Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Five *N*′-benzylidene-*N*-methylpyrazine-2-carbohydrazides

Ligia R. Gomes,[a] John Nicolson Low,[b]* Ana S. M. C. Rodrigues,[c] James L. Wardell,[b,d] Camillo H. da Silva Lima[d] and Marcus V. N. de Souza[d]

[a]REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre 687, P-4169-007 Porto, Portugal, [b]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, [c]Centro de Investigação em Química, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre 687, P-4169-007 Porto, Portugal, and [d]Instituto de Tecnología em Fármacos–Farmanguinhos, FioCruz – Fundação Oswaldo Cruz, R. Sizenando Nabuco 100, Manguinhos, 21041-250 Rio de Janeiro, RJ, Brazil
Correspondence e-mail: jnlow111@gmail.com

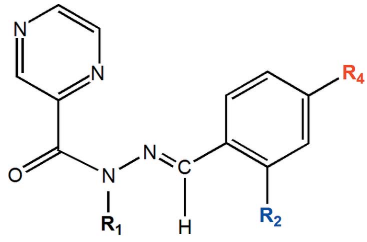
Received 2 April 2013
Accepted 11 April 2013

The compounds *N*′-benzylidene-*N*-methylpyrazine-2-carbohydrazide, $C_{13}H_{12}N_4O$, (II*a*), *N*′-(2-methoxybenzylidene)-*N*-methylpyrazine-2-carbohydrazide, $C_{14}H_{14}N_4O_2$, (II*b*), *N*′-(4-cyanobenzylidene)-*N*-methylpyrazine-2-carbohydrazide dihydrate, $C_{14}H_{11}N_5O{\cdot}2H_2O$, (II*c*), *N*-methyl-*N*′-(2-nitrobenzylidene)pyrazine-2-carbohydrazide, $C_{13}H_{11}N_5O_3$, (II*d*), and *N*-methyl-*N*′-(4-nitrobenzylidene)pyrazine-2-carbohydrazide, $C_{13}H_{11}N_5O_3$, (II*e*), have dihedral angles between the pyrazine rings and the benzene rings in the range 55–78°. These methylated pyrazine-2-carbohydrazides have supramolecular structures which are formed by weak C—H···O/N hydrogen bonds, with the exception of (II*c*) which is hydrated. There are π–π stacking interactions in all five compounds. Three of these structures are compared with their nonmethylated counterparts, which have dihedral angles between the pyrazine rings and the benzene rings in the range 0–6°.

Comment

Pyrazine derivatives exhibit a wide range of biological activities. Recent studies have revealed that pyrazine-2-carbohydrazides, (I) (see Scheme; Vergara *et al.*, 2009; Lima *et al.*, 2011), have moderate antituberculosis properties. The crystal structures of various pyrazine-2-carbohydrazides have been reported (Baddeley *et al.*, 2009; Howie *et al.*, 2010*a*,*b*,*c*; Howie, de Souza *et al.*, 2010; de Souza *et al.*, 2011). In continuation of these studies, the synthesis and antituberculosis activities of a series of methylated pyrazine-2-carbohydrazide derivatives, (II) (see Scheme), have been studied. It is worth noting that methylation of (I) occurred at the imine N atom rather than at the pyridine N atom. However, none of the compounds (II) was found to exhibit antituberculosis properties (de Souza, 2013).

A recently reported study of mono- and diesters of 3-(pyrazin-2-ylcarbonyl)dithiocarbazic acid suggested that the planarity of pyrazine derivatives may be a prerequisite for tubercolostatic activity (Szczesio *et al.*, 2011; Orlewska *et al.*, 2001). This prompted crystal structure determinations of the five title methylated pyrazine-2-carbohydrazide derivatives, namely *N*′-benzylidene-*N*-methylpyrazine-2-carbohydrazide, (II*a*) (Fig. 1), *N*′-(2-methoxybenzylidene)-*N*-methylpyrazine-2-carbohydrazide, (II*b*) (Fig. 2), *N*′-(4-cyanobenzylidene)-*N*-methylpyrazine-2-carbohydrazide dihydrate, (II*c*) (Fig. 3), *N*-methyl-*N*′-(2-nitrobenzylidene)pyrazine-2-carbohydrazide, (II*d*) (Fig. 4), and *N*-methyl-*N*′-(4-nitrobenzylidene)pyrazine-2-carbohydrazide, (II*e*) (Fig. 5). A comparative analysis of the structures of these inactive compounds on the one hand with,



(I*b*) R_1=R_4= H; R_2= OCH_3
(I*c*) R_1=R_2= H; R_4= CN
(I*d*) R_1=R_4= H; R_2= NO_2

(II*a*) R_1= CH_3; R_2=R_4=H
(II*b*) R_1= CH_3; R_4= H; R_2= OCH_3
(II*c*) R_1= CH_3; R_2= H; R_4= CN
(II*d*) R_1= CH_3; R_4= H; R_2= NO_2
(II*e*) R_1= CH_3; R_2= H; R_4= NO_2

on the other, those of moderately active *N*′-benzylidenepyrazine-2-carbohydrazide, (I*b*) (de Souza *et al.*, 2011), *N*′-(4-cyanobenzylidene)pyrazine-2-carbohydrazide, (I*c*) (Howie *et al.*, 2010*a*), and *N*′-(2-nitrobenzylidene)pyrazine-2-carbohydrazide, (I*d*) (Howie *et al.*, 2010*a*), will be a useful contribution to the understanding of the correlation between structure and activity.

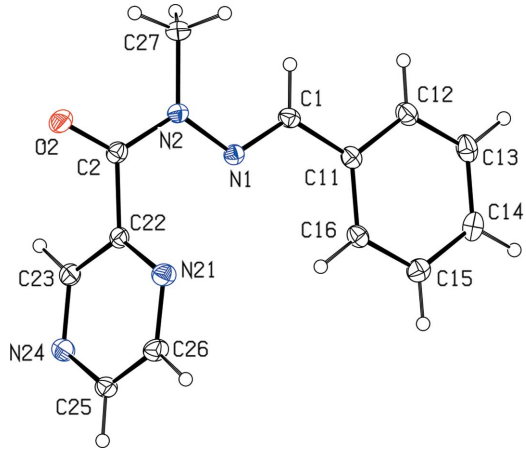


Figure 1
The molecular structure of (II*a*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

 doi:10.1107/S0108270113010056

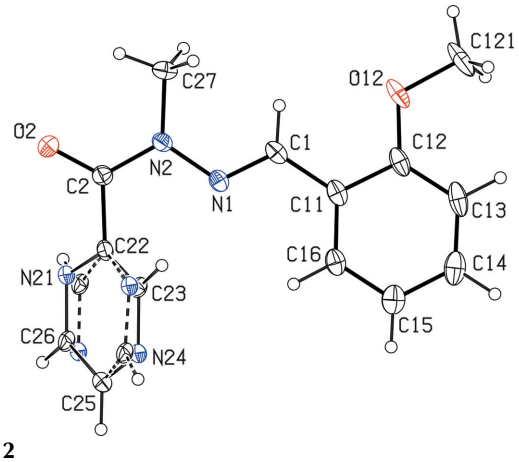


Figure 2
The molecular structure of (II*b*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The dashed lines show the minor disorder component of the pyrazine ring.

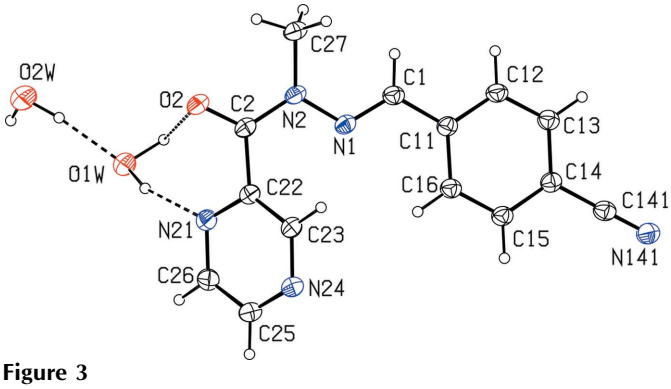


Figure 3
The molecular structure of (II*c*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Dashed lines indicate hydrogen bonding to the solvent water molecules.

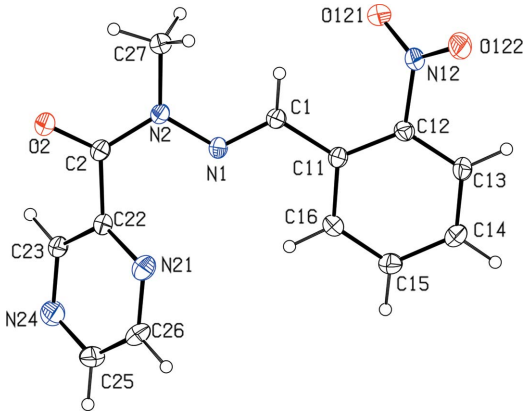


Figure 4
The molecular structure of (II*d*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

As will be shown, derivatives (II*a*)–(II*e*) are not planar, unlike the analogous compounds (I*b*)–(I*d*). A search of the Cambridge Structural Database (CSD, Version 5.34; Allen, 2002) revealed that pyrazine-2-carbohydrazides of type (I) exhibit a preference for conformations having the carbonyl

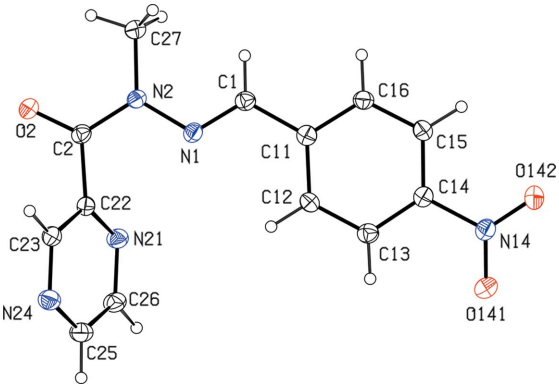


Figure 5
The molecular structure of (II*e*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

group *trans* to the H—N(pyrazinamide) bond, shown as conformation *E*(1) in Fig. 6. Furthermore, a short intramolecular pyrazine–hydrazide *ortho*-N···H—N′ contact is observed for the majority of these structures [see, for example, Baddeley *et al.* (2009), Howie *et al.* (2010*a*,*b*,*c*), Howie, de Souza *et al.* (2010) and de Souza *et al.* (2011)]. These two effects constrain the relative positions of the pyrazine N atoms with respect to the hydrazine group. Hyperconjugation from the heteroaryl ring to the benzene ring *via* the hydrazine unit has been suggested as the main contributor to the near planarity of type (I) compounds and this is reinforced by the intramolecular N—H···N hydrogen bond (Szczesio *et al.*, 2011). However, this planarity can be dramatically influenced by the nature and position of the substituents on the benzene ring.

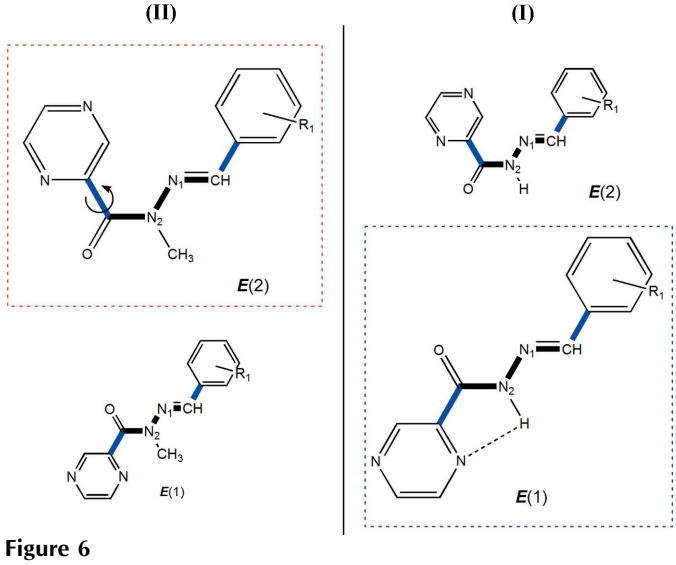


Figure 6
The conformations of *N*′-[(*E*)-aryl]pyrazine-2-carbohydrazides, where *E*(1) and *E*(2) are the *trans* and *cis* arrangements of the C=O and H—N2 bonds, respectively. The *E*(1) form is preferred by *N*′-arylpyrazine-2-carbohydrazides (de Souza *et al.*, 2011; Howie *et al.*, 2010*a*) and the *E*(2) form is adopted by the *N*-methyl-*N*′-arylpyrazine-2-carbohydrazides characterized in this study.

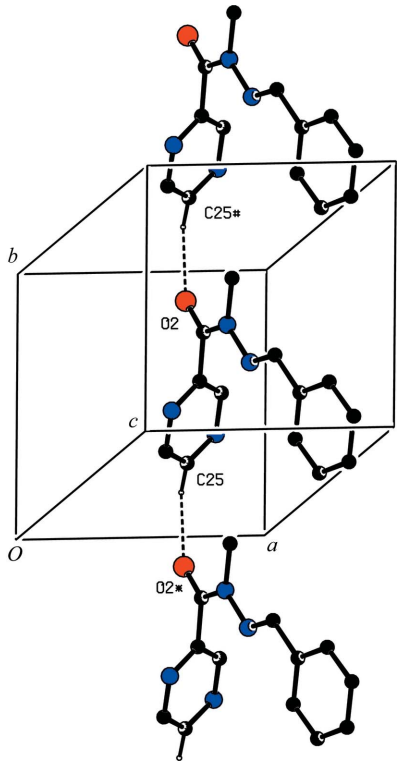


Figure 7
Part of the crystal structure of (II*a*), showing the chain which runs parallel to the *b* axis. Atoms labelled with an asterisk (*) or a hash symbol (#) are at the symmetry positions (x, $y-1$, z) and (x, $y+1$, z), respectively. H atoms not involved in hydrogen bonding (dashed lines) have been omitted.

