# (2E)-2-[(2-Hydroxy-4-methoxyphenyl)-(phenyl)methylidene]-N-phenyl-hydrazinecarboxamide dimethyl-formamide monosolvate

C. F. Annie,[a] Jinsa Mary Jacob,[a] M. Sithambaresan[b]* and M. R. Prathapachandra Kurup[a]

[a]Department of Applied Chemistry, Cochin University of Science and Technology, Kochi 682 022, India, and [b]Department of Chemistry, Faculty of Science, Eastern University, Sri Lanka, Chenkalady, Sri Lanka

Correspondence e-mail: eesans@yahoo.com

The title compound, $C_{21}H_{19}N_3O_3 \cdot C_3H_7NO$, adopts an $E$ conformation with respect to the azomethine bond and crystallizes in the amide form. The dihedral angle between the rings lined to the C=N bond is 88.60 (12)°. The dimethylformamide solvent molecule is disordered over two orientations with site occupancies of 0.684 (3) and 0.316 (3). The two N atoms of the hydrazinecarboxamide group are involved in intermolecular N—H⋯O hydrogen bonds in which the dimethylformamide O atom acts as acceptor. The structure also features $\pi$–$\pi$ interactions, with a centroid–centroid distance of 3.6561 (13) Å. Classical and non-classical intramolecular O—H⋯N and C—H⋯O hydrogen bonds are also present.

## Related literature

For applications of hydrazinecarboxamide and its derivatives, see: Afrasiabi et al. (2005); Alam et al. (2010). For related structures, see: Siji et al. (2010); Reena & Kurup (2010); Sithambaresan & Kurup (2011). For standard bond-length data, see: March (1992); Kala et al. (2007). For the synthesis, see: Sreekanth et al. (2004).
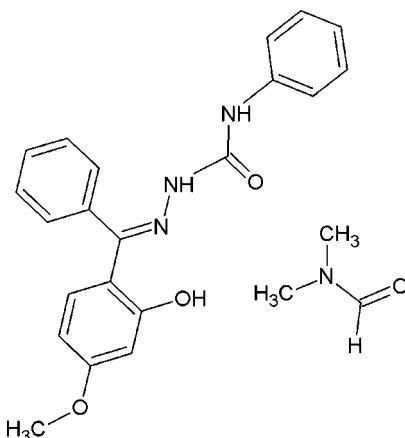
## Experimental

### Crystal data

| | |
|---|---|
| $C_{21}H_{19}N_3O_3 \cdot C_3H_7NO$ | $V$ = 2302.2 (2) Å$^3$ |
| $M_r$ = 434.49 | $Z$ = 4 |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation |
| $a$ = 13.1155 (7) Å | $\mu$ = 0.09 mm$^{-1}$ |
| $b$ = 16.9619 (11) Å | $T$ = 296 K |
| $c$ = 10.7399 (5) Å | 0.35 × 0.30 × 0.25 mm |
| $\beta$ = 105.509 (3)° | |

### Data collection

| | |
|---|---|
| Bruker Kappa APEXII CCD diffractometer | 17400 measured reflections |
| Absorption correction: multi-scan (SADABS; Bruker, 2004) | 4061 independent reflections |
| $T_{min}$ = 0.970, $T_{max}$ = 0.978 | 2875 reflections with $I > 2\sigma(I)$ |
| | $R_{int}$ = 0.069 |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.052 | 10 restraints |
| $wR(F^2)$ = 0.158 | H-atom parameters constrained |
| $S$ = 1.02 | $\Delta\rho_{max}$ = 0.18 e Å$^{-3}$ |
| 4061 reflections | $\Delta\rho_{min}$ = −0.19 e Å$^{-3}$ |
| 311 parameters | |

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

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| O1—H1⋯N1 | 0.89 | 1.78 | 2.5655 (18) | 147 |
| N2—H2′⋯O4A | 0.87 | 2.19 | 2.941 (12) | 145 |
| N2—H2′⋯O4B | 0.87 | 2.22 | 2.96 (3) | 143 |
| N3—H3′⋯O4A | 0.85 | 2.00 | 2.830 (7) | 165 |
| N3—H3′⋯O4B | 0.85 | 2.07 | 2.882 (18) | 161 |
| C24A—H24C⋯O3$^i$ | 0.96 | 2.62 | 3.400 (4) | 139 |
| C23B—H23E⋯O3$^i$ | 0.96 | 2.31 | 3.157 (13) | 147 |
| C23B—H23F⋯O1$^i$ | 0.96 | 2.59 | 3.473 (13) | 153 |

