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1-Methyl-4-nitraminopyridinium nitrate and 4-nitraminopyridinium methanesulfonate

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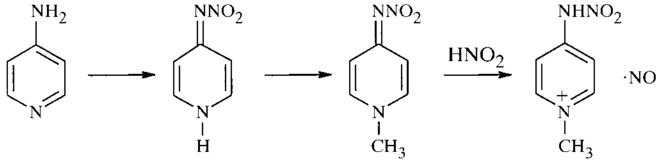
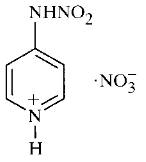
In the title compounds, $C_6H_8N_3O_2^+\cdot NO_3^-$ and $C_5H_6N_3O_2^+\cdot CH_3SO_3^-$, respectively, the cations are almost planar; the twist of the nitramino group about the C—N and N—N bonds does not exceed 10°. The deviations from coplanarity are accounted for by intermolecular N—H···O interactions. The coplanarity of the $NHNO_2$ group and the phenyl ring leads to the deformation of the nitramino group. The C—N—N angle and one C—C—N angle at the junction of the phenyl ring and the nitramino group are increased from 120° by *ca* 6°, whereas the other junction C—C—N angle is decreased by *ca* 5°. Within the nitro group, the O—N—O angle is increased by *ca* 5° and one O—N—N angle is decreased by *ca* 5°, whereas the other O—N—N angle remains almost unchanged. The cations are connected to the anions by relatively strong N—H···O hydrogen bonds [shortest H···O separations 1.77 (2)–1.81 (3) Å] and much weaker C—H···O hydrogen bonds [H···O separations 2.30 (2)–2.63 (3) Å].

Comment

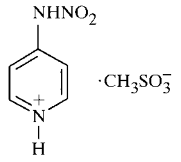
The reaction of primary nitramines with nitrous acid provides the same products as diazotation of the corresponding parent amines. When *N*-methylnitramine is treated with sodium nitrite in acidic solution, methanol and *N*,*N*-dimethylnitramine are formed. The latter is formed as a result of methylation of the substrate with diazomethane, the intermediate being formed in the first step of the reaction. Because of the relative stability of aromatic diazonium salts, they are the principal products, often formed quantitatively, of reactions of *N*-arylnitramines with nitrous acid (Wright, 1969). We have assumed that this rule is applicable to the *N*-pyridylnitramines as well. Nitration of 4-aminopyridine with mixed acids provides the corresponding nitrimine, (I), in good yield (Deady & Korytsky, 1983). Methylation of (I) gives the nitrimine, (II), as the only product; the isomeric secondary nitramine has been obtained *via* another route (Daszkiewicz *et al.*, 1997). The protonation of (II) must provide a cation, (III), containing a primary nitramino group bound to the positively charged aromatic ring. Its reaction with nitrous acid should give 1-methyl-4-pyridone as the main product. To our surprise, compound (II) is resistant to the action of nitrous acid and its rapid disproportionation gives 1-methyl-4-nitraminopyridinium nitrate, (III), as the only product. Compound (II) cannot be rearranged like a typical nitramine under the influence of concentrated sulfuric acid, so the stability of its protonated form in (III) is not surprising. On the other hand, the primary nitramine is susceptible to rearrangement and forms 4-amino-3-nitropyridine in strongly acidic media. In spite of this, we were able to prepare from (I) the salt 4-nitraminopyridinium methanesulfonate, (V), and to determine its structure, which is presented here with the structure of (III). The result confirms Deady & Korytsky's supposition that the rearrangement of pyridylnitramines requires double protonation of a substrate.