As expected, the substitution of a methyl group on N2 in the pyrazine-2-carbohydrazide system induces significant structural change. The major changes are in the relative positions of the pyrazine ring and carbonyl groups, and in the nonplanarity of the methylated compounds. The methyl group precludes the formation of the intramolecular hydrogen bond observed in the compounds of type (I) and imposes steric hindrance near the pyrazine ring, with the result that the conformation of the compounds of type (II) is *E*(2) (Fig. 6), in contrast with the *E*(1) conformation assumed by nonmethylated compounds (I). The overall planarity is lost, probably due to the loss of hyperconjugation within the C(O)NMeN=C group. The deviations from planarity of (II*a*)–(II*e*) arise fundamentally from the rotation of the pyrazine (py) ring about the C(py)—C(=O) axis. Various torsion and other angles determined for (I) and (II) are listed in Table 1. The molecule of (I*b*) (de Souza *et al.*, 2011) is planar and lies on a crystallographic mirror plane, while that of (I*c*) (Howie *et al.*, 2010*a*) is nearly planar [$\theta = 5.82\ (7)^\circ$]. In contrast, θ values for compounds (II) are in the range 55–78° (Table 1). The rotation of the pyrazine ring about the C22—C2 axis is the main contributor to the nonplanarity of the methylated compounds, since the benzene rings are largely coplanar with the CNNC spacer group. Compound (II*a*) exhibits the largest dihedral angle and the greatest deviation of atom C2 from the mean plane through the pyrazine ring. The angle the pyrazine ring makes with the C22—C2 bond is probably due to the participation of atom C25 as a donor in an intermolecular hydrogen bond.

Compound (II*b*) exhibits conformational disorder. The pyrazine ring is rotated anticlockwise by 51.10 (3)° for the major component and clockwise by 67.14 (3)° for the minor one. These rotations are based on the torsion angle φ_1 in Table 1 for both the major and minor components. It is interesting to note that atom N21 of the major component participates as an acceptor in a weak N···H—C intermolecular interaction, while the equivalent interaction is absent in the minor component.

Compound (II*c*) crystallizes as a dihydrate. The asymmetric unit was selected such that the three molecules form a hydrogen-bonded unit. The water molecules are involved in hydrogen-bonded chains with atoms N21.

In compound (II*d*), the plane of the benzene ring is practically coplanar with the plane of the CNNC spacer group, the dihedral angle being 5.3 (3)°. The dihedral angle between the plane of the CNNC spacer group and the mean plane of the pyrazine ring is 53.0 (2)°, a clockwise rotation, with reference to atom N21, around the C2—C22 axis. The nitro group is twisted out of the plane of the benzene ring by 45.8 (4)°. In spite of this, there is a short contact between atoms O121 and H1 of 2.40 Å, with an angle at atom H1 of 112°. The twist of this nitro group may result as a compromise between this weak intramolecular interaction and a weak intermolecuar interaction involving atom O122 of the nitro group.

In isomeric compound (II*e*), the dihedral angle between the benzene-ring mean plane and the CNNC spacer group is 8.26 (17)°, and the dihedral angle between the CNNC spacer group and the mean plane of the pyrazine ring is 59.65 (17)°, again a clockwise rotation, with reference to atom N21, around the C2—C22 axis. In contrast with (II*d*), the nitro substituent is twisted out of the plane of the benzene ring plane by only 7.1 (2)°.

Only in hydrated (II*c*) are strong hydrogen bonds present. For the other compounds studied here, the intermolecular arrangements are formed by weak C—H···O/N hydrogen bonds and π–π stacking interactions.

For compound (II*a*), a weak C25–H25···O2(x, $y-1$, z) hydrogen bond links the molecules into a *C*(7) chain (Bernstein *et al.*, 1995), which runs parallel to the *b* axis (Table 2 and Fig. 7). There is a π–π short contact between the pyrazine rings, lying across the centre of symmetry at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$); the centroid–centroid distance is 3.6631 (7) Å, the perpendicular distance between the rings is 3.6415 (5) Å and the slippage is 0.395 Å.

In compound (II*b*), the intermolecular short contacts (Table 3) involve atom C13 as a donor and atom N21 of the major disordered pyrazine ring as an acceptor. There are no similar contacts for the minor component. This suggests that this interaction does not play any significant part in the supramolecular structure of this compound. The other short intermolecular contacts involve the methyl H atoms (Table 3). There is a π–π short contact between the pyrazine rings, which stack above each other with unit translation along the *a* axis; for the major component, the centroid–centroid distance is

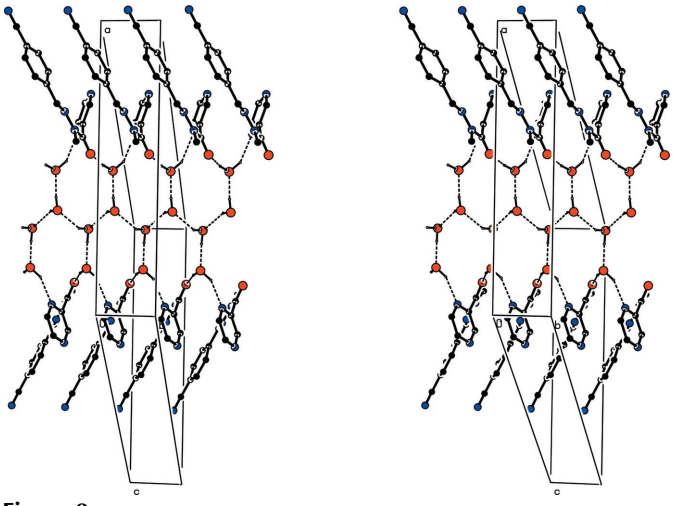


Figure 8
A stereoview of (II*c*), showing the structure formed by the rings generated by the water chain, which runs parallel to the *b* axis. H atoms not involved in hydrogen bonding (dashed lines) have been omitted.

4.032 (7) Å, the perpendicular distance between the rings is 3.600 (3) Å and the slippage is 1.816 Å, while for minor component, the centroid–centroid distance is 4.033 (8) Å, the perpendicular distance between the rings is 3.164 (4) Å and the slippage is 2.500 Å. The benzene rings also stack above each other with unit translation along the *a* axis; the centroid–centroid distance is 4.032 (6) Å, the perpendicular distance between the rings is 3.4489 (9) Å and the slippage is 2.088 Å.

For compound (II*c*), water molecule O1*W* links the molecules into a $C_2^2(7)$ chain *via* O1*W*—H1*WB*···N21 (within the defined asymmetric unit) and O1*W*—H1*WA*···O2(x, $y-1$, z) hydrogen bonds. This chain runs parallel to the *b* axis. The O2*W* water molecules are linked into a *C*2 chain by an O2—H2*WB*···O2*W*($-x+1$, $y-\frac{1}{2}$, $-z+\frac{1}{2}$) hydrogen bond. This chain of water molecules links two antiparallel chains together to form a ribbon which runs parallel to the *b* axis (Table 4 and Fig. 8). These chains are linked into a three-dimensional structure by weak C13—H13···O1*W*(x, $-y+\frac{1}{2}$, $z+\frac{1}{2}$) and C26—H26···N141(x, $-y+\frac{1}{2}$, $-z-\frac{1}{2}$) hydrogen bonds (Table 4). There is a π–π short contact between the pyrazine rings, which stack above each other along the *b* axis; the centroid–centroid distance is 3.9517 (15) Å, the perpendicular distance between the rings is 3.5627 (10) Å and the slippage is 1.710 Å. The benzene rings also stack above each other with unit translation along the *a* axis; the centroid–centroid distance is 3.9516 (15) Å, the perpendicular distance between the rings is 3.4128 (10) Å and the slippage is 2.088 Å.

For compound (II*d*), a weak C14—H14···O2($x+1$, y, $z-1$) hydrogen bond links the molecules into a $C(10)$ chain, which is formed by unit translations along the *a* and *c* axes; this chain and a centrosymetrically antiparallel chain are linked by a C13—H13···O122($-x+2$, $-y+1$, $-z$) hydrogen bond and its centrosymetrically related bond, so forming an $R_2^2(10)$ ring, linking the molecules into ribbons which lie parallel to (101) (Fig. 9 and Table 5). There is a π–π short contact between the pyrazine rings, which stack above each other along the *a* axis; the centroid–centroid distance is 3.797 (2) Å, the perpendicular distance between the rings is 3.3838 (15) Å and the slippage is 1.723 Å. The benzene rings also stack above each other with unit translation along the *a* axis; the centroid–centroid distance is 3.797 (2) Å, the perpendicular distance between the rings is 3.5009 (14) Å and the slippage is 2.471 Å,

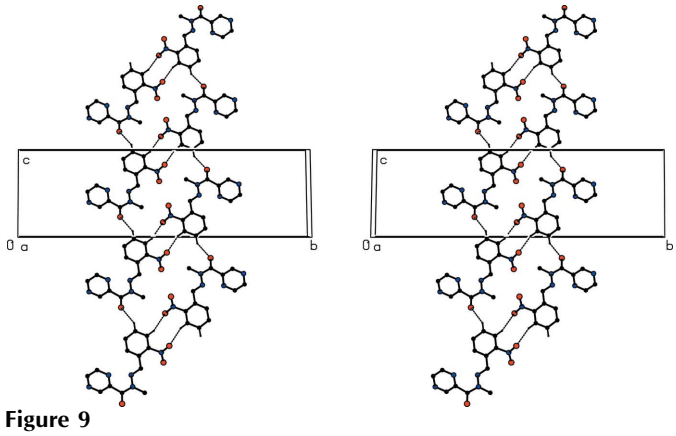


Figure 9
A stereoview of (II*d*), showing the ribbon structure formed by the linking of centrosymmetric dimers. This ribbon runs parallel to the (101) plane. H atoms not involved in hydrogen bonding (dashed lines) have been omitted.

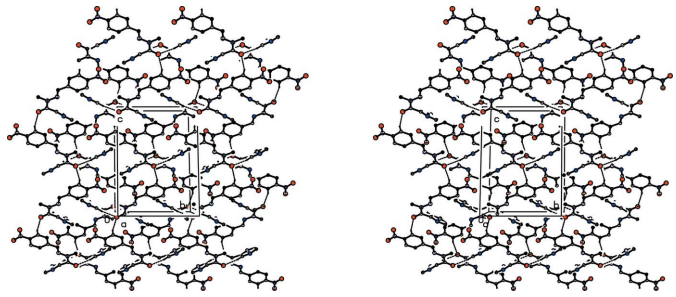


Figure 10
A stereoview of (II*e*), showing the double-sided sheet which runs parallel to the ($\bar{1}$01) plane. H atoms not involved in hydrogen bonding (dashed lines) have been omitted.

For compound (II*e*), a C15—H15···O2($x+\frac{1}{2}$, $-y+\frac{1}{2}$, $z+\frac{1}{2}$) hydrogen bond links the molecules into a $C(9)$ chain. The molecules are linked across a centre of symmetry at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) by a C23—H23···O2($-x+1$, $-y+1$, $-z+1$) hydrogen bond. These two interactions combine the molecules into a double-sided sheet which runs parallel to the ($\bar{1}$01) plane (Fig. 10 and Table 6). The pyrazine rings stack above each other across a centre of symmetry at ($\frac{1}{2}$, 0, $\frac{1}{2}$); the centroid–centroid distance is 4.1331 (7) Å, the perpendicular distance between the rings is 3.4738 (11) Å and the slippage is 2.240 Å.

Experimental

A reaction mixture of the appropriate *N*′-[(*E*)-benzylidene]pyrazine-2-carbohydrazide derivative (0.75 mmol; Vergara *et al.*, 2009; Lima *et al.*, 2011), Na_2CO_3 (*ca* 4 mmol) and MeI (3 mmol) in acetone (4 ml) was heated at 313 K for 18 h under a nitrogen atmosphere. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure to leave a residue, which was added to ice–water. The solid which separated was collected and washed with cold Et_2O (3 × 10 ml), yielding the *N*-methylpyrazine-2-carbohydrazide deri-

Table 1
Comparison of selected geometric parameters (°).

θ is the dihedral angle between the pyrazine ring and the phenyl ring, φ_1 and φ_2 are the torsion angles N21—C22—C2—N2 and N1—C1—C11—C12, respectively, and φ_3 is the angular deviation of atom C2 from the mean plane of the pyrazine ring. In (I*b*), the molecule sits on a mirror plane.