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

Data collection: APEX2 (Bruker, 2004); cell refinement: APEX2 and SAINT (Bruker, 2004); data reduction: SAINT and XPREP (Bruker, 2004); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997) and DIAMOND (Brandenburg, 2010); software used to prepare material for publication: SHELXL97 and publCIF (Westrip, 2010).

# organic compounds

## References

Afrasiabi, Z., Sinn, E., Lin, W., Ma, Y., Campana, C. & Padhye, S. (2005). *J. Inorg. Biochem.* **99**, 1526–1531.

Alam, O., Mullick, P., Verma, S. P., Gilani, S. J., Khan, S. A., Siddiqui, N. & Ahsan, W. (2010). *Eur. J. Med. Chem.* **45**, 2467–2472.

Brandenburg, K. (2010). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Bruker (2004). *SADABS*, *APEX2*, *XPREP* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Kala, U. L., Suma, S., Kurup, M. R. P., Suja, K. & Rohith, P. J. (2007). *Polyhedron*, **26**, 1427–1435.

March, J. (1992). *Advanced Organic Chemistry, Reactions, Mechanisms and Structure*, 4th ed. New York: Wiley.

Reena, T. A. & Kurup, M. R. P. (2010). *J. Chem. Crystallogr.* **40**, 927–932.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Siji, V. L., Sudarsanakumar, M. R. & Suma, S. (2010). *Polyhedron*, **29**, 2035–2040.

Sithambaresan, M. & Kurup, M. R. P. (2011). *Acta Cryst.* E**67**, o2972.

Sreekanth, A., Kala, U. L., Nayar, C. R. & Kurup, M. R. P. (2004). *Polyhedron*, **23**, 41–47.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

# supplementary materials

## (2*E*)-2-[(2-Hydroxy-4-methoxyphenyl)(phenyl)methylidene]-*N*-phenyl-hydrazinecarboxamide dimethylformamide monosolvate

### C. F. Annie, Jinsa Mary Jacob, M. Sithambaresan and M. R. Prathapachandra Kurup

### Comment

Semicarbazones are compounds with versatile structural features (Siji *et al.*, 2010) and exhibit a wide range of bioactivities including anticancer (Afrasiabi *et al.*, 2005) and antiviral properties. Some of them are found to exhibit anticonvulsant activity with less neurotoxicity (Alam *et al.*, 2010).

The compound crystallizes in monoclinic $P2_1/c$ space group. The molecule exists in the *E* configuration with respect to C7=N1 bond (Sithambaresan and Kurup, 2011) which is confirmed by the torsion angle of -179.56 (15)° of N2—N1—C7—C6 moiety (Fig. 1). The torsion angle value of -3.9 (3)° corresponding to N1—N2—C8—O3 moiety supports the *cis* configuration of the O3 atom with respect to the nitrogen atom N1. Also the torsion angles of -1.6 (3)° and -1.2 (3)° for O1—C1—C6—C7 and C1—C6—C7—N1 moieties respectively confirm the *cis* configuration of phenolic oxygen O1 and azomethine nitrogen N1 and it favors intramolecular hydrogen bonding between N1 and H attached to O1.

The C7–N1 bond distance [1.290 (2) Å] is in conformity with a formal C=N bond [1.28 Å] (March, 1992) confirming the azomethine bond formation. The existence of semicarbazone in the amido form in the solid state is confirmed by the observed bond length of 1.210 (2) Å for C8–O3 bond which is identical to a formal C=O bond length [1.21 Å] (Kala *et al.*, 2007). The N1–N2 and N2–C8 bond distances of 1.364 (2) Å and 1.377 (2) Å respectively are greater than that for a double bond and less than that for a single bond which indicate appreciable delocalization of π-electron density over the semicarbazone chain (Reena & Kurup, 2010). Rings *Cg*1[ii] (comprising atoms C1—C6) and *Cg*2[iii] (comprising atoms C9—C14) make a dihedral angle of 14.43 (12)° with each other while rings *Cg*1[ii] and *Cg*3[iv] (comprising atoms C15—C20) are twisted away from each other by a dihedral angle of 88.60 (12)° [symmetry codes: (ii)1 - *x*,1 - *y*,1 - *z*; (iii)1 + *x*,3/2 - *y*,1/2 + *z*; (iv)*x*,3/2 - *y*,1/2 + *z*]. The dimethylformamide solvent molecule is disordered with site occupancies of 0.684 (3) and 0.316 (3).