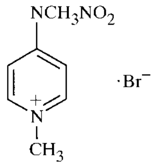
(I) (II) (III)



(IV)



(V)



(VI)

The molecular structures of (III) and (V) are shown in Figs. 1 and 2. Compound (V) crystallizes with two independent molecules, *A* and *B*, in the asymmetric unit. The pyridine ring in (III) and (V) is not affected by the methyl substituent on N1, the positive charge or the character of the *N*-nitro group (primary, secondary or nitrimine). The C2—C3 and C5—C6 bonds are shorter (mean 1.356 Å) than the remaining C—C bonds (mean 1.396 Å) (Fig. 1). Another common feature is a decreased valence angle centred on C4, and slightly increased angles centred on C2 and C6. It is an inductive effect of the *N*-nitro group that is responsible for this apparent deformation. The Ar—N bonds are of the same length in all the

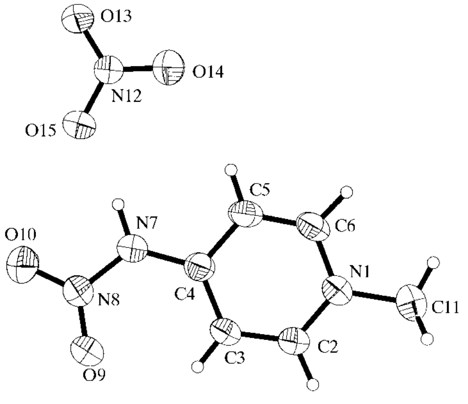


Figure 1
The molecular structure of (III) showing the atom-numbering scheme and with 50% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii.

molecules; the differences of *ca* 0.01 Å are incompatible with the expected differences between the formally single [(IV): Meiyappan *et al.*, 1999; (III) and (V): present work] and double bonds [(I) and (II): Anulewicz *et al.*, 1993; Krygowski *et al.*, 1996].

An interesting geometric parameter of all aromatic nitramines is the torsion angle along the Ar—N bond. This angle may be considered a gauge of the mesomeric interaction between the nitramine π-electron system and the aromatic sextet. Nitrimines (I) and (II) are planar or nearly planar, indicating conjugation between the ring and the substituent. It can be expected that protonation of the amide N9 atom can disconnect the conjugation, but this is not what has been observed; the molecules of (III) and (V) are nearly planar. The twist of the nitramino group about the C—N and N—N bonds does not exceed 10°. The deviations from coplanarity are accounted for with non-valence interactions.

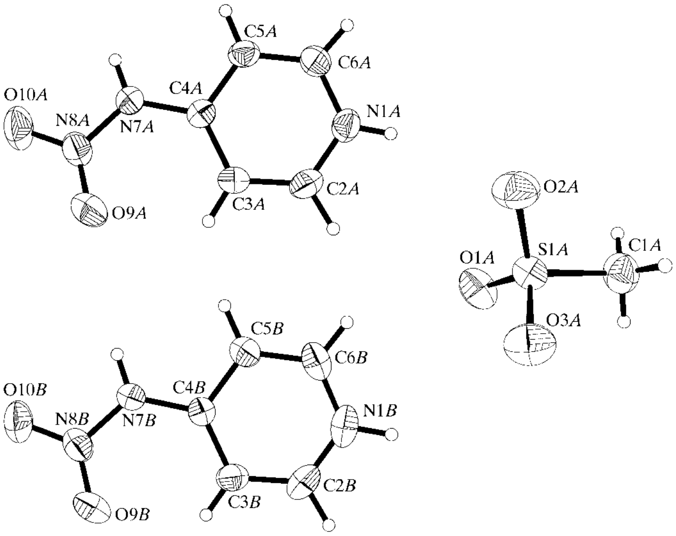


Figure 2
The structures of the cations of molecules *A* and *B* of (V) and of the anion of molecule *A*, showing the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii.