Compound	R_1	θ	φ_1	φ_2	φ_3
(II*a*)	H	77.46 (6)	72.83 (14)	175.16 (10)	6.77 (8)
(II*b*)	*o*-OCH_3 (major)	58.1 (3)	−128.9 (4)	168.73 (18)	3.2 (3)
	o-OCH_3 (minor)	69.5 (3)	67.1 (6)	n/a	4.1 (3)
(II*c*)	[*p*-CN]·$2H_2O$	55.43 (12)	−135.8 (2)	169.8 (2)	4.06 (14)
(II*d*)	*o*-NO_2	48.51(17	54.6 (4)	178.7 (3)	6.3 (2)
(II*e*)	*p*-NO_2	55.39 (9)	−62.3 (2)	3.5 (3)	4.59 (13)
(I*b*)	*o*-OCH_3	0.0	0.0	0.0	0.0
(I*c*)	(*p*-CN	5.82 (7)	−3.76 (18)	176.21 (17)	1.56 (9)
(I*d*)	(*o*-NO_2	0.54 (5)	−12.72 (15)	−169.90 (10)	1.49 (7)

vative as a colourless crystalline solid. Further recrystallizations of the *N*-methylpyrazine-2-carbohydrazides were carried out from appropriate solvents. A consistent recrystallization solvent, which could provide suitable crystals for the X-ray study for the five derivatives reported here, was not found. None of the solvents used was specially dried.

Compound (II*a*) (yield 54%, m.p. 391–393 K) was recrystallized from EtOH for the X-ray analysis, (II*b*) (yield 63%, 378–380 K) from $MeOCH_2CH_2OH$, (II*c*) (yield 73%, m.p. 383–384 K) from dimethyl sulfoxide, (II*d*) (yield 66%, m.p. 424–425 K) from EtOH and (II*e*) (yield 58%, m.p. 458–460 K) from EtOH.

Compound (II*a*)

Crystal data

$C_{13}H_{12}N_4O$
M_r = 240.27
Triclinic, $P\overline{1}$
a = 7.4961 (3) Å
b = 7.6923 (3) Å
c = 10.8821 (7) Å
α = 73.421 (5)°
β = 84.844 (6)°
γ = 88.530 (6)°
V = 598.97 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 120 K
0.56 × 0.43 × 0.23 mm

Data collection

Rigaku R-AXIS conversion diffractometer
Absorption correction: multi-scan (*CrystalClear-SM Expert*; Rigaku, 2011)
T_{min} = 0.952, T_{max} = 0.980
7672 measured reflections
2712 independent reflections
2270 reflections with $I > 2\sigma(I)$
R_{int} = 0.016

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.119
S = 1.17
2712 reflections
164 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 2
Hydrogen-bond geometry (Å, °) for (II*a*).

D—H···A	D—H	H···A	D···A	D—H···A
C25—H25···O2^{i}	0.95	2.59	3.1823 (16)	121

Symmetry code: (i) $x, y-1, z$.

Table 3
Hydrogen-bond geometry (Å, °) for (II*b*).

D—H···A	D—H	H···A	D···A	D—H···A
C13—H13···N21^{i}	0.95	2.61	3.514 (8)	159

Symmetry code: (i) $x-1, y+1, z$.

Compound (II*b*)

Crystal data

$C_{14}H_{14}N_4O_2$
M_r = 270.29
Triclinic, $P\overline{1}$
a = 4.032 (5) Å
b = 10.628 (15) Å
c = 15.034 (19) Å
α = 94.08 (3)°
β = 90.36 (3)°
γ = 92.07 (3)°
V = 642.2 (15) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 100 K
0.18 × 0.13 × 0.12 mm

Data collection

Rigaku Saturn724+ diffractometer
Absorption correction: multi-scan (*CrystalClear-SM Expert*; Rigaku, 2011)
T_{min} = 0.983, T_{max} = 0.988
4990 measured reflections
2246 independent reflections
1859 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.159
S = 1.10
2246 reflections
185 parameters
6 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Compound (II*c*)

Crystal data

$C_{14}H_{11}N_5O·2H_2O$
M_r = 301.31
Monoclinic, $P2_1/c$
a = 19.395 (3) Å
b = 3.9517 (5) Å
c = 23.270 (3) Å
β = 124.890 (9)°
V = 1462.9 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 120 K
0.56 × 0.23 × 0.08 mm

Data collection

Rigaku R-AXIS conversion diffractometer
Absorption correction: multi-scan (*CrystalClear-SM Expert*; Rigaku, 2011)
T_{min} = 0.946, T_{max} = 0.992
12564 measured reflections
3341 independent reflections
2189 reflections with $I > 2\sigma(I)$
R_{int} = 0.053

Table 4
Hydrogen-bond geometry (Å, °) for (II*c*).

D—H···A	D—H	H···A	D···A	D—H···A
O1*W*—H1*WB*···N21	0.96	2.08	2.963 (2)	153
O2*W*—H2*WA*···O1*W*	0.91	1.84	2.745 (3)	172
O1*W*—H1*WA*···O2^{i}	0.99	1.83	2.807 (2)	167
O2*W*—H2*WB*···O2*W*^{ii}	0.84	1.96	2.649 (3)	138
C13—H13···O1*W*^{iii}	0.95	2.59	3.465 (3)	152
C26—H26···N141^{iv}	0.95	2.62	3.480 (3)	150

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

Table 5
Hydrogen-bond geometry (Å, °) for (II*d*).

D—H···A	D—H	H···A	D···A	D—H···A
C13—H13···O122^{i}	0.95	2.54	3.439 (5)	157
C14—H14···O2^{ii}	0.95	2.58	3.428 (4)	150

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

Table 6
Hydrogen-bond geometry (Å, °) for (II*e*).

D—H···A	D—H	H···A	D···A	D—H···A
C15—H15···O2^{i}	0.95	2.42	3.325 (2)	159
C23—H23···O2^{ii}	0.95	2.36	3.290 (2)	166

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

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.063	202 parameters
$wR(F^2)$ = 0.248	H-atom parameters constrained
S = 1.23	$\Delta\rho_{max}$ = 0.40 e Å^{-3}
3341 reflections	$\Delta\rho_{min}$ = −0.33 e Å^{-3}

Compound (II*d*)

Crystal data

$C_{13}H_{11}N_5O_3$	V = 1261.33 (11) Å^3
M_r = 285.27	Z = 4
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 3.7974 (2) Å	μ = 0.11 mm^{-1}
b = 33.3126 (17) Å	T = 120 K
c = 10.0959 (5) Å	0.40 × 0.10 × 0.02 mm
β = 99.027 (2)°	

Data collection

Nonius KappaCCD area-detector diffractometer	11176 measured reflections 2168 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	1563 reflections with $I > 2\sigma(I)$ R_{int} = 0.071
T_{min} = 0.957, T_{max} = 0.998	

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.080	191 parameters
$wR(F^2)$ = 0.196	H-atom parameters constrained
S = 1.10	$\Delta\rho_{max}$ = 0.32 e Å^{-3}
2168 reflections	$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Compound (II*e*)

Crystal data

$C_{13}H_{11}N_5O_3$	V = 2628.7 (5) Å^3
M_r = 285.27	Z = 8
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
a = 17.510 (2) Å	μ = 0.11 mm^{-1}
b = 10.5421 (11) Å	T = 120 K
c = 14.9638 (14) Å	0.42 × 0.24 × 0.16 mm
β = 107.887 (8)°	

Data collection

Rigaku R-AXIS conversion diffractometer	7284 measured reflections 3000 independent reflections
Absorption correction: multi-scan (*CrystalClear-SM Expert*; Rigaku, 2011)	2610 reflections with $I > 2\sigma(I)$ R_{int} = 0.042
T_{min} = 0.956, T_{max} = 0.983	

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.060	191 parameters
$wR(F^2)$ = 0.169	H-atom parameters constrained
S = 1.08	$\Delta\rho_{max}$ = 0.31 e Å^{-3}
3000 reflections	$\Delta\rho_{min}$ = −0.26 e Å^{-3}

In all five title compounds, H atoms were treated as riding, with C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic H atoms, or C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms. In (II*c*), the water H atoms were located in a difference map and allowed to ride at these positions, with U_{iso}(H) = 1.5U_{eq}(O). The positions of the H atoms, methyl groups and water molecules were checked on difference maps during the refinement and after the refinement was complete. Initially, the disordered components of (II*b*) were located on a difference map. The disordered ring were found to be rotated by approximately 180° with respect to each other. In (II*b*), both disordered rings were restrained to be planar. Atoms N21, N24, N21*A* and N24*A* were constrained to have the same anisotropic displacement parameters, as were atoms C23, C26, C23*A* and C26*A*. The site-occupation factor for the major component was 0.529 (9). No constraints were appled to the bond lengths and angles.

Data collection: *CrystalClear-SM Expert* (Rigaku, 2011) for (II*a*), (II*b*), (II*c*) and (II*e*); *COLLECT* (Nonius, 2000) for (II*d*). Cell refinement: *CrystalClear-SM Expert* for (II*a*), (II*b*), (II*c*) and (II*e*); *SCALEPACK* (Otwinowski & Minor, 1997) for (II*d*). Data reduction: *CrystalClear-SM Expert* for (II*a*), (II*b*), (II*c*) and (II*e*); *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK* for (II*d*). For all compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *OSCAIL* (McArdle *et al.*, 2004) and *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *OSCAIL* and *SHELXL97*.

The authors thank the staff at the National Crystallographic Service, University of Southampton, for the data collection, and for help and advice (Coles & Gale, 2012).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3484). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Baddeley, T. C., Howie, R. A., Lima, C. H. da S., Kaiser, C. R., de Souza, M. V. N., James, L., Wardell, J. L. & Wardell, S. M. S. V. (2009). *Z. Kristallogr.* **224**, 506–514.
Bernstein, J., Davis, R. E., Shimoni, I. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Coles, S. J. & Gale, P. A. (2012). *Chem. Sci.* **3**, 683–689.
Howie, R. A., de Souza, M. V. N., Wardell, S. M. S. V., Wardell, J. L. & Tiekink, E. R. T. (2010). *Acta Cryst.* E**66**, o178–o179.
Howie, R. A., Lima, C. H. S., Kaiser, C. R., de Souza, M. V. N., Wardell, J. L. & Wardell, S. M. S. V. (2010*a*). *Z. Kristallogr.* **225**, 19–28.
Howie, R. A., Lima, C. H. S., Kaiser, C. R., de Souza, M. V. N., Wardell, J. L. & Wardell, S. M. S. (2010*b*). *Z. Kristallogr.* **225**, 158–166.
Howie, R. A., Lima, C. H. S., Kaiser, C. R., de Souza, M. V. N., Wardell, J. L. & Wardell, S. M. S. (2010*c*). *Z. Kristallogr.* **225**, 349–358.
Lima, C. H. S., Henriques, M. G. M. O., Candea, A. L. P., Lourenco, M. C. S., Bezerra, F. A. F. M., Ferreira, M. L., Kaiser, C. R. & de Souza, M. V. N. (2011). *Med. Chem.* **7**, 245–249.

McArdle, P., Gilligan, K., Cunningham, D., Dark, R. & Mahon, M. (2004). *CrystEngComm*, **6**, 303–309.
Nonius (2000). *COLLECT*. Nonius BV, Delft, The Netherlands.
Orlewska, C., Foks, H., Sowinski, P., Martynowski, D., Olczak, A. & Glówka, M. L. (2001). *Pol. J. Chem.* **75**, 1237–1245.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Rigaku (2011). *CrystalClear-SM Expert*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Souza, M. V. N. de (2013). Unpublished results.
Souza, M. V. N. de, Lima, C. H. da S., Wardell, J. L., Wardell, S. M. S. V. & Tiekink, E. R. T. (2011). *Acta Cryst.* E**67**, o1714–o1715.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Szczesio, M., Olczak, A., Gołka, J., Gobis, K., Foks, H. & Główka, M. L. (2011). *Acta Cryst.* C**67**, o235–o240.
Vergara, F. M. F., Lima, C. H. da S., Henriques, M. das G. M. de O., Candéa, A. L. P., Lourenço, M. C. S., Ferreira, M. de L., Kaiser, C. R. & de Souza, M. V. N. (2009). *Eur. J. Med. Chem.* **44**, 4954–4959.

supplementary materials

Acta Cryst. (2013). C**69**, 549-555 [doi:10.1107/S0108270113010056]

Five *N*′-benzylidene-*N*-methylpyrazine-2-carbohydrazides

Ligia R. Gomes, John Nicolson Low, Ana S. M. C. Rodrigues, James L. Wardell, Camillo H. da Silva Lima and Marcus V. N. de Souza

(IIa) *N*′-Benzylidene-*N*-methylpyrazine-2-carbohydrazide

Crystal data

$C_{13}H_{12}N_4O$
$M_r = 240.27$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 7.4961$ (3) Å
$b = 7.6923$ (3) Å
$c = 10.8821$ (7) Å
$\alpha = 73.421$ (5)°
$\beta = 84.844$ (6)°
$\gamma = 88.530$ (6)°
$V = 598.97$ (5) Å^3
$Z = 2$
$F(000) = 252$
$D_x = 1.332$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å
Cell parameters from 6254 reflections
$\theta = 3.2$–27.4°
$\mu = 0.09$ mm^{-1}
$T = 120$ K
Block, orange
0.56 × 0.43 × 0.23 mm

Data collection

Rigaku R-AXIS conversion diffractometer
Radiation source: Sealed tube
Graphite monochromator
Detector resolution: 10.0000 pixels mm^{-1}
profile data from ω–scans
Absorption correction: multi-scan (*CrystalClear*-SM Expert; Rigaku, 2011)
$T_{min} = 0.952$, $T_{max} = 0.980$
7672 measured reflections
2712 independent reflections
2270 reflections with $I > 2\sigma(I)$
$R_{int} = 0.016$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.2°$
$h = -9\rightarrow9$
$k = -9\rightarrow9$
$l = -14\rightarrow14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.119$
$S = 1.17$
2712 reflections
164 parameters
0 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0656P)^2 + 0.0688P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Special details