Fig. 2 shows the packing diagram of the title compound along *c* axis. The nitrogen atoms, N2 and N3 of the hydrazine carboxamide moiety form classical intermolecular hydrogen bonds N2–H2′···O4[i] and N3–H3′···O4[i] respectively in which oxygen atom of the solvent dimethylformamide functions as acceptor and two non classical intramolecular hydrogen bonding interactions also found in the molecule and the DMFsolvent (Table 1). A prominent π···π interaction is observed with a centroid-centroid distance of 3.6561 (13) Å between the *Cg*1[ii] rings of two molecules. Other short ring interactions are weak as they correspond to a distance greater than 4 Å. Two types of C–H···π interactions with H···π distances of 3.3114 and 3.3197 Å are also present in the crystal system.

### Experimental

The title compound was prepared by adapting a reported procedure (Sreekanth *et al.*, 2004). To a warm methanolic solution of *N*-phenylsemicarbazide (0.302 g, 2 mmol), a methanolic solution of 2-hydroxy-4-methoxybenzophenone (0.456 g, 2 mmol) was added and the resulting solution was refluxed for 2 h after adding a drop of conc. HCl. On cooling

the solution colorless crystals were separated out. Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of its solution in a 1:1 mixture of methanol and DMF.

## Refinement

All H atoms on C were placed in calculated positions, guided by difference maps, with C–H bond distances 0.93–0.97 Å. H atoms were assigned as $U_{iso}$=1.2Ueq (1.5 for Me). N2–H2′, N3–H3′ and O1–H1 H atoms were located from difference maps and restrained using *DFIX* instructions. All the C, N and O atoms of the dimethylformamide molecule are disordered over two sites A and B with relative occupancies of 0.637 (4) and 0.363 (4) respectively..

## Computing details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT* (Bruker, 2004); data reduction: *SAINT* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).
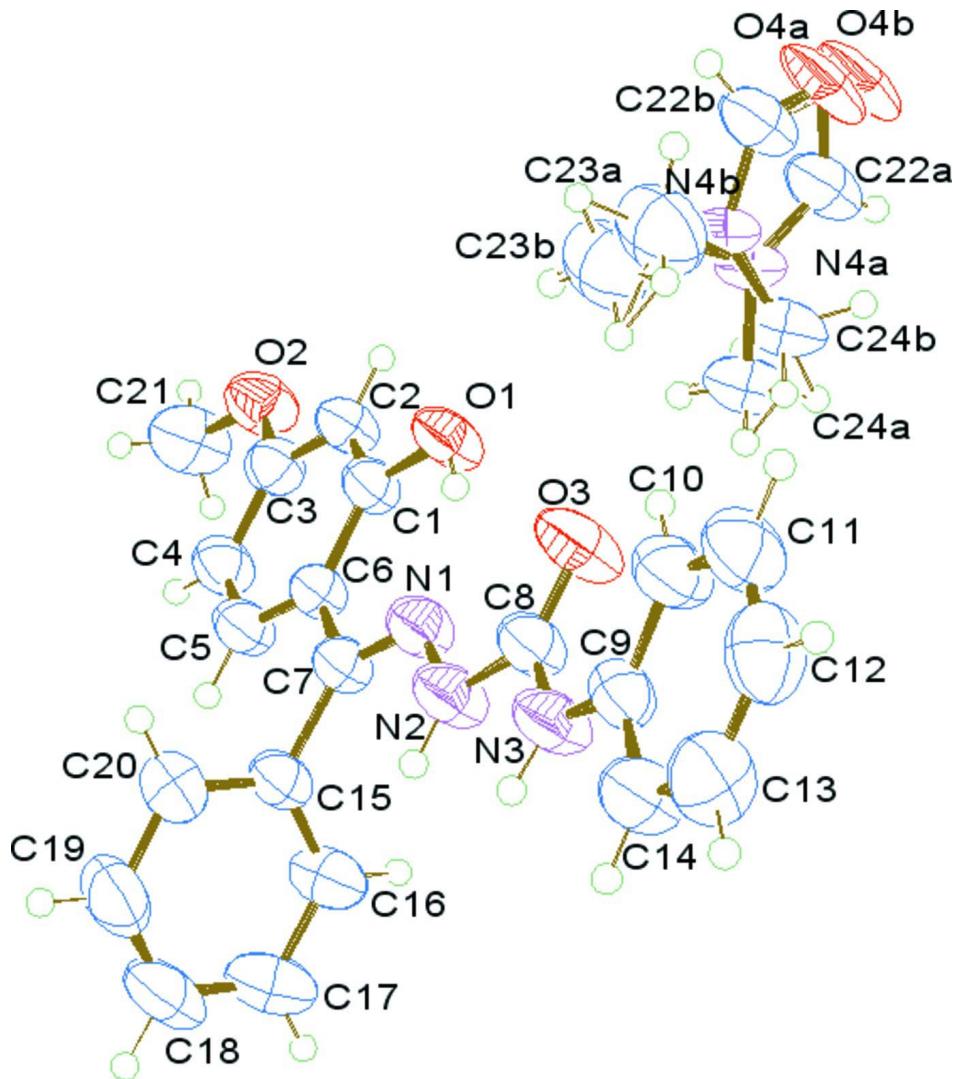
**Figure 1**

