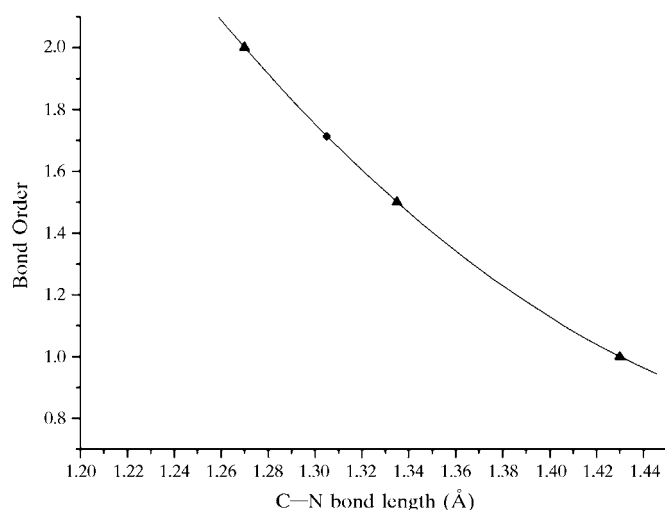


Figure 6

The dependence of the C–N bond order on its bond length. The curve was calculated by a polynomial fit $y = A + Bx + Cx^2$, where *y* is bond order and *x* is the bond length ($A = 37.50987$, $B = -47.24290$ and $C = 15.18219$). Bond lengths are from BZAZIN11 and PYRDNA01, with the average values from AZBENC01 and AZOBEN (the triangles). The positions of (I) and (II) are superimposed (rhombus).

Experimental

Compound (I) was isolated from the commercial pesticide GOLTIX WP 70 (Bayer) by repeated recrystallization from methanol. The melting point (441.5–442.0 K) agrees well with that (438–440 K) of the analytical standard Metamitron-Pestanal (Riedel-de Haen AG, 2005). The structure was confirmed by ^1H and ^{13}C NMR as well as by IR spectroscopic analysis; purity was tested by thin-layer chromatography. Compound (II) was prepared according to the method described by Neunhoeffer *et al.* (1992). The isolated substance was characterized by ^1H and ^{13}C NMR spectroscopic analysis and purity was checked by high-pressure liquid chromatography.

Compound (I)

Crystal data

$\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}$	$V = 1907.54 (7) \text{ \AA}^3$
$M_r = 202.22$	$Z = 8$
Orthorhombic, <i>Pbca</i>	Mo $K\alpha$ radiation
$a = 9.5433 (2) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$b = 9.1416 (2) \text{ \AA}$	$T = 150 (1) \text{ K}$
$c = 21.8652 (4) \text{ \AA}$	$0.35 \times 0.16 \times 0.10 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer	1816 reflections with $I > 2\sigma(I)$
4037 measured reflections	$R_{\text{int}} = 0.015$
2172 independent reflections	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.099$	$\Delta\rho_{\text{max}} = 0.19 \text{ e \AA}^{-3}$
$S = 1.07$	$\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$
2172 reflections	
146 parameters	

Table 1

Hydrogen-bond and short-contact geometry (Å, °) for (I).

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N14—H141 \cdots O15	0.960 (18)	2.169 (17)	2.6856 (14)	112.3 (12)
N14—H141 \cdots O15 ⁱ	0.960 (18)	2.398 (17)	2.8749 (13)	110.2 (12)
N14—H142 \cdots N1 ⁱⁱ	0.928 (19)	2.245 (19)	3.1663 (15)	171.3 (14)
N14—H142 \cdots N2 ⁱⁱ	0.928 (19)	2.418 (18)	3.1643 (15)	137.4 (13)
C12—H12 \cdots O15	0.93	2.29	2.8883 (16)	122

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

Compound (II)

Crystal data

$\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}$	$V = 921.46 (4) \text{ \AA}^3$
$M_r = 202.22$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 11.6164 (3) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$b = 7.1361 (2) \text{ \AA}$	$T = 150 \text{ K}$
$c = 12.0604 (3) \text{ \AA}$	$0.25 \times 0.17 \times 0.08 \text{ mm}$
$\beta = 112.8259 (15)^\circ$	