Experimental. Compound (II*a*): ^{1}H NMR (500 MHz, $CDCl_3$, δ, p.p.m.): 8.85 (, s, H_3), 8.69 (1H, s, H_5), 8.66 (1H, s, H_6), 7.81 (1H, N═CH), 7.39–7.33 (5H, m, phenyl), 3.62 (3H, s, NCH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ, p.p.m.): 167.5, 150.2, 144.9, 144.7, 143.8, 141.1, 133.8, 130.2, 128.8, 127.3, 28.5; IR (KBr, v, cm^{-1}): 1676 (C═O), 1606 (–N═C–CH_3). LC/MS: m/z [M]$^-$: 240.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness 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 threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *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}
O2	0.59462 (13)	0.82450 (11)	0.15785 (9)	0.0353 (2)
N1	0.71743 (12)	0.48356 (12)	0.42370 (9)	0.0222 (2)
N2	0.65947 (12)	0.65306 (12)	0.35592 (9)	0.0233 (2)
N21	0.51069 (14)	0.38869 (14)	0.21804 (10)	0.0300 (2)
N24	0.78603 (14)	0.37332 (14)	0.02828 (10)	0.0313 (3)
C1	0.75771 (14)	0.46307 (16)	0.53921 (10)	0.0239 (2)
H1	0.7479	0.5633	0.5740	0.029*
C2	0.62923 (15)	0.67640 (15)	0.23037 (11)	0.0244 (2)
C11	0.81848 (14)	0.28776 (16)	0.61799 (10)	0.0237 (2)
C12	0.87332 (16)	0.27812 (17)	0.73924 (11)	0.0299 (3)
H12	0.8700	0.3838	0.7680	0.036*
C13	0.93248 (17)	0.11570 (19)	0.81768 (12)	0.0338 (3)
H13	0.9713	0.1109	0.8993	0.041*
C14	0.93520 (16)	−0.03992 (18)	0.77750 (12)	0.0321 (3)
H14	0.9753	−0.1514	0.8316	0.039*
C15	0.87901 (16)	−0.03243 (17)	0.65759 (12)	0.0295 (3)
H15	0.8799	−0.1393	0.6303	0.035*
C16	0.82177 (15)	0.13007 (16)	0.57781 (11)	0.0256 (3)
H16	0.7847	0.1345	0.4957	0.031*
C22	0.64153 (15)	0.51242 (15)	0.18023 (10)	0.0223 (2)
C23	0.77724 (16)	0.50456 (16)	0.08704 (11)	0.0277 (3)
H23	0.8673	0.5955	0.0639	0.033*
C25	0.65355 (16)	0.25194 (16)	0.06350 (11)	0.0267 (3)
H25	0.6518	0.1578	0.0230	0.032*
C26	0.51892 (16)	0.25938 (17)	0.15723 (12)	0.0302 (3)
H26	0.4283	0.1690	0.1796	0.036*
C27	0.65016 (16)	0.80741 (16)	0.40887 (12)	0.0285 (3)
H27A	0.6018	0.9128	0.3468	0.043*
H27B	0.7705	0.8357	0.4262	0.043*
H27C	0.5719	0.7775	0.4892	0.043*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0499 (6)	0.0231 (5)	0.0324 (5)	0.0007 (4)	−0.0118 (4)	−0.0049 (3)
N1	0.0209 (5)	0.0222 (5)	0.0234 (5)	−0.0011 (3)	−0.0015 (3)	−0.0066 (4)
N2	0.0255 (5)	0.0208 (5)	0.0245 (5)	−0.0013 (4)	−0.0028 (4)	−0.0079 (4)
N21	0.0280 (5)	0.0304 (5)	0.0331 (5)	−0.0066 (4)	0.0022 (4)	−0.0124 (4)
N24	0.0354 (6)	0.0316 (6)	0.0280 (5)	−0.0056 (4)	0.0015 (4)	−0.0111 (4)
C1	0.0231 (5)	0.0262 (6)	0.0248 (5)	−0.0027 (4)	−0.0009 (4)	−0.0111 (4)
C2	0.0230 (5)	0.0233 (6)	0.0266 (6)	−0.0028 (4)	−0.0034 (4)	−0.0061 (4)
C11	0.0189 (5)	0.0298 (6)	0.0229 (5)	−0.0031 (4)	0.0002 (4)	−0.0084 (4)
C12	0.0324 (6)	0.0348 (7)	0.0241 (6)	−0.0039 (5)	−0.0024 (5)	−0.0105 (5)
C13	0.0345 (7)	0.0422 (7)	0.0230 (6)	−0.0044 (5)	−0.0060 (5)	−0.0052 (5)
C14	0.0264 (6)	0.0333 (7)	0.0300 (6)	−0.0015 (5)	−0.0025 (5)	0.0018 (5)
C15	0.0259 (6)	0.0288 (6)	0.0333 (6)	−0.0015 (5)	−0.0005 (5)	−0.0087 (5)
C16	0.0228 (5)	0.0314 (6)	0.0237 (5)	−0.0016 (4)	−0.0022 (4)	−0.0094 (5)
C22	0.0248 (5)	0.0220 (5)	0.0199 (5)	−0.0009 (4)	−0.0067 (4)	−0.0040 (4)
C23	0.0305 (6)	0.0261 (6)	0.0261 (6)	−0.0076 (5)	0.0003 (4)	−0.0067 (5)
C25	0.0313 (6)	0.0255 (6)	0.0254 (6)	−0.0007 (4)	−0.0072 (4)	−0.0089 (4)
C26	0.0273 (6)	0.0286 (6)	0.0368 (6)	−0.0074 (5)	−0.0020 (5)	−0.0122 (5)
C27	0.0307 (6)	0.0254 (6)	0.0331 (6)	−0.0008 (5)	−0.0044 (5)	−0.0138 (5)

Geometric parameters (Å, º)

O2—C2	1.2233 (14)	C13—C14	1.3858 (19)
N1—C1	1.2841 (14)	C13—H13	0.9500
N1—N2	1.3830 (13)	C14—C15	1.3921 (17)
N2—C2	1.3652 (14)	C14—H14	0.9500
N2—C27	1.4579 (13)	C15—C16	1.3858 (17)
N21—C22	1.3376 (15)	C15—H15	0.9500
N21—C26	1.3402 (15)	C16—H16	0.9500
N24—C25	1.3341 (15)	C22—C23	1.3833 (16)
N24—C23	1.3378 (15)	C23—H23	0.9500
C1—C11	1.4628 (16)	C25—C26	1.3811 (17)
C1—H1	0.9500	C25—H25	0.9500
C2—C22	1.5084 (15)	C26—H26	0.9500
C11—C12	1.3984 (15)	C27—H27A	0.9800
C11—C16	1.4008 (16)	C27—H27B	0.9800
C12—C13	1.3846 (18)	C27—H27C	0.9800
C12—H12	0.9500		
C1—N1—N2	117.51 (9)	C16—C15—C14	120.36 (11)
C2—N2—N1	116.86 (9)	C16—C15—H15	119.8
C2—N2—C27	120.23 (9)	C14—C15—H15	119.8
N1—N2—C27	122.54 (9)	C15—C16—C11	120.10 (10)
C22—N21—C26	115.12 (10)	C15—C16—H16	119.9
C25—N24—C23	115.75 (10)	C11—C16—H16	119.9
N1—C1—C11	121.02 (10)	N21—C22—C23	122.18 (10)
N1—C1—H1	119.5	N21—C22—C2	118.63 (10)
C11—C1—H1	119.5	C23—C22—C2	118.84 (10)

O2—C2—N2	122.49 (10)	N24—C23—C22	122.30 (10)
O2—C2—C22	119.42 (10)	N24—C23—H23	118.9
N2—C2—C22	118.09 (9)	C22—C23—H23	118.9
C12—C11—C16	119.02 (11)	N24—C25—C26	121.81 (10)
C12—C11—C1	118.09 (10)	N24—C25—H25	119.1
C16—C11—C1	122.89 (10)	C26—C25—H25	119.1
C13—C12—C11	120.51 (11)	N21—C26—C25	122.81 (10)
C13—C12—H12	119.7	N21—C26—H26	118.6
C11—C12—H12	119.7	C25—C26—H26	118.6
C12—C13—C14	120.21 (11)	N2—C27—H27A	109.5
C12—C13—H13	119.9	N2—C27—H27B	109.5
C14—C13—H13	119.9	H27A—C27—H27B	109.5
C13—C14—C15	119.79 (11)	N2—C27—H27C	109.5
C13—C14—H14	120.1	H27A—C27—H27C	109.5
C15—C14—H14	120.1	H27B—C27—H27C	109.5
C1—N1—N2—C2	175.51 (10)	C12—C11—C16—C15	−0.11 (17)
C1—N1—N2—C27	2.55 (15)	C1—C11—C16—C15	−179.28 (10)
N2—N1—C1—C11	179.41 (9)	C26—N21—C22—C23	−1.31 (16)
N1—N2—C2—O2	−172.75 (10)	C26—N21—C22—C2	171.88 (10)
C27—N2—C2—O2	0.38 (17)	O2—C2—C22—N21	−107.86 (13)
N1—N2—C2—C22	6.53 (14)	N2—C2—C22—N21	72.83 (14)
C27—N2—C2—C22	179.66 (9)	O2—C2—C22—C23	65.56 (15)
N1—C1—C11—C12	175.16 (10)	N2—C2—C22—C23	−113.74 (12)
N1—C1—C11—C16	−5.65 (17)	C25—N24—C23—C22	1.21 (17)
C16—C11—C12—C13	0.94 (17)	N21—C22—C23—N24	0.31 (18)
C1—C11—C12—C13	−179.85 (10)	C2—C22—C23—N24	−172.87 (10)
C11—C12—C13—C14	−1.04 (19)	C23—N24—C25—C26	−1.67 (17)
C12—C13—C14—C15	0.31 (19)	C22—N21—C26—C25	0.85 (17)
C13—C14—C15—C16	0.52 (18)	N24—C25—C26—N21	0.68 (19)
C14—C15—C16—C11	−0.62 (18)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C25—H25···O2^{i}	0.95	2.59	3.1823 (16)	121

Symmetry code: (i) *x*, *y*−1, *z*.

(IIb) *N′*-(2-Methoxybenzylidene)-*N*-methylpyrazine-2-carbohydrazide

Crystal data

$C_{14}H_{14}N_4O_2$
$M_r = 270.29$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 4.032$ (5) Å
$b = 10.628$ (15) Å
$c = 15.034$ (19) Å
$\alpha = 94.08$ (3)°
$\beta = 90.36$ (3)°
$\gamma = 92.07$ (3)°
$V = 642.2$ (15) Å^3
$Z = 2$
$F(000) = 284$
$D_x = 1.394$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å
Cell parameters from 1623 reflections
$\theta = 2.4$–31.2°
$\mu = 0.10$ mm^{-1}

T = 100 K
Block, brown

0.18 × 0.13 × 0.12 mm

Data collection

Rigaku Saturn724+ diffractometer
Radiation source: Rotating anode
Confocal monochromator
Detector resolution: 28.5714 pixels mm^{-1}
profile data from ω–scans
Absorption correction: multi-scan (*CrystalClear*-SM Expert; Rigaku, 2011)
T_{min} = 0.983, T_{max} = 0.988

4990 measured reflections
2246 independent reflections
1859 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 25.0°, θ_{min} = 3.2°
h = −3→4
k = −12→12
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.159
S = 1.10
2246 reflections
185 parameters
6 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0898P)^2 + 0.0839P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Special details

Experimental. Compound (II*b*): ^{1}H NMR (500 MHz, $CDCl_3$, δ, p.p.m.): 8.85 (1H, s, H_3), 8.69 (1H, s, H_5), 8.64 (1H, s, H_6), 8.23 (1H, s, N═CH), 7.35–7.30 (2H, m, $H_{4'}$ and $H_{5'}$), 6.90–6.82 (2H, m, $H_{3'}$ and $H_{6'}$), 3.88 (3H, s, OCH_3), 3.62 (3H, s, NCH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ, p.p.m.): 167.6, 158.2, 150.5, 145.1, 144.7, 143.9, 137.5, 131.6, 126.1, 122.4, 121.0, 111.1, 55.6, 28.8; IR (KBr, ν, cm^{-1}): 1680 (C═O), 1600 (–N═C–CH_3). LC/MS: m/z $[M + H]^+$: 271.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness 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 threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *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 (Å²)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
O2	0.8377 (4)	0.40652 (13)	0.38061 (9)	0.0375 (4)	
O12	−0.0014 (4)	0.97966 (14)	0.37116 (11)	0.0457 (5)	
N1	0.4082 (4)	0.65216 (15)	0.29794 (10)	0.0274 (4)	
N2	0.5864 (4)	0.59046 (15)	0.35931 (10)	0.0274 (4)	
C1	0.3178 (5)	0.76459 (18)	0.31972 (13)	0.0296 (5)	
H1	0.3606	0.8017	0.3782	0.035*	
C2	0.6893 (5)	0.47329 (18)	0.33125 (12)	0.0284 (5)	
C11	0.1489 (5)	0.83521 (18)	0.25415 (14)	0.0312 (5)	
C12	−0.0030 (5)	0.94854 (18)	0.28078 (16)	0.0367 (5)	
C13	−0.1466 (6)	1.0204 (2)	0.21866 (19)	0.0460 (6)	
H13	−0.2464	1.0974	0.2374	0.055*	