The molecular structure of the title compound, showing the disordered DMF solvent molecule.
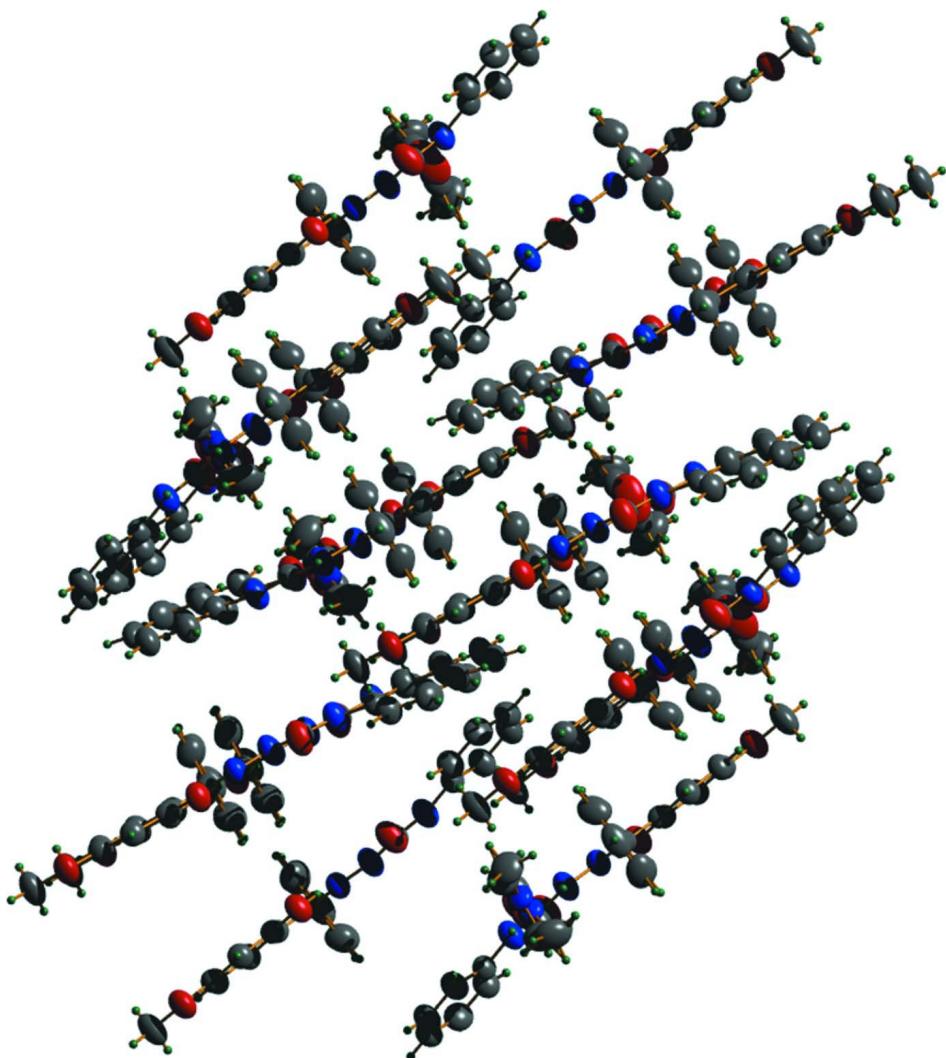