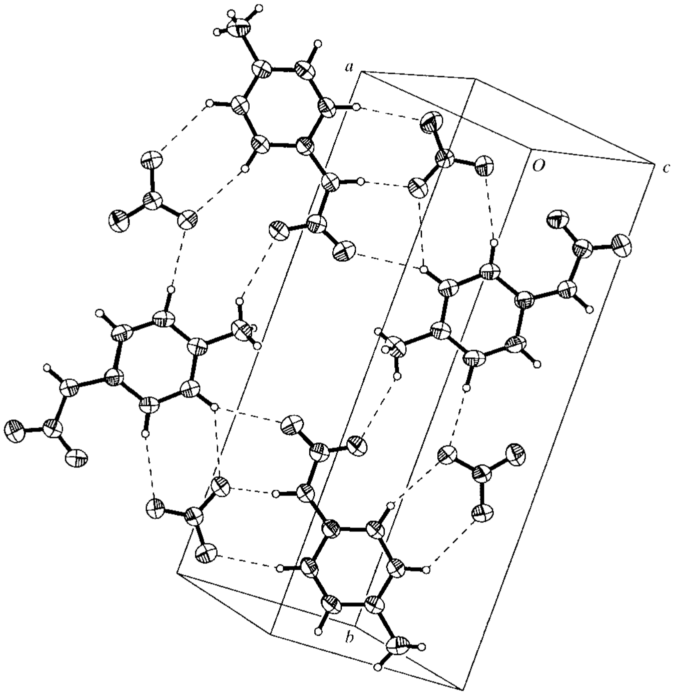


Figure 3
The packing diagram for (III). Hydrogen bonds are shown as dashed lines.

In typical secondary nitramines in the benzene (Bujak *et al.*, 1998; Ejsmont *et al.*, 1998) and pyridine series (Zaleski *et al.*, 1999*a*,*b*), the nitramino group is also almost planar. It is twisted with respect to the phenyl ring by *ca* 60° about the C—N bond [(VI): Zaleski *et al.*, 1999*a*]. The C—N bond is *ca* 0.025 Å longer, whereas the length of the N—N bond is almost the same as the corresponding bonds in the primary nitrimines, (I) and (II), and nitramines, (III) and (V). The twist of the nitramino group relative to the phenyl ring is steric in origin. It is impossible to accommodate the H_3CNNO_2 group and the phenyl ring on the same plane. Even when the methyl group is substituted by an H atom, coplanarity of the $NHNO_2$ group and a phenyl ring leads to the deformation of the bond angles within the NNO_2 group from 120°. The C4—N7—N8 and C3—C4—N7 angles are increased by *ca* 6°, whereas the C5—C4—N7 angle is decreased by *ca* 5°. Within the nitro group, there is an increase of *ca* 5° in the O9—N8—O10 angle and a decrease of the O10—N8—N7 angle, whereas the O9—N8—N7 angle remains close to 120°.

It should be mentioned that in the nitrimines, (I) and (II), a slightly different deformation of the NNO_2 group is observed. The C4—N7—N8 angle remains close to 120°, whereas the C3—C4—N7 angle is more enlarged (by *ca* 10–11°). In the NO_2 group as well, it is the O9—N8—N7 angle that is increased by *ca* 4°, whereas the O9—N8—O10 angle remains close to 120°. The reason for the observed differences is not clear. One possible explanation is an interaction between the lone electron pair on N7 and the NO_2 group. Its relatively large size may lead to the increase of the valence angle centred on N8, rather than N7 as in the nitrimines (I) and (II).

The 1-methyl-4-nitraminopyridinium cations in (III) are connected to the nitrate anions by relatively strong N—H···O

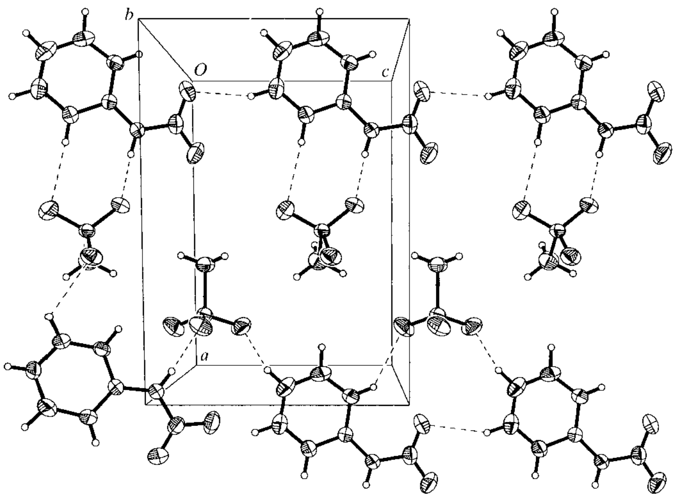


Figure 4
The packing diagram for (V). Hydrogen bonds are shown as dashed lines.