C14	−0.1441 (6)	0.9796 (2)	0.12891 (19)	0.0471 (6)	
H14	−0.2417	1.0289	0.0861	0.056*	
C15	0.0005 (5)	0.8673 (2)	0.10160 (16)	0.0417 (6)	
H15	−0.0001	0.8389	0.0402	0.050*	
C16	0.1455 (5)	0.79676 (19)	0.16372 (14)	0.0347 (5)	
H16	0.2453	0.7201	0.1443	0.042*	
C27	0.6666 (5)	0.6458 (2)	0.44850 (12)	0.0340 (5)	
H27A	0.8087	0.5893	0.4790	0.051*	
H27B	0.4614	0.6577	0.4822	0.051*	
H27C	0.7836	0.7276	0.4443	0.051*	
C22	0.6213 (5)	0.42870 (17)	0.23544 (12)	0.0258 (4)	
C25	0.5341 (5)	0.34126 (19)	0.06766 (13)	0.0317 (5)	
H25	0.4943	0.3080	0.0081	0.038*	
C23	0.749 (3)	0.4998 (11)	0.1676 (9)	0.0271 (13)	0.527 (9)
H23	0.8672	0.5776	0.1818	0.032*	0.527 (9)
C26	0.419 (2)	0.2706 (9)	0.1407 (4)	0.0271 (13)	0.527 (9)
H26	0.3043	0.1917	0.1279	0.032*	0.527 (9)
N21	0.4691 (17)	0.3124 (6)	0.2250 (3)	0.0282 (13)	0.527 (9)
N24	0.702 (2)	0.4571 (6)	0.0834 (6)	0.0282 (13)	0.527 (9)
N21A	0.779 (3)	0.4873 (10)	0.1712 (8)	0.0282 (13)	0.473 (9)
N24A	0.376 (2)	0.2812 (8)	0.1252 (4)	0.0282 (13)	0.473 (9)
C23A	0.420 (2)	0.3263 (9)	0.2109 (5)	0.0271 (13)	0.473 (9)
H23A	0.3059	0.2846	0.2561	0.032*	0.473 (9)
C26A	0.742 (3)	0.4378 (8)	0.0867 (8)	0.0271 (13)	0.473 (9)
H26A	0.8665	0.4728	0.0405	0.032*	0.473 (9)
C121	−0.1477 (7)	1.0963 (2)	0.4016 (2)	0.0682 (9)	
H12A	−0.1318	1.1074	0.4668	0.102*	
H12B	−0.3816	1.0941	0.3832	0.102*	
H12C	−0.0295	1.1668	0.3755	0.102*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0508 (10)	0.0342 (8)	0.0286 (8)	0.0079 (7)	0.0002 (7)	0.0066 (6)
O12	0.0437 (9)	0.0239 (8)	0.0672 (11)	0.0052 (7)	0.0078 (8)	−0.0161 (7)
N1	0.0256 (9)	0.0229 (9)	0.0333 (9)	−0.0010 (6)	0.0042 (7)	0.0004 (7)
N2	0.0311 (9)	0.0247 (9)	0.0260 (9)	0.0004 (7)	0.0017 (7)	−0.0016 (6)
C1	0.0263 (10)	0.0239 (10)	0.0374 (11)	−0.0035 (8)	0.0093 (8)	−0.0038 (8)
C2	0.0307 (11)	0.0283 (11)	0.0264 (10)	0.0009 (8)	0.0048 (8)	0.0031 (8)
C11	0.0242 (10)	0.0215 (10)	0.0474 (12)	−0.0032 (8)	0.0089 (9)	0.0009 (8)
C12	0.0276 (11)	0.0194 (10)	0.0622 (14)	−0.0026 (8)	0.0083 (10)	−0.0031 (10)
C13	0.0318 (12)	0.0197 (11)	0.0870 (19)	0.0006 (9)	0.0094 (12)	0.0069 (11)
C14	0.0351 (12)	0.0328 (13)	0.0756 (17)	−0.0032 (10)	0.0025 (11)	0.0220 (12)
C15	0.0337 (12)	0.0368 (13)	0.0557 (14)	−0.0024 (9)	0.0055 (10)	0.0127 (10)
C16	0.0301 (11)	0.0262 (11)	0.0481 (13)	0.0011 (8)	0.0090 (9)	0.0054 (9)
C27	0.0387 (12)	0.0363 (12)	0.0255 (10)	−0.0044 (9)	0.0010 (8)	−0.0051 (8)
C22	0.0293 (10)	0.0194 (10)	0.0292 (10)	0.0063 (8)	0.0042 (8)	0.0025 (8)
C25	0.0399 (12)	0.0273 (11)	0.0282 (10)	0.0080 (9)	0.0018 (8)	−0.0006 (8)
C23	0.036 (2)	0.022 (2)	0.0249 (18)	0.0044 (17)	0.0028 (16)	0.0102 (14)
C26	0.036 (2)	0.022 (2)	0.0249 (18)	0.0044 (17)	0.0028 (16)	0.0102 (14)

N21	0.042 (2)	0.0186 (17)	0.0245 (16)	0.0060 (15)	−0.0020 (14)	0.0014 (15)
N24	0.042 (2)	0.0186 (17)	0.0245 (16)	0.0060 (15)	−0.0020 (14)	0.0014 (15)
N21A	0.042 (2)	0.0186 (17)	0.0245 (16)	0.0060 (15)	−0.0020 (14)	0.0014 (15)
N24A	0.042 (2)	0.0186 (17)	0.0245 (16)	0.0060 (15)	−0.0020 (14)	0.0014 (15)
C23A	0.036 (2)	0.022 (2)	0.0249 (18)	0.0044 (17)	0.0028 (16)	0.0102 (14)
C26A	0.036 (2)	0.022 (2)	0.0249 (18)	0.0044 (17)	0.0028 (16)	0.0102 (14)
C121	0.0519 (16)	0.0407 (15)	0.106 (2)	0.0179 (12)	−0.0098 (15)	−0.0408 (15)

Geometric parameters (Å, º)

O2—C2	1.230 (3)	C27—H27C	0.9800
O12—C12	1.375 (3)	C22—N21A	1.337 (13)
O12—C121	1.439 (3)	C22—N21	1.359 (7)
N1—C1	1.283 (3)	C22—C23A	1.362 (9)
N1—N2	1.382 (3)	C22—C23	1.402 (14)
N2—C2	1.366 (3)	C25—N24A	1.273 (7)
N2—C27	1.455 (3)	C25—C26A	1.315 (10)
C1—C11	1.460 (3)	C25—N24	1.388 (8)
C1—H1	0.9500	C25—C26	1.443 (8)
C2—C22	1.504 (3)	C25—H25	0.9500
C11—C16	1.391 (3)	C23—N24	1.324 (10)
C11—C12	1.405 (3)	C23—H23	0.9500
C12—C13	1.385 (4)	C26—N21	1.324 (7)
C13—C14	1.388 (4)	C26—H26	0.9500
C13—H13	0.9500	N21A—C26A	1.346 (10)
C14—C15	1.385 (4)	N24A—C23A	1.351 (8)
C14—H14	0.9500	C23A—H23A	0.9500
C15—C16	1.379 (3)	C26A—H26A	0.9500
C15—H15	0.9500	C121—H12A	0.9800
C16—H16	0.9500	C121—H12B	0.9800
C27—H27A	0.9800	C121—H12C	0.9800
C27—H27B	0.9800		

C12—O12—C121	117.3 (2)	N21—C22—C23	126.6 (5)
C1—N1—N2	118.49 (17)	C23A—C22—C23	117.6 (7)
C2—N2—N1	116.06 (16)	N21A—C22—C2	118.9 (5)
C2—N2—C27	121.02 (16)	N21—C22—C2	113.6 (3)
N1—N2—C27	122.91 (17)	C23A—C22—C2	122.9 (3)
N1—C1—C11	119.65 (19)	C23—C22—C2	119.3 (5)
N1—C1—H1	120.2	N24A—C25—C26A	124.7 (6)
C11—C1—H1	120.2	N24A—C25—N24	126.0 (4)
O2—C2—N2	122.42 (18)	C26A—C25—C26	117.4 (6)
O2—C2—C22	120.34 (18)	N24—C25—C26	120.9 (5)
N2—C2—C22	117.22 (16)	N24A—C25—H25	113.4
C16—C11—C12	117.9 (2)	C26A—C25—H25	121.8
C16—C11—C1	121.83 (19)	N24—C25—H25	119.6
C12—C11—C1	120.3 (2)	C26—C25—H25	119.6
O12—C12—C13	123.8 (2)	N24—C23—C22	119.1 (8)
O12—C12—C11	115.3 (2)	N24—C23—H23	120.4
C13—C12—C11	120.9 (2)	C22—C23—H23	120.4

C12—C13—C14	119.7 (2)	N21—C26—C25	122.0 (5)
C12—C13—H13	120.1	N21—C26—H26	119.0
C14—C13—H13	120.1	C25—C26—H26	119.0
C15—C14—C13	120.2 (2)	C26—N21—C22	114.0 (4)
C15—C14—H14	119.9	C23—N24—C25	117.2 (5)
C13—C14—H14	119.9	C22—N21A—C26A	118.0 (7)
C16—C15—C14	119.8 (2)	C25—N24A—C23A	115.6 (5)
C16—C15—H15	120.1	N24A—C23A—C22	123.0 (5)
C14—C15—H15	120.1	N24A—C23A—H23A	118.5
C15—C16—C11	121.6 (2)	C22—C23A—H23A	118.5
C15—C16—H16	119.2	C25—C26A—N21A	120.4 (7)
C11—C16—H16	119.2	C25—C26A—H26A	119.8
N2—C27—H27A	109.5	N21A—C26A—H26A	119.8
N2—C27—H27B	109.5	O12—C121—H12A	109.5
H27A—C27—H27B	109.5	O12—C121—H12B	109.5
N2—C27—H27C	109.5	H12A—C121—H12B	109.5
H27A—C27—H27C	109.5	O12—C121—H12C	109.5
H27B—C27—H27C	109.5	H12A—C121—H12C	109.5
N21A—C22—N21	125.2 (5)	H12B—C121—H12C	109.5
N21A—C22—C23A	118.0 (6)		

C1—N1—N2—C2	−177.12 (16)	N21—C22—C23—N24	5.1 (8)
C1—N1—N2—C27	2.1 (3)	C23A—C22—C23—N24	−7.8 (13)
N2—N1—C1—C11	175.87 (15)	C2—C22—C23—N24	176.8 (4)
N1—N2—C2—O2	−176.87 (17)	N24A—C25—C26—N21	−120 (4)
C27—N2—C2—O2	3.9 (3)	C26A—C25—C26—N21	11.9 (11)
N1—N2—C2—C22	4.6 (2)	N24—C25—C26—N21	−0.2 (6)
C27—N2—C2—C22	−174.65 (16)	C25—C26—N21—C22	3.1 (6)
N1—C1—C11—C16	−14.3 (3)	N21A—C22—N21—C26	−14.9 (10)
N1—C1—C11—C12	168.73 (18)	C23A—C22—N21—C26	49 (2)
C121—O12—C12—C13	−2.3 (3)	C23—C22—N21—C26	−5.6 (7)
C121—O12—C12—C11	178.69 (19)	C2—C22—N21—C26	−177.7 (3)
C16—C11—C12—O12	177.98 (17)	C22—C23—N24—C25	−1.6 (8)
C1—C11—C12—O12	−4.9 (3)	N24A—C25—N24—C23	11.7 (8)
C16—C11—C12—C13	−1.0 (3)	C26A—C25—N24—C23	−76 (4)
C1—C11—C12—C13	176.06 (18)	C26—C25—N24—C23	−0.6 (6)
O12—C12—C13—C14	−178.22 (19)	N21—C22—N21A—C26A	11.1 (12)
C11—C12—C13—C14	0.7 (3)	C23A—C22—N21A—C26A	−3.2 (7)
C12—C13—C14—C15	0.2 (3)	C23—C22—N21A—C26A	−92 (8)
C13—C14—C15—C16	−0.7 (3)	C2—C22—N21A—C26A	173.1 (4)
C14—C15—C16—C11	0.4 (3)	C26A—C25—N24A—C23A	3.0 (7)
C12—C11—C16—C15	0.5 (3)	N24—C25—N24A—C23A	−10.6 (10)
C1—C11—C16—C15	−176.56 (18)	C26—C25—N24A—C23A	56 (3)
O2—C2—C22—N21A	−111.5 (6)	C25—N24A—C23A—C22	−0.3 (7)
N2—C2—C22—N21A	67.1 (6)	N21A—C22—C23A—N24A	0.6 (7)
O2—C2—C22—N21	52.5 (4)	N21—C22—C23A—N24A	−123 (3)
N2—C2—C22—N21	−128.9 (4)	C23—C22—C23A—N24A	9.2 (12)
O2—C2—C22—C23A	64.6 (6)	C2—C22—C23A—N24A	−175.6 (4)
N2—C2—C22—C23A	−116.8 (5)	N24A—C25—C26A—N21A	−5.9 (7)

O2—C2—C22—C23	−120.2 (6)	N24—C25—C26A—N21A	95 (4)
N2—C2—C22—C23	58.4 (6)	C26—C25—C26A—N21A	−16.2 (9)
N21A—C22—C23—N24	87 (7)	C22—N21A—C26A—C25	5.8 (7)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C13—H13···N21^{i}	0.95	2.61	3.514 (8)	159

Symmetry code: (i) *x*−1, *y*+1, *z*.