**Figure 2**

A view of the unit cell along *c* axis.

**(2*E*)-2-[(2-Hydroxy-4-methoxyphenyl)(phenyl)methylidene]-*N*- phenylhydrazinecarboxamide**

**dimethylformamide monosolvate**

*Crystal data*
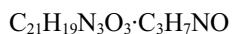
| | |
|---|---|
| $C_{21}H_{19}N_3O_3 \cdot C_3H_7NO$ | $F(000) = 920$ |
| $M_r = 434.49$ | $D_x = 1.254$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -P 2ybc | Cell parameters from 5896 reflections |
| $a = 13.1155$ (7) Å | $\theta = 2.4–28.2°$ |
| $b = 16.9619$ (11) Å | $\mu = 0.09$ mm$^{-1}$ |
| $c = 10.7399$ (5) Å | $T = 296$ K |
| $\beta = 105.509$ (3)° | Block, colourless |
| $V = 2302.2$ (2) Å$^3$ | $0.35 \times 0.30 \times 0.25$ mm |
| $Z = 4$ | |

*Data collection*

| | |
|---|---|
| Bruker Kappa APEXII CCD diffractometer | 17400 measured reflections |
| Radiation source: fine-focus sealed tube | 4061 independent reflections |
| Graphite monochromator | 2875 reflections with $I > 2\sigma(I)$ |
| $\omega$ and $\varphi$ scan | $R_{int} = 0.069$ |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2004) | $\theta_{max} = 25.0°$, $\theta_{min} = 2.3°$ |
| $T_{min} = 0.970$, $T_{max} = 0.978$ | $h = -15 \rightarrow 15$ |
| | $k = -19 \rightarrow 20$ |
| | $l = -12 \rightarrow 12$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.052$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.158$ | |
| $S = 1.02$ | H-atom parameters constrained |
| 4061 reflections | $w = 1/[\sigma^2(F_o^2) + (0.0824P)^2 + 0.2581P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 311 parameters | |
| 10 restraints | $(\Delta/\sigma)_{max} < 0.001$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{max} = 0.18$ e Å$^{-3}$ |
| | $\Delta\rho_{min} = -0.19$ e Å$^{-3}$ |

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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$^2$ > 2sigma(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$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}*/U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| O1 | 0.84998 (10) | 0.61778 (8) | 1.04160 (12) | 0.0666 (4) | |
| H1 | 0.7974 | 0.6191 | 0.9700 | 0.100* | |
| O2 | 1.21655 (11) | 0.59166 (9) | 1.18461 (13) | 0.0740 (4) | |
| O3 | 0.57307 (11) | 0.63119 (10) | 0.84928 (12) | 0.0826 (5) | |
| N1 | 0.75944 (12) | 0.61397 (9) | 0.79832 (14) | 0.0588 (4) | |
| N2 | 0.66741 (12) | 0.61639 (10) | 0.70205 (14) | 0.0655 (5) | |
| H2′ | 0.6700 | 0.6187 | 0.6222 | 0.079* | |
| N3 | 0.48988 (12) | 0.63420 (11) | 0.63350 (14) | 0.0663 (5) | |
| H3′ | 0.5040 | 0.6304 | 0.5610 | 0.080* | |
| C1 | 0.94202 (14) | 0.60977 (10) | 1.00767 (16) | 0.0520 (4) | |
| C2 | 1.03416 (15) | 0.60499 (11) | 1.10594 (16) | 0.0581 (5) | |
| H2 | 1.0311 | 0.6074 | 1.1914 | 0.070* | |
| C3 | 1.13084 (14) | 0.59664 (11) | 1.07944 (17) | 0.0559 (4) | |
| C4 | 1.13607 (15) | 0.59357 (12) | 0.95264 (17) | 0.0609 (5) | |
| H4 | 1.2009 | 0.5881 | 0.9338 | 0.073* | |
| C5 | 1.04372 (14) | 0.59881 (11) | 0.85454 (17) | 0.0575 (5) | |
| H5 | 1.0479 | 0.5971 | 0.7695 | 0.069* | |