hydrogen bonds [H$\cdots$O 1.77 (2) Å], forming pairs (Fig. 3). These pairs are interconnected with each other by much weaker C—H$\cdots$O hydrogen bonds, forming layers close to the [101] plane. In salt (V), each 4-nitraminopyridinium cation is connected to two methanesulfonate anions by N—H$\cdots$O hydrogen bonds [N$\cdots$O 2.665 (2)–2.771 (2) Å], forming chains (Fig. 4). These hydrogen bonds are assisted by much weaker C—H$\cdots$O bonds [C$\cdots$O 3.072 (3)–3.369 (3) Å], interconnecting the molecules into a three-dimensional structure. It should be mentioned that the hydrogen bonds binding one of the two independent cations are stronger than those in the other molecule; the H$\cdots$O separations for the cation of molecule *B* are *ca* 0.06–0.12 Å shorter than those for the cation of molecule *A*.

Experimental

The title compounds were prepared from readily accessible *N*-(4-pyridyl)nitramine and its methylated derivative. 1,4-Dihydro-1-methyl-4-nitriminopyridine (3.06 g, 20 mmol) was dissolved in 20% sulfuric acid (10 ml). A saturated aqueous solution of sodium nitrite (2.80 g, 40 mmol) was added dropwise slowly at room temperature. The solution was stirred at 298–303 K until evolution of gases ceased, and then cooled. The crude product (3.95 g, 91%) was collected by filtration, washed with iced water and dried *in vacuo* (m.p. 431–437 K). Crystallization from methanol (45 ml) provided light-yellow prisms of (III) (2.18 g) suitable for X-ray diffraction studies. Pure (III) melted at 433–436 K with decomposition. From the mother liquor, another crop of the product was isolated; it was contaminated with some inorganic salts. Spectroscopic analysis: IR (KBr, ν, cm^{-1}): 3100–2350 (broad, intense band with several sub-maxima, hydrogen-bonded N—H group), 1385, 1336, 1316, 1296 and 1254 (N—O stretching vibrations in the nitrate anion and NO_2 group); ^{1}H NMR (DMSO-d_6, δ, p.p.m.): 12.1 (*s*, NH), 8.65 (*d*, 2H), 7.77 (*d*, ^3J = 7.5 Hz, 2H, aromatic H), 4.15 (*s*, 3H, *N*-methyl group); ^{13}C NMR (DMSO-d_6, δ, p.p.m.): 153.1 (C4), 145.2 (C2, C6), 113.9 (C3, C5), 45.8 (NCH_3). *N*-(4-Pyridyl)nitramine (1.39 g, 0.01 mol) was dissolved in 70% aqueous methanesulfonic acid (5.0 ml) and left for 12 h at room temperature. 4-Nitraminopyridinium methanesulfonate was collected by filtration, washed with tetrahydrofuran and dried *in vacuo*. The product formed large colourless prisms of (V) (m.p. 436–439 K) suitable for X-ray diffraction studies. From the liquor, another crop of the salt was obtained after dilution with tetrahydrofuran and cooling (total yield 1.71 g, 73%). Spectroscopic analysis: IR (KBr, ν, cm^{-1}): 1451, 1338 (N—NO_2 stretching vibrations), 761, 753 (N—NO_2 deformations); ^{1}H NMR (DMSO-d_6, δ, p.p.m.): 10.6 (*s*, NH), 8.69 (*d*, 2H), 7.82 (*d*, ^3J = 7.5 Hz, 2H, aromatic H), 2.49 (*s*, 3H, *S*-methyl group); ^{13}C NMR (DMSO-d_6, δ, p.p.m.): 152.8 (C4), 142.2 (C2, C6), 113.4 (C3, C5), 39.6 (SCH_3).