(IIc) *N′*-(4-Cyanobenzylidene)-*N*-methylpyrazine-2-carbohydrazide dihydrate

Crystal data

$C_{14}H_{11}N_5O·2H_2O$
M_r = 301.31
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 19.395 (3) Å
b = 3.9517 (5) Å
c = 23.270 (3) Å
β = 124.890 (9)°
V = 1462.9 (3) Å^3
Z = 4
$F(000)$ = 632
D_x = 1.368 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71075 Å
Cell parameters from 5437 reflections
θ = 3.1–27.5°
μ = 0.10 mm^{-1}
T = 120 K
Lath, yellow
0.56 × 0.23 × 0.08 mm

Data collection

Rigaku R-AXIS conversion diffractometer
Radiation source: Sealed tube
Graphite monochromator
Detector resolution: 10.0000 pixels mm^{-1}
profile data from ω scans
Absorption correction: multi-scan (*CrystalClear*-SM Expert; Rigaku, 2011)
T_{min} = 0.946, T_{max} = 0.992
12564 measured reflections
3341 independent reflections
2189 reflections with $I > 2\sigma(I)$
R_{int} = 0.053
θ_{max} = 27.5°, θ_{min} = 3.1°
h = −25→25
k = −4→5
l = −30→30

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.248
S = 1.23
3341 reflections
202 parameters
0 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.1408P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.026 (7)

Special details

Experimental. Compound (II*c*): ^{1}H NMR (500 MHz, $CDCl_3$, δ, p.p.m.): 8.84 (1H, s, H_3), 8.70 (2H, s, H_5 and H_6), 7.80 (1H, s, N═CH), 7.61 (2H, J = 8.0 Hz, $H_{2'}$ and $H_{6'}$), 7.47 (2H, J = 8.0 Hz, $H_{3'}$ and $H_{5'}$), 3.63 (3H, s, NCH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ, p.p.m.): 157.8, 150.0, 145.2, 144.9, 143.9, 138.7, 138.3, 132.7, 127.7, 118.5, 113.5, 28.9; IR (KBr, ν, cm^{-1}): 2232 (CN), 1683 (C═O), 1608 (–N═C–CH_3). LC/MS: m/z $[M + H]^+$: 266.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness 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 threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *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}
O2	0.39035 (9)	1.2988 (4)	0.41661 (8)	0.0470 (5)
N1	0.30755 (10)	0.9113 (5)	0.49844 (9)	0.0357 (5)
N2	0.36554 (10)	1.0804 (5)	0.49269 (9)	0.0370 (5)
N21	0.23766 (11)	0.9867 (5)	0.30927 (9)	0.0394 (5)
N24	0.10404 (12)	1.2139 (6)	0.31377 (10)	0.0483 (6)
N141	0.04799 (12)	0.0201 (5)	0.60153 (9)	0.0466 (5)
C1	0.32763 (13)	0.8270 (6)	0.55927 (11)	0.0373 (5)
H1	0.3823	0.8754	0.5996	0.045*
C2	0.34103 (13)	1.1709 (6)	0.42715 (11)	0.0368 (5)
C11	0.26632 (12)	0.6565 (6)	0.56652 (10)	0.0351 (5)
C12	0.29262 (13)	0.5177 (6)	0.63124 (10)	0.0390 (6)
H12	0.3499	0.5367	0.6695	0.047*
C13	0.23719 (13)	0.3541 (6)	0.64061 (11)	0.0387 (5)
H13	0.2560	0.2609	0.6849	0.046*
C14	0.15273 (13)	0.3263 (6)	0.58410 (11)	0.0361 (5)
C15	0.12524 (13)	0.4653 (6)	0.51940 (10)	0.0373 (5)
H15	0.0679	0.4462	0.4812	0.045*
C16	0.18116 (13)	0.6307 (6)	0.51062 (11)	0.0363 (5)
H16	0.1620	0.7278	0.4665	0.044*
C22	0.25017 (12)	1.1206 (6)	0.36732 (11)	0.0356 (5)
C23	0.18423 (13)	1.2354 (6)	0.36886 (12)	0.0419 (6)
H23	0.1962	1.3342	0.4109	0.050*
C25	0.09194 (14)	1.0692 (7)	0.25688 (12)	0.0494 (7)
H25	0.0361	1.0421	0.2166	0.059*
C26	0.15733 (14)	0.9580 (6)	0.25457 (11)	0.0449 (6)
H26	0.1452	0.8571	0.2127	0.054*
C27	0.45005 (13)	1.1569 (6)	0.55350 (11)	0.0431 (6)
H27A	0.4802	1.2881	0.5387	0.065*
H27B	0.4803	0.9453	0.5753	0.065*
H27C	0.4465	1.2886	0.5874	0.065*
C141	0.09456 (13)	0.1544 (6)	0.59335 (11)	0.0394 (6)
O1W	0.35816 (10)	0.6041 (5)	0.29459 (8)	0.0515 (5)
H1WA	0.3690	0.4650	0.3345	0.077*

H1WB	0.3254	0.7863	0.2941	0.077*
O2W	0.49138 (13)	0.6383 (11)	0.28335 (12)	0.1346 (15)
H2WA	0.4499	0.6147	0.2904	0.202*
H2WB	0.4701	0.4964	0.2503	0.202*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0315 (8)	0.0599 (11)	0.0496 (10)	−0.0051 (7)	0.0231 (7)	0.0029 (8)
N1	0.0289 (9)	0.0376 (10)	0.0404 (10)	0.0008 (7)	0.0198 (8)	−0.0030 (8)
N2	0.0265 (8)	0.0419 (11)	0.0408 (10)	−0.0033 (7)	0.0183 (8)	−0.0033 (8)
N21	0.0369 (10)	0.0420 (11)	0.0404 (10)	−0.0028 (8)	0.0228 (8)	−0.0017 (8)
N24	0.0318 (10)	0.0682 (14)	0.0425 (10)	0.0048 (9)	0.0199 (8)	0.0063 (9)
N141	0.0374 (11)	0.0518 (13)	0.0448 (11)	−0.0006 (9)	0.0202 (9)	0.0032 (9)
C1	0.0308 (10)	0.0417 (13)	0.0352 (10)	0.0033 (9)	0.0164 (9)	−0.0032 (9)
C2	0.0300 (10)	0.0381 (12)	0.0431 (11)	0.0016 (8)	0.0213 (9)	−0.0012 (9)
C11	0.0312 (10)	0.0376 (12)	0.0365 (11)	0.0061 (8)	0.0195 (9)	−0.0015 (9)
C12	0.0290 (10)	0.0466 (14)	0.0359 (11)	0.0051 (9)	0.0154 (9)	−0.0014 (9)
C13	0.0355 (11)	0.0404 (12)	0.0362 (11)	0.0033 (9)	0.0182 (9)	0.0005 (9)
C14	0.0335 (10)	0.0354 (12)	0.0389 (11)	0.0028 (8)	0.0205 (9)	−0.0018 (9)
C15	0.0316 (10)	0.0406 (13)	0.0373 (11)	0.0046 (9)	0.0183 (9)	−0.0010 (9)
C16	0.0325 (10)	0.0386 (12)	0.0346 (10)	0.0025 (9)	0.0173 (9)	−0.0013 (9)
C22	0.0316 (10)	0.0355 (11)	0.0389 (11)	−0.0009 (8)	0.0198 (9)	0.0005 (9)
C23	0.0335 (11)	0.0523 (14)	0.0416 (11)	0.0052 (9)	0.0225 (10)	0.0026 (10)
C25	0.0316 (11)	0.0669 (17)	0.0418 (12)	−0.0029 (10)	0.0165 (10)	0.0054 (11)
C26	0.0431 (13)	0.0505 (15)	0.0389 (11)	−0.0080 (10)	0.0222 (10)	−0.0049 (10)
C27	0.0286 (10)	0.0492 (14)	0.0446 (12)	−0.0037 (9)	0.0169 (10)	−0.0042 (10)
C141	0.0355 (11)	0.0395 (12)	0.0364 (11)	0.0056 (9)	0.0166 (9)	0.0006 (9)
O1W	0.0424 (9)	0.0672 (12)	0.0487 (9)	0.0053 (8)	0.0283 (8)	0.0012 (8)
O2W	0.0439 (12)	0.301 (5)	0.0627 (14)	0.0041 (18)	0.0324 (11)	0.0090 (19)

Geometric parameters (Å, º)

O2—C2	1.224 (3)	C13—H13	0.9500
N1—C1	1.279 (3)	C14—C15	1.391 (3)
N1—N2	1.379 (2)	C14—C141	1.435 (3)
N2—C2	1.360 (3)	C15—C16	1.378 (3)
N2—C27	1.458 (3)	C15—H15	0.9500
N21—C22	1.337 (3)	C16—H16	0.9500
N21—C26	1.339 (3)	C22—C23	1.377 (3)
N24—C25	1.334 (3)	C23—H23	0.9500
N24—C23	1.337 (3)	C25—C26	1.372 (3)
N141—C141	1.154 (3)	C25—H25	0.9500
C1—C11	1.458 (3)	C26—H26	0.9500
C1—H1	0.9500	C27—H27A	0.9800
C2—C22	1.509 (3)	C27—H27B	0.9800
C11—C12	1.396 (3)	C27—H27C	0.9800
C11—C16	1.404 (3)	O1W—H1WA	0.9935
C12—C13	1.375 (3)	O1W—H1WB	0.9568
C12—H12	0.9500	O2W—H2WA	0.9136

C13—C14	1.400 (3)	O2W—H2WB	0.8438
C1—N1—N2	118.99 (18)	C14—C15—H15	120.0
C2—N2—N1	117.06 (16)	C15—C16—C11	120.37 (19)
C2—N2—C27	120.75 (18)	C15—C16—H16	119.8
N1—N2—C27	122.18 (17)	C11—C16—H16	119.8
C22—N21—C26	115.71 (19)	N21—C22—C23	121.49 (19)
C25—N24—C23	115.25 (19)	N21—C22—C2	115.18 (18)
N1—C1—C11	119.76 (19)	C23—C22—C2	122.99 (19)
N1—C1—H1	120.1	N24—C23—C22	122.8 (2)
C11—C1—H1	120.1	N24—C23—H23	118.6
O2—C2—N2	121.41 (19)	C22—C23—H23	118.6
O2—C2—C22	120.23 (18)	N24—C25—C26	122.3 (2)
N2—C2—C22	118.33 (18)	N24—C25—H25	118.9
C12—C11—C16	118.7 (2)	C26—C25—H25	118.9
C12—C11—C1	119.17 (18)	N21—C26—C25	122.3 (2)
C16—C11—C1	122.09 (18)	N21—C26—H26	118.8
C13—C12—C11	121.29 (19)	C25—C26—H26	118.8
C13—C12—H12	119.4	N2—C27—H27A	109.5
C11—C12—H12	119.4	N2—C27—H27B	109.5
C12—C13—C14	119.28 (19)	H27A—C27—H27B	109.5
C12—C13—H13	120.4	N2—C27—H27C	109.5
C14—C13—H13	120.4	H27A—C27—H27C	109.5
C15—C14—C13	120.2 (2)	H27B—C27—H27C	109.5
C15—C14—C141	120.13 (18)	N141—C141—C14	178.9 (2)
C13—C14—C141	119.63 (18)	H1WA—O1W—H1WB	102.2
C16—C15—C14	120.06 (19)	H2WA—O2W—H2WB	94.2
C16—C15—H15	120.0		
C1—N1—N2—C2	−178.76 (19)	C14—C15—C16—C11	0.8 (3)
C1—N1—N2—C27	2.0 (3)	C12—C11—C16—C15	−1.3 (3)
N2—N1—C1—C11	178.30 (18)	C1—C11—C16—C15	179.5 (2)
N1—N2—C2—O2	−174.4 (2)	C26—N21—C22—C23	−3.0 (3)
C27—N2—C2—O2	4.8 (3)	C26—N21—C22—C2	−176.47 (19)
N1—N2—C2—C22	7.5 (3)	O2—C2—C22—N21	46.1 (3)
C27—N2—C2—C22	−173.25 (19)	N2—C2—C22—N21	−135.8 (2)
N1—C1—C11—C12	169.8 (2)	O2—C2—C22—C23	−127.3 (2)
N1—C1—C11—C16	−11.0 (3)	N2—C2—C22—C23	50.8 (3)
C16—C11—C12—C13	0.9 (3)	C25—N24—C23—C22	0.7 (4)
C1—C11—C12—C13	−179.9 (2)	N21—C22—C23—N24	1.6 (4)
C11—C12—C13—C14	0.0 (3)	C2—C22—C23—N24	174.6 (2)
C12—C13—C14—C15	−0.5 (3)	C23—N24—C25—C26	−1.6 (4)
C12—C13—C14—C141	179.7 (2)	C22—N21—C26—C25	2.1 (3)
C13—C14—C15—C16	0.1 (3)	N24—C25—C26—N21	0.1 (4)
C141—C14—C15—C16	179.93 (19)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WB*···N21	0.96	2.08	2.963 (2)	153