Data collection

Nonius KappaCCD diffractometer	1803 reflections with $I > 2\sigma(I)$
3998 measured reflections	$R_{\text{int}} = 0.016$
2108 independent reflections	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.099$	$\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$
$S = 1.05$	$\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$
2108 reflections	
146 parameters	

Table 2
Hydrogen-bond and short-contact geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N14—H141 \cdots O15	0.917 (16)	2.148 (15)	2.6633 (13)	114.6 (12)
N14—H141 \cdots N1 ⁱ	0.917 (16)	2.321 (15)	3.0081 (13)	131.5 (12)
N14—H142 \cdots N2 ⁱⁱ	0.917 (15)	2.149 (15)	3.0550 (13)	169.3 (12)
C12—H12 \cdots N14	0.93	2.52	2.9564 (16)	109

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

Table 3
Selected bond lengths (Å) in (I), (II) and (III).

Bond	(I)	Bond	(II)	Bond	(III)
C6—C7	1.4854 (15)	C3—C7	1.4874 (14)	—	—
C6—N1	1.3069 (14)	C3—N2	1.3112 (13)	C1—N2	1.315 (7)
N1—N2	1.3729 (13)	N1—N2	1.3729 (12)	N1—N2	1.358 (7)
N2—C3	1.3081 (15)	N1—C6	1.3013 (14)	N1—C3	1.303 (7)
C3—N4	1.3582 (15)	C3—N4	1.3666 (13)	C1—N3	1.376 (7)
N4—C5	1.3850 (14)	N4—C5	1.3910 (14)	C2—N3	1.381 (6)
C5—C6	1.4638 (16)	C5—C6	1.4551 (15)	C2—C3	1.504 (7)
C3—C13	1.4893 (16)	C6—C13	1.4927 (15)	C3—C5	1.488 (7)
N4—N14	1.4163 (13)	N4—N14	1.4155 (12)	N3—N4	1.397 (6)
C5—O15	1.2254 (14)	C5—O15	1.2270 (13)	C2—O1	1.203 (7)

Table 4
The representative structures containing the motif C—N—N—C with varying order of C—N and N—N bonds and with the corresponding bond lengths (Å).

The structures contain no disorder and are not flagged with errors.

Refcode	C—N bond length	Bond order	N—N bond length	Bond order
AZBENC01 ^a	1.443	1	1.251	2
AZOBEN12 ^b	1.430	1	1.256	2
	1.430	1	1.249	2
AZOBEN13 ^c	1.431	1	1.256	2
	1.431	1	1.249	2
BZAZIN11 ^d	1.269	2	1.413	1
PYRDNA01 ^e	1.336	1.5	—	—
TRIZIN01 ^f	1.317	0.5	—	—

Notes: (a) *cis*-azobenzene (Mostad & Römning, 1971); (b) *trans*-azobenzene (Harada & Ogawa, 2004); (c) *trans*-azobenzene (Harada & Ogawa, 2004); (d) benzalazine (Burke-Laing & Laing, 1976); (e) pyridine (Mootz & Wussow, 1981), average values from four independent molecules (the average C—C bond length corresponding to the bond order 1.5 is 1.379 Å); (f) *s*-triazine (Coppens, 1967). (a), (d), (f) were determined at room temperature, (e) at 153 K, and (b) and (c) at 90 K.

In both structures, all H atoms were discernible in difference Fourier maps; however, they were constrained by the riding-model approximation [methyl C—H = 0.96 Å and aryl C—H = 0.93 Å; $U_{iso}(H) = 1.5U_{eq}(\text{methyl C})$ and $1.2U_{eq}(\text{aryl C})$]. For the NH₂ groups in both compounds, the positional parameters of the H atoms were

constrained to idealized tetrahedral geometry by the command AFIX 3 in *SHELXL97* (Sheldrick, 1997). The isotropic displacement parameters of the NH₂ H atoms were freely refined.

For both compounds, data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; 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: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3068). Services for accessing these data are described at the back of the journal.

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