Compound (III)

Crystal data

$C_6H_8N_3O_2^+\cdot NO_3^-$
$M_r = 216.16$
Monoclinic, $P2_1/c$
$a = 7.108\ (1)$ Å
$b = 17.598\ (4)$ Å
$c = 7.246\ (1)$ Å
$\beta = 90.33\ (3)^\circ$
$V = 906.4\ (3)$ Å^3
$Z = 4$

$D_x = 1.584$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 35 reflections
$\theta = 12$–14°
$\mu = 0.14$ mm^{-1}
$T = 293\ (2)$ K
Prism, light yellow
0.5 × 0.4 × 0.4 mm

Data collection

Kuma KM-4 diffractometer
ω scans
2824 measured reflections
2640 independent reflections
1746 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.014$
$\theta_{\rm max} = 30.1^\circ$

$h = -10 \rightarrow 10$
$k = 0 \rightarrow 24$
$l = -10 \rightarrow 0$
2 standard reflections
every 50 reflections
intensity decay: 1.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.141$
$S = 1.03$
2640 reflections

168 parameters
All H-atom parameters refined
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.30$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.18$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (III).

C4—N7	1.377 (2)	N8—O9	1.206 (2)
N7—N8	1.364 (2)	N8—O10	1.214 (2)
C2—N1—C6	119.7 (1)	C6—C5—C4	120.0 (1)
N1—C2—C3	122.0 (1)	N1—C6—C5	121.3 (1)
C2—C3—C4	119.0 (1)	N8—N7—C4	125.7 (1)
N7—C4—C3	126.8 (1)	O9—N8—O10	125.3 (1)
N7—C4—C5	115.2 (1)	O9—N8—N7	119.2 (1)
C3—C4—C5	118.0 (1)	O10—N8—N7	115.5 (1)
C3—C4—N7—N8	9.8 (3)	C4—N7—N8—O9	4.5 (3)
C5—C4—N7—N8	−171.0 (2)	C4—N7—N8—O10	−175.3 (2)

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

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
N7—H7$\cdots$O15	0.94 (2)	1.77 (2)	2.700 (2)	171 (2)
C3—H3$\cdots$O13$^{\rm i}$	0.90 (2)	2.39 (2)	3.270 (2)	165 (2)
C2—H2$\cdots$O15$^{\rm i}$	0.94 (2)	2.52 (2)	3.226 (2)	131 (2)
C2—H2$\cdots$O10$^{\rm i}$	0.94 (2)	2.51 (2)	3.396 (2)	156 (2)
C5—H5$\cdots$O14	0.92 (2)	2.37 (2)	3.265 (2)	166 (2)
C6—H6$\cdots$O13$^{\rm ii}$	0.95 (2)	2.30 (2)	3.229 (2)	168 (2)
C11—H11*C*$\cdots$O9$^{\rm iii}$	0.93 (3)	2.52 (3)	3.330 (2)	146 (2)

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

Compound (V)

Crystal data

$C_5H_6N_3O_2^+\cdot CH_3SO_3^-$
$M_r = 235.22$
Monoclinic, $P2_1/n$
$a = 11.824\ (2)$ Å
$b = 8.138\ (2)$ Å
$c = 20.125\ (4)$ Å
$\beta = 97.36\ (3)^\circ$
$V = 1920.5\ (7)$ Å^3
$Z = 8$

$D_x = 1.627$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 27 reflections
$\theta = 10$–14°
$\mu = 0.35$ mm^{-1}
$T = 293\ (2)$ K
Prism, colourless
0.45 × 0.40 × 0.35 mm

Data collection

Kuma KM-4 diffractometer
ω scans
3500 measured reflections
3402 independent reflections
3022 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\rm max} = 25.1^\circ$

$h = -13 \rightarrow 14$
$k = -9 \rightarrow 0$
$l = -23 \rightarrow 0$
2 standard reflections
every 50 reflections
intensity decay: 2.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.099$
$S = 1.08$
3402 reflections
272 parameters
H-atom parameters constrained
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0140 (10)

Table 3
Selected geometric parameters (Å, °) for (V).