O2*W*—H2*WA*···O1*W*	0.91	1.84	2.745 (3)	172
O1*W*—H1*WA*···O2^{i}	0.99	1.83	2.807 (2)	167
O2*W*—H2*WB*···O2*W*^{ii}	0.84	1.96	2.649 (3)	138
C13—H13···O1*W*^{iii}	0.95	2.59	3.465 (3)	152
C26—H26···N141^{iv}	0.95	2.62	3.480 (3)	150

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

(IId) *N*-Methyl-*N*′-(2-nitrobenzylidene)pyrazine-2-carbohydrazide

Crystal data

$C_{13}H_{11}N_5O_3$
M_r = 285.27
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 3.7974 (2) Å
b = 33.3126 (17) Å
c = 10.0959 (5) Å
β = 99.027 (2)°
V = 1261.33 (11) Å^3
Z = 4
$F(000)$ = 592
D_x = 1.502 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 14894 reflections
θ = 2.9–27.5°
μ = 0.11 mm^{-1}
T = 120 K
Lath, yellow
0.40 × 0.10 × 0.02 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Vertically mounted graphite crystal monochromator
Detector resolution: 9 pixels mm^{-1}
CCD scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.957, T_{max} = 0.998
11176 measured reflections
2168 independent reflections
1563 reflections with $I > 2\sigma(I)$
R_{int} = 0.071
θ_{max} = 25.0°, θ_{min} = 3.2°
h = −4→4
k = −39→39
l = −11→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.080
$wR(F^2)$ = 0.196
S = 1.10
2168 reflections
191 parameters
0 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0855P)^2 + 1.4865P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Special details

Experimental. Compound (II*d*): ^{1}H NMR (500 MHz, $CDCl_3$, δ, p.p.m.): 8.84 (1H, s, H_3), 8.69 (2H, m, H_5 and H_6), 8.39 (1H, s, N═CH), 8.02(1H, d, N═CH), 7.57–7.48 (3H, m), 3.65 (3H, s, NCH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ, p.p.m.): 167.8, 150.0, 148.4, 145.1, 144.8, 143.9, 136.8, 133.6, 130.4, 128.8, 128.3, 125.0, 29.1; IR (KBr, ν, cm^{-1}): 1672 (C═O), 1597 (–N═C–CH_3). LC/MS: m/z [M + Na]$^-$: 281.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness 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 threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O2	0.3911 (7)	0.65099 (7)	0.7717 (2)	0.0403 (7)
O121	1.0540 (8)	0.51292 (8)	0.3594 (3)	0.0452 (8)
O122	0.7448 (8)	0.49513 (8)	0.1686 (3)	0.0519 (8)
N1	0.6819 (7)	0.62022 (8)	0.4785 (3)	0.0265 (7)
N2	0.5626 (7)	0.61611 (8)	0.5997 (3)	0.0273 (7)
N12	0.9002 (8)	0.52058 (9)	0.2455 (3)	0.0350 (8)
C1	0.7285 (8)	0.58864 (10)	0.4111 (3)	0.0255 (8)
H1	0.6922	0.5626	0.4452	0.031*
C2	0.4829 (9)	0.65095 (10)	0.6602 (3)	0.0289 (8)
C11	0.8402 (8)	0.59398 (10)	0.2788 (3)	0.0248 (8)
C12	0.9069 (8)	0.56205 (10)	0.1962 (3)	0.0263 (8)
C13	0.9867 (9)	0.56702 (11)	0.0685 (3)	0.0320 (9)
H13	1.0223	0.5443	0.0152	0.038*
C14	1.0141 (9)	0.60516 (11)	0.0193 (3)	0.0325 (8)
H14	1.0737	0.6092	−0.0676	0.039*
C15	0.9528 (10)	0.63778 (11)	0.0990 (4)	0.0347 (9)
H15	0.9742	0.6643	0.0663	0.042*
C16	0.8617 (9)	0.63219 (10)	0.2247 (4)	0.0312 (8)
H16	0.8125	0.6549	0.2755	0.037*
N21	0.3203 (8)	0.69483 (10)	0.4634 (3)	0.0375 (8)
C22	0.5046 (9)	0.69004 (10)	0.5885 (3)	0.0268 (8)
C23	0.6829 (9)	0.72100 (10)	0.6577 (3)	0.0283 (8)
H23	0.8081	0.7163	0.7454	0.034*
N24	0.6860 (9)	0.75790 (10)	0.6050 (3)	0.0455 (9)
C25	0.4941 (11)	0.76297 (12)	0.4819 (4)	0.0408 (10)
H25	0.4794	0.7890	0.4430	0.049*
C26	0.3203 (10)	0.73189 (12)	0.4112 (4)	0.0351 (9)
H26	0.1969	0.7366	0.3232	0.042*
C27	0.5144 (9)	0.57723 (10)	0.6605 (3)	0.0316 (8)
H27A	0.4352	0.5812	0.7474	0.047*
H27B	0.7410	0.5626	0.6735	0.047*
H27C	0.3345	0.5617	0.6015	0.047*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0600 (18)	0.0346 (16)	0.0289 (15)	0.0014 (12)	0.0152 (13)	−0.0012 (12)
O121	0.0686 (19)	0.0348 (16)	0.0322 (15)	0.0115 (13)	0.0081 (13)	0.0045 (12)
O122	0.087 (2)	0.0298 (16)	0.0413 (17)	−0.0150 (15)	0.0180 (16)	−0.0102 (13)
N1	0.0307 (15)	0.0264 (16)	0.0218 (15)	−0.0015 (12)	0.0021 (12)	−0.0032 (12)
N2	0.0364 (16)	0.0253 (16)	0.0211 (15)	−0.0010 (12)	0.0070 (12)	0.0011 (12)
N12	0.0507 (19)	0.0271 (17)	0.0290 (17)	0.0007 (14)	0.0119 (15)	−0.0038 (14)

C1	0.0280 (17)	0.0245 (18)	0.0235 (18)	0.0007 (14)	0.0021 (14)	−0.0002 (14)
C2	0.0341 (19)	0.031 (2)	0.0216 (18)	0.0004 (15)	0.0036 (15)	−0.0010 (15)
C11	0.0257 (16)	0.0269 (19)	0.0208 (17)	−0.0004 (13)	0.0009 (13)	−0.0016 (14)
C12	0.0288 (18)	0.0238 (19)	0.0261 (18)	−0.0013 (14)	0.0035 (14)	−0.0015 (14)
C13	0.039 (2)	0.033 (2)	0.0239 (18)	0.0020 (16)	0.0033 (15)	−0.0058 (15)
C14	0.0332 (19)	0.039 (2)	0.0265 (18)	0.0000 (16)	0.0078 (15)	0.0029 (16)
C15	0.044 (2)	0.027 (2)	0.034 (2)	−0.0013 (16)	0.0066 (17)	0.0057 (16)
C16	0.038 (2)	0.0241 (19)	0.032 (2)	0.0019 (15)	0.0067 (16)	−0.0013 (15)
N21	0.0359 (17)	0.045 (2)	0.0310 (17)	−0.0018 (14)	0.0032 (13)	−0.0005 (15)
C22	0.0289 (17)	0.0293 (19)	0.0225 (17)	0.0014 (14)	0.0053 (14)	−0.0022 (14)
C23	0.0356 (19)	0.0279 (19)	0.0209 (17)	0.0000 (15)	0.0024 (14)	−0.0012 (15)
N24	0.060 (2)	0.037 (2)	0.041 (2)	−0.0051 (16)	0.0131 (17)	−0.0024 (16)
C25	0.052 (2)	0.032 (2)	0.041 (2)	0.0042 (18)	0.0155 (19)	0.0076 (18)
C26	0.036 (2)	0.043 (2)	0.0254 (19)	0.0013 (16)	0.0036 (16)	0.0092 (17)
C27	0.039 (2)	0.028 (2)	0.0283 (19)	0.0007 (16)	0.0073 (15)	0.0017 (15)

Geometric parameters (Å, º)

O2—C2	1.230 (4)	C14—H14	0.9500
O121—N12	1.232 (4)	C15—C16	1.379 (5)
O122—N12	1.235 (4)	C15—H15	0.9500
N1—C1	1.280 (4)	C16—H16	0.9500
N1—N2	1.377 (4)	N21—C26	1.343 (5)
N2—C2	1.367 (4)	N21—C22	1.353 (4)
N2—C27	1.457 (4)	C22—C23	1.365 (5)
N12—C12	1.470 (4)	C23—N24	1.340 (5)
C1—C11	1.474 (5)	C23—H23	0.9500
C1—H1	0.9500	N24—C25	1.350 (5)
C2—C22	1.498 (5)	C25—C26	1.367 (5)
C11—C16	1.393 (5)	C25—H25	0.9500
C11—C12	1.399 (4)	C26—H26	0.9500
C12—C13	1.380 (5)	C27—H27A	0.9800
C13—C14	1.374 (5)	C27—H27B	0.9800
C13—H13	0.9500	C27—H27C	0.9800
C14—C15	1.393 (5)		

C1—N1—N2	118.9 (3)	C16—C15—H15	119.5
C2—N2—N1	116.0 (3)	C14—C15—H15	119.5
C2—N2—C27	121.0 (3)	C15—C16—C11	121.5 (3)
N1—N2—C27	122.9 (3)	C15—C16—H16	119.2
O121—N12—O122	123.7 (3)	C11—C16—H16	119.2
O121—N12—C12	118.7 (3)	C26—N21—C22	116.3 (3)
O122—N12—C12	117.7 (3)	N21—C22—C23	122.1 (3)
N1—C1—C11	117.8 (3)	N21—C22—C2	119.6 (3)
N1—C1—H1	121.1	C23—C22—C2	118.0 (3)
C11—C1—H1	121.1	N24—C23—C22	121.7 (3)
O2—C2—N2	121.6 (3)	N24—C23—H23	119.2
O2—C2—C22	119.1 (3)	C22—C23—H23	119.2
N2—C2—C22	119.3 (3)	C23—N24—C25	116.3 (3)
C16—C11—C12	115.7 (3)	N24—C25—C26	122.2 (4)

C16—C11—C1	120.6 (3)	N24—C25—H25	118.9
C12—C11—C1	123.6 (3)	C26—C25—H25	118.9
C13—C12—C11	123.5 (3)	N21—C26—C25	121.4 (3)
C13—C12—N12	116.5 (3)	N21—C26—H26	119.3
C11—C12—N12	119.9 (3)	C25—C26—H26	119.3
C14—C13—C12	119.3 (3)	N2—C27—H27A	109.5
C14—C13—H13	120.4	N2—C27—H27B	109.5
C12—C13—H13	120.4	H27A—C27—H27B	109.5
C13—C14—C15	118.9 (3)	N2—C27—H27C	109.5
C13—C14—H14	120.6	H27A—C27—H27C	109.5
C15—C14—H14	120.6	H27B—C27—H27C	109.5
C16—C15—C14	121.0 (3)		

C1—N1—N2—C2	−173.5 (3)	N12—C12—C13—C14	−176.9 (3)
C1—N1—N2—C27	5.2 (4)	C12—C13—C14—C15	−1.3 (5)
N2—N1—C1—C11	177.2 (3)	C13—C14—C15—C16	−0.8 (5)
N1—N2—C2—O2	−176.3 (3)	C14—C15—C16—C11	2.4 (5)
C27—N2—C2—O2	5.0 (5)	C12—C11—C16—C15	−1.7 (5)
N1—N2—C2—C22	4.2 (4)	C1—C11—C16—C15	−177.6 (3)
C27—N2—C2—C22	−174.5 (3)	C26—N21—C22—C23	−0.4 (5)
N1—C1—C11—C16	−5.8 (5)	C26—N21—C22—C2	172.9 (3)
N1—C1—C11—C12	178.7 (3)	O2—C2—C22—N21	−124.9 (4)
C16—C11—C12—C13	−0.5 (5)	N2—C2—C22—N21	54.6 (4)
C1—C11—C12—C13	175.2 (3)	O2—C2—C22—C23	48.7 (5)
C16—C11—C12—N12	178.4 (3)	N2—C2—C22—C23	−131.8 (3)
C1—C11—C12—N12	−5.9 (5)	N21—C22—C23—N24	−0.2 (5)
O121—N12—C12—C13	133.6 (3)	C2—C22—C23—N24	−173.6 (3)
O122—N12—C12—C13	−45.1 (4)	C22—C23—N24—C25	2.0 (5)
O121—N12—C12—C11	−45.3 (4)	C23—N24—C25—C26	−3.2 (6)
O122—N12—C12—C11	135.9 (3)	C22—N21—C26—C25	−0.8 (5)
C11—C12—C13—C14	2.0 (5)	N24—C25—C26—N21	2.7 (6)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C13—H13···O122^{i}	0.95	2.54	3.439 (5)	157
C14—H14···O2^{ii}	0.95	2.58	3.428 (4)	150

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

(IIe) *N*-Methyl-*N*′-(4-nitrobenzylidene)pyrazine-2-carbohydrazide

Crystal data

$C_{13}H_{11}N_5O_3$	V = 2628.7 (5) Å^3
M_r = 285.27	Z = 8
Monoclinic, *C*2/*c*	F(000) = 1184
Hall symbol: -C 2yc	D_x = 1.442 Mg m^{-3}
a = 17.510 (2) Å	Mo $K\alpha$ radiation, λ = 0.71075 Å
b = 10.5421 (11) Å	Cell parameters from 3733 reflections
c = 14.9638 (14) Å	θ = 3.1–27.4°
β = 107.887 (8)°	μ = 0.11 mm^{-1}