| | | | | |
|---|---|---|---|---|
| C6 | 0.94474 (13) | 0.60652 (10) | 0.87711 (15) | 0.0496 (4) |
| C7 | 0.84867 (14) | 0.60951 (10) | 0.76958 (16) | 0.0509 (4) |
| C8 | 0.57499 (15) | 0.62767 (12) | 0.73737 (17) | 0.0590 (5) |
| C9 | 0.38600 (14) | 0.65561 (11) | 0.63201 (16) | 0.0561 (5) |
| C10 | 0.35631 (16) | 0.68054 (13) | 0.73941 (19) | 0.0705 (6) |
| H10 | 0.4059 | 0.6834 | 0.8194 | 0.085* |
| C11 | 0.25230 (18) | 0.70127 (14) | 0.7270 (2) | 0.0804 (6) |
| H11 | 0.2324 | 0.7176 | 0.7998 | 0.097* |
| C12 | 0.17775 (17) | 0.69846 (14) | 0.6102 (2) | 0.0794 (6) |
| H12 | 0.1080 | 0.7128 | 0.6036 | 0.095* |
| C13 | 0.20729 (17) | 0.67438 (15) | 0.5040 (2) | 0.0811 (6) |
| H13 | 0.1576 | 0.6724 | 0.4240 | 0.097* |
| C14 | 0.31036 (16) | 0.65306 (14) | 0.51496 (19) | 0.0722 (6) |
| H14 | 0.3295 | 0.6365 | 0.4418 | 0.087* |
| C15 | 0.85612 (14) | 0.60722 (11) | 0.63283 (16) | 0.0527 (4) |
| C16 | 0.85331 (16) | 0.53656 (13) | 0.57021 (17) | 0.0710 (6) |
| H16 | 0.8457 | 0.4899 | 0.6124 | 0.085* |
| C17 | 0.86165 (18) | 0.53419 (16) | 0.4453 (2) | 0.0847 (7) |
| H17 | 0.8602 | 0.4861 | 0.4033 | 0.102* |
| C18 | 0.87206 (17) | 0.60280 (18) | 0.3829 (2) | 0.0831 (7) |
| H18 | 0.8780 | 0.6014 | 0.2986 | 0.100* |
| C19 | 0.87374 (19) | 0.67305 (17) | 0.4443 (2) | 0.0896 (7) |
| H19 | 0.8803 | 0.7196 | 0.4012 | 0.108* |
| C20 | 0.86589 (17) | 0.67617 (14) | 0.56947 (19) | 0.0748 (6) |
| H20 | 0.8672 | 0.7245 | 0.6109 | 0.090* |
| C21 | 1.31791 (17) | 0.58519 (18) | 1.1620 (2) | 0.0898 (7) |
| H21A | 1.3203 | 0.5388 | 1.1116 | 0.135* |
| H21B | 1.3708 | 0.5815 | 1.2431 | 0.135* |
| H21C | 1.3312 | 0.6309 | 1.1160 | 0.135* |
| O4A | 0.5772 (14) | 0.6210 (6) | 0.4203 (10) | 0.100 (2) | 0.684 (3) |
| N4A | 0.6036 (4) | 0.59304 (18) | 0.2263 (4) | 0.0615 (10) | 0.684 (3) |
| C22A | 0.5958 (2) | 0.5725 (2) | 0.3396 (3) | 0.0780 (9) | 0.684 (3) |
| H22A | 0.6043 | 0.5196 | 0.3627 | 0.094* | 0.684 (3) |
| C23A | 0.6011 (5) | 0.6733 (3) | 0.1866 (5) | 0.1115 (15) | 0.684 (3) |
| H23A | 0.5797 | 0.7059 | 0.2481 | 0.167* | 0.684 (3) |
| H23B | 0.5517 | 0.6791 | 0.1032 | 0.167* | 0.684 (3) |
| H23C | 0.6703 | 0.6888 | 0.1818 | 0.167* | 0.684 (3) |
| C24A | 0.6284 (3) | 0.5357 (2) | 0.1380 (4) | 0.0957 (11) | 0.684 (3) |
| H24A | 0.6188 | 0.4834 | 0.1672 | 0.144* | 0.684 (3) |
| H24B | 0.7005 | 0.5423 | 0.1356 | 0.144* | 0.684 (3) |
| H24C | 0.5822 | 0.5435 | 0.0530 | 0.144* | 0.684 (3) |
| O4B | 0.576 (3) | 0.5968 (15) | 0.421 (2) | 0.100 (2) | 0.316 (3) |
| N4B | 0.6081 (12) | 0.6247 (6) | 0.2322 (10) | 0.0615 (10) | 0.316 (3) |
| C22B | 0.5949 (5) | 0.6475 (5) | 0.3420 (6) | 0.0780 (9) | 0.316 (3) |
| H22B | 0.5990 | 0.7008 | 0.3633 | 0.094* | 0.316 (3) |
| C23B | 0.6333 (13) | 0.6804 (8) | 0.1434 (12) | 0.1115 (15) | 0.316 (3) |
| H23D | 0.6241 | 0.7331 | 0.1712 | 0.167* | 0.316 (3) |
| H23E | 0.5872 | 0.6720 | 0.0586 | 0.167* | 0.316 (3) |
| H23F | 0.7054 | 0.6731 | 0.1413 | 0.167* | 0.316 (3) |