C4*A*—N7*A*	1.380 (3)	C4*B*—N7*B*	1.374 (3)
N7*A*—N8*A*	1.352 (2)	N7*B*—N8*B*	1.361 (2)
N8*A*—O9*A*	1.210 (3)	N8*B*—O10*B*	1.214 (2)
N8*A*—O10*A*	1.222 (3)	N8*B*—O9*B*	1.220 (2)
C6*A*—N1*A*—C2*A*	120.9 (2)	C2*B*—N1*B*—C6*B*	120.7 (2)
N1*A*—C6*A*—C5*A*	120.4 (2)	N1*B*—C6*B*—C5*B*	120.9 (2)
C6*A*—C5*A*—C4*A*	119.8 (2)	C6*B*—C5*B*—C4*B*	119.1 (2)
N7*A*—C4*A*—C5*A*	115.2 (2)	N7*B*—C4*B*—C3*B*	126.4 (2)
N7*A*—C4*A*—C3*A*	126.1 (2)	N7*B*—C4*B*—C5*B*	114.8 (2)
C5*A*—C4*A*—C3*A*	118.7 (2)	C3*B*—C4*B*—C5*B*	118.8 (2)
C2*A*—C3*A*—C4*A*	118.4 (2)	C2*B*—C3*B*—C4*B*	118.2 (2)
N1*A*—C2*A*—C3*A*	121.9 (2)	N1*B*—C2*B*—C3*B*	122.3 (2)
N8*A*—N7*A*—C4*A*	125.9 (2)	N8*B*—N7*B*—C4*B*	125.4 (2)
O9*A*—N8*A*—O10*A*	125.2 (2)	O10*B*—N8*B*—O9*B*	125.3 (2)
O9*A*—N8*A*—N7*A*	119.4 (2)	O10*B*—N8*B*—N7*B*	115.4 (2)
O10*A*—N8*A*—N7*A*	115.3 (2)	O9*B*—N8*B*—N7*B*	119.2 (2)
C5*A*—C4*A*—N7*A*—N8*A*	−175.3 (2)	C3*B*—C4*B*—N7*B*—N8*B*	9.6 (3)
C3*A*—C4*A*—N7*A*—N8*A*	5.4 (3)	C5*B*—C4*B*—N7*B*—N8*B*	−170.9 (2)
C4*A*—N7*A*—N8*A*—O9*A*	11.6 (3)	C4*B*—N7*B*—N8*B*—O10*B*	−178.0 (2)
C4*A*—N7*A*—N8*A*—O10*A*	−170.9 (2)	C4*B*—N7*B*—N8*B*—O9*B*	3.6 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N7*A*—H7*AA*···O2*B*$^{\rm i}$	0.90	1.83	2.734 (2)	176
N7*B*—H7*BA*···O3*A*$^{\rm ii}$	0.90	1.77	2.665 (2)	172
N1*A*—H1*AE*···O1*A*	0.90	1.94	2.771 (2)	154
N1*B*—H1*BE*···O1*B*	0.90	1.82	2.668 (2)	157
C3*A*—H3*AB*···O9*A*	0.96	2.16	2.737 (3)	117
C3*B*—H3*BB*···O9*B*	0.96	2.15	2.716 (3)	117
C5*A*—H5*AA*···O1*A*$^{\rm iii}$	0.96	2.62	3.176 (3)	117
C6*A*—H6*AA*···O1*A*$^{\rm iii}$	0.96	2.39	3.072 (3)	127
C3*B*—H3*BB*···O3*B*$^{\rm i}$	0.96	2.46	3.169 (3)	131
C5*B*—H5*BA*···O2*A*$^{\rm ii}$	0.96	2.41	3.369 (3)	173
C6*B*—H6*BA*···O10*A*$^{\rm iv}$	0.96	2.66	3.306 (3)	125

Symmetry codes: (i) $x, 1+y, z$; (ii) $\frac{5}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iv) $x, y-1, z$.

In compound (III), all the H-atom coordinates were refined, leading to C—H distances in the range 0.90 (3)–0.95 (2) Å, N—H distances of 0.94 (2) Å, and H—C—H angles in the range 97 (2)–115 (2)°. In compound (V), all the H atoms were treated as riding, with C—H = 0.96 Å and N—H = 0.90 Å.

For both compounds, cell refinement: *Kuma Diffraction Software* (Kuma Diffraction, 1997); data reduction: *Kuma Diffraction Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*); 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: GD1147). Services for accessing these data are described at the back of the journal.

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