T = 120 K
Prism, orange

0.42 × 0.24 × 0.16 mm

Data collection

Rigaku R-AXIS conversion diffractometer
Radiation source: Sealed tube
Graphite monochromator
Detector resolution: 10.0000 pixels mm^{-1}
profile data from ω scans
Absorption correction: multi-scan (*CrystalClear*-SM Expert; Rigaku, 2011)
T_{min} = 0.956, T_{max} = 0.983

7284 measured reflections
3000 independent reflections
2610 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 27.5°, θ_{min} = 3.1°
h = −22→22
k = −13→13
l = −19→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.169
S = 1.08
3000 reflections
191 parameters
0 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0773P)^2 + 2.8776P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Special details

Experimental. Compound (II*e*): ^{1}H NMR (400 MHz, $CDCl_3$, δ, p.p.m.): 8.85 (1H, s, H_3), 8.70 (2H, m, H_5 and H_6), 8.17 (2H, d, J = 8.0Hz, $H_{3'}$ and $H_{5'}$), 7.84 (1H, s, N═CH), 7.52 (2H, d, J = 8.0Hz, $H_{2'}$ and $H_{6'}$), 3.64 (3H, s, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ, p.p.m.): 167.7, 149.8, 148.4, 145.2, 144.8, 143.8, 139.9, 138.1, 128.8, 127.8, 124.2, 28.9.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness 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 threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *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}
O2	0.57061 (8)	0.47908 (13)	0.45169 (10)	0.0343 (3)
O141	0.86046 (10)	−0.34850 (14)	0.71616 (12)	0.0430 (4)
O142	0.95959 (9)	−0.26236 (14)	0.82272 (11)	0.0400 (4)
N1	0.69672 (9)	0.24637 (14)	0.58377 (11)	0.0289 (4)
N2	0.67240 (9)	0.36628 (15)	0.55006 (11)	0.0288 (4)
N14	0.89617 (10)	−0.25541 (15)	0.75878 (12)	0.0330 (4)
N21	0.57793 (10)	0.16583 (15)	0.41024 (12)	0.0331 (4)
N24	0.42373 (10)	0.15461 (17)	0.43127 (13)	0.0374 (4)
C1	0.76619 (11)	0.23431 (18)	0.64385 (13)	0.0293 (4)
H1	0.7979	0.3071	0.6677	0.035*
C2	0.59832 (11)	0.37657 (17)	0.48461 (13)	0.0284 (4)

C11	0.79675 (11)	0.10698 (18)	0.67581 (13)	0.0291 (4)
C12	0.75341 (11)	−0.00272 (18)	0.63833 (13)	0.0296 (4)
H12	0.7015	0.0047	0.5939	0.035*
C13	0.78555 (12)	−0.12142 (19)	0.66549 (14)	0.0319 (4)
H13	0.7566	−0.1960	0.6398	0.038*
C14	0.86118 (11)	−0.12919 (18)	0.73113 (13)	0.0294 (4)
C15	0.90534 (11)	−0.02318 (19)	0.77173 (13)	0.0303 (4)
H15	0.9563	−0.0314	0.8178	0.036*
C16	0.87229 (11)	0.09528 (19)	0.74256 (14)	0.0306 (4)
H16	0.9015	0.1695	0.7684	0.037*
C22	0.54957 (11)	0.25722 (17)	0.45338 (12)	0.0282 (4)
C23	0.47319 (11)	0.25233 (18)	0.46330 (14)	0.0320 (4)
H23	0.4557	0.3204	0.4937	0.038*
C25	0.45238 (13)	0.0629 (2)	0.38884 (16)	0.0393 (5)
H25	0.4195	−0.0088	0.3651	0.047*
C26	0.52813 (12)	0.06823 (19)	0.37812 (15)	0.0362 (4)
H26	0.5453	0.0005	0.3470	0.043*
C27	0.72305 (12)	0.47763 (18)	0.58082 (14)	0.0319 (4)
H27A	0.6958	0.5526	0.5469	0.048*
H27B	0.7741	0.4652	0.5678	0.048*
H27C	0.7333	0.4900	0.6484	0.048*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0341 (7)	0.0258 (7)	0.0408 (8)	0.0033 (5)	0.0084 (6)	−0.0002 (6)
O141	0.0461 (9)	0.0295 (7)	0.0499 (9)	0.0008 (6)	0.0097 (7)	−0.0035 (7)
O142	0.0357 (8)	0.0374 (8)	0.0425 (8)	0.0062 (6)	0.0054 (6)	0.0064 (6)
N1	0.0289 (8)	0.0252 (8)	0.0337 (8)	0.0017 (6)	0.0115 (6)	0.0012 (6)
N2	0.0281 (8)	0.0237 (8)	0.0340 (8)	−0.0004 (6)	0.0088 (6)	−0.0011 (6)
N14	0.0337 (8)	0.0294 (9)	0.0370 (9)	0.0028 (7)	0.0127 (7)	0.0021 (7)
N21	0.0332 (8)	0.0292 (8)	0.0372 (9)	−0.0006 (6)	0.0114 (7)	−0.0054 (7)
N24	0.0305 (8)	0.0345 (9)	0.0467 (10)	−0.0022 (7)	0.0110 (7)	−0.0065 (7)
C1	0.0283 (9)	0.0291 (9)	0.0319 (9)	−0.0019 (7)	0.0112 (7)	−0.0006 (7)
C2	0.0302 (9)	0.0255 (9)	0.0309 (9)	0.0013 (7)	0.0113 (7)	−0.0025 (7)
C11	0.0282 (9)	0.0315 (9)	0.0299 (9)	0.0003 (7)	0.0124 (7)	0.0001 (7)
C12	0.0245 (8)	0.0326 (10)	0.0305 (9)	−0.0012 (7)	0.0068 (7)	−0.0005 (7)
C13	0.0310 (9)	0.0311 (10)	0.0346 (9)	−0.0022 (7)	0.0118 (8)	−0.0022 (8)
C14	0.0303 (9)	0.0290 (9)	0.0307 (9)	0.0015 (7)	0.0119 (7)	0.0016 (7)
C15	0.0264 (9)	0.0335 (10)	0.0298 (9)	−0.0002 (7)	0.0071 (7)	0.0008 (7)
C16	0.0293 (9)	0.0289 (9)	0.0330 (9)	−0.0034 (7)	0.0087 (7)	−0.0021 (7)
C22	0.0288 (9)	0.0257 (9)	0.0275 (8)	0.0019 (7)	0.0050 (7)	0.0004 (7)
C23	0.0289 (9)	0.0280 (9)	0.0373 (10)	0.0030 (7)	0.0076 (7)	−0.0042 (7)
C25	0.0351 (10)	0.0329 (10)	0.0475 (12)	−0.0044 (8)	0.0095 (9)	−0.0077 (9)
C26	0.0373 (10)	0.0290 (10)	0.0427 (11)	−0.0002 (8)	0.0128 (8)	−0.0089 (8)
C27	0.0325 (9)	0.0273 (9)	0.0354 (10)	−0.0030 (7)	0.0096 (8)	−0.0012 (8)

Geometric parameters (Å, º)

O2—C2	1.224 (2)	C12—C13	1.381 (3)
O141—N14	1.231 (2)	C12—H12	0.9500
O142—N14	1.225 (2)	C13—C14	1.388 (3)
N1—C1	1.278 (3)	C13—H13	0.9500
N1—N2	1.379 (2)	C14—C15	1.388 (3)
N2—C2	1.369 (2)	C15—C16	1.389 (3)
N2—C27	1.458 (2)	C15—H15	0.9500
N14—C14	1.470 (2)	C16—H16	0.9500
N21—C22	1.337 (2)	C22—C23	1.391 (3)
N21—C26	1.339 (3)	C23—H23	0.9500
N24—C25	1.336 (3)	C25—C26	1.385 (3)
N24—C23	1.336 (3)	C25—H25	0.9500
C1—C11	1.470 (3)	C26—H26	0.9500
C1—H1	0.9500	C27—H27A	0.9800
C2—C22	1.512 (3)	C27—H27B	0.9800
C11—C16	1.397 (3)	C27—H27C	0.9800
C11—C12	1.402 (3)		

C1—N1—N2	117.97 (16)	C15—C14—N14	118.52 (17)
C2—N2—N1	116.92 (15)	C14—C15—C16	117.64 (17)
C2—N2—C27	120.87 (15)	C14—C15—H15	121.2
N1—N2—C27	122.20 (15)	C16—C15—H15	121.2
O142—N14—O141	123.44 (17)	C15—C16—C11	121.04 (18)
O142—N14—C14	118.25 (16)	C15—C16—H16	119.5
O141—N14—C14	118.30 (16)	C11—C16—H16	119.5
C22—N21—C26	115.43 (17)	N21—C22—C23	122.45 (17)
C25—N24—C23	115.58 (17)	N21—C22—C2	119.39 (16)
N1—C1—C11	119.52 (17)	C23—C22—C2	117.89 (16)
N1—C1—H1	120.2	N24—C23—C22	121.90 (17)
C11—C1—H1	120.2	N24—C23—H23	119.0
O2—C2—N2	121.95 (17)	C22—C23—H23	119.0
O2—C2—C22	119.60 (17)	N24—C25—C26	122.57 (19)
N2—C2—C22	118.44 (16)	N24—C25—H25	118.7
C16—C11—C12	119.38 (17)	C26—C25—H25	118.7
C16—C11—C1	118.91 (17)	N21—C26—C25	122.05 (18)
C12—C11—C1	121.66 (17)	N21—C26—H26	119.0
C13—C12—C11	120.53 (17)	C25—C26—H26	119.0
C13—C12—H12	119.7	N2—C27—H27A	109.5
C11—C12—H12	119.7	N2—C27—H27B	109.5
C12—C13—C14	118.41 (18)	H27A—C27—H27B	109.5
C12—C13—H13	120.8	N2—C27—H27C	109.5
C14—C13—H13	120.8	H27A—C27—H27C	109.5
C13—C14—C15	122.98 (18)	H27B—C27—H27C	109.5
C13—C14—N14	118.50 (17)		

C1—N1—N2—C2	178.94 (16)	C13—C14—C15—C16	−1.8 (3)
C1—N1—N2—C27	−0.1 (3)	N14—C14—C15—C16	178.07 (16)
N2—N1—C1—C11	−175.23 (15)	C14—C15—C16—C11	1.0 (3)

N1—N2—C2—O2	178.58 (16)	C12—C11—C16—C15	0.5 (3)
C27—N2—C2—O2	−2.4 (3)	C1—C11—C16—C15	−176.98 (17)
N1—N2—C2—C22	−0.8 (2)	C26—N21—C22—C23	−0.8 (3)
C27—N2—C2—C22	178.22 (15)	C26—N21—C22—C2	−174.73 (17)
N1—C1—C11—C16	−179.05 (17)	O2—C2—C22—N21	118.3 (2)
N1—C1—C11—C12	3.5 (3)	N2—C2—C22—N21	−62.3 (2)
C16—C11—C12—C13	−1.3 (3)	O2—C2—C22—C23	−55.9 (2)
C1—C11—C12—C13	176.12 (17)	N2—C2—C22—C23	123.49 (19)
C11—C12—C13—C14	0.6 (3)	C25—N24—C23—C22	−0.4 (3)
C12—C13—C14—C15	1.0 (3)	N21—C22—C23—N24	0.9 (3)
C12—C13—C14—N14	−178.83 (16)	C2—C22—C23—N24	174.98 (18)
O142—N14—C14—C13	−173.56 (17)	C23—N24—C25—C26	−0.3 (3)
O141—N14—C14—C13	6.8 (3)	C22—N21—C26—C25	0.2 (3)
O142—N14—C14—C15	6.6 (3)	N24—C25—C26—N21	0.4 (4)
O141—N14—C14—C15	−173.05 (17)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15···O2^{i}	0.95	2.42	3.325 (2)	159
C23—H23···O2^{ii}	0.95	2.36	3.290 (2)	166

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

Comparison of selected geometric parameters (°)

θ is the dihedral angle between pyrazine ring and the phenyl ring, φ_1 and φ_2 are the torsion angles N21—C22—C2—N2 and N1—C1—C11—C12, respectively, and φ_3 is the angular deviation of atom C2 from the mean plane of the pyrazine ring. In (I*b*), the molecule sits on a mirror plane.

Compound	R_1	θ	φ_1	φ_2	φ_3
(II*a*)	H	77.46 (6)	72.83 (14)	175.16 (10)	6.77 (8)
(II*b*)	*o*OCH_3 (major)	58.1 (3)	-128.9 (4)	168.73 (18)	3.2 (3)
	oOCH_3 (minor)	69.5 (3)	67.1 (6)	n/a	′4.1 (3)
(II*c*)	[*p*CN].2H_2O	55.43 (12)	-135.8 (2)	169.8 (2)	4.06 (14)
(II*d*)	*o*NO_2	48.51(17	54.6 (5)	178.7 (3)	6.3 (2)
(II*e*)	*p*NO_2	55.39 (9)	-62.3 (2)	3.5 (3)	4.59 (13)
(I*b*)	*o*OCH_3	0.0	0.0	0.0	0.0
(I*c*)	(*p*CN	5.82 (7)	-3.76 (18)	176.21 (17)	1.56 (9)
(I*d*)	(*o*NO_2	0.54 (5)	-12.72 (15)	-169.90 (10)	1.49 (7)