| | | | | | |
|---|---|---|---|---|---|
| C24B | 0.5982 (9) | 0.5433 (6) | 0.1957 (9) | 0.0957 (11) | 0.316 (3) |
| H24D | 0.5607 | 0.5157 | 0.2478 | 0.144* | 0.316 (3) |
| H24E | 0.6673 | 0.5207 | 0.2085 | 0.144* | 0.316 (3) |
| H24F | 0.5599 | 0.5390 | 0.1062 | 0.144* | 0.316 (3) |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0586 (8) | 0.0987 (11) | 0.0499 (7) | 0.0052 (6) | 0.0275 (6) | −0.0003 (6) |
| O2 | 0.0609 (8) | 0.1036 (11) | 0.0558 (8) | 0.0070 (7) | 0.0124 (6) | 0.0008 (7) |
| O3 | 0.0688 (9) | 0.1380 (14) | 0.0465 (8) | 0.0131 (8) | 0.0250 (6) | 0.0061 (7) |
| N1 | 0.0527 (9) | 0.0780 (11) | 0.0483 (8) | 0.0002 (7) | 0.0181 (7) | −0.0024 (7) |
| N2 | 0.0509 (9) | 0.1028 (13) | 0.0464 (8) | 0.0032 (8) | 0.0191 (7) | −0.0020 (7) |
| N3 | 0.0544 (9) | 0.1032 (13) | 0.0464 (8) | 0.0042 (8) | 0.0224 (7) | −0.0056 (8) |
| C1 | 0.0570 (10) | 0.0564 (11) | 0.0489 (9) | −0.0002 (8) | 0.0249 (8) | −0.0001 (7) |
| C2 | 0.0648 (12) | 0.0707 (12) | 0.0426 (9) | 0.0019 (9) | 0.0208 (8) | 0.0010 (8) |
| C3 | 0.0565 (11) | 0.0599 (11) | 0.0506 (10) | 0.0009 (8) | 0.0132 (8) | 0.0013 (8) |
| C4 | 0.0533 (11) | 0.0763 (13) | 0.0577 (11) | 0.0004 (9) | 0.0230 (9) | −0.0020 (9) |
| C5 | 0.0578 (11) | 0.0731 (13) | 0.0466 (9) | −0.0014 (9) | 0.0224 (8) | −0.0018 (8) |
| C6 | 0.0557 (10) | 0.0525 (10) | 0.0446 (9) | −0.0014 (8) | 0.0204 (8) | −0.0013 (7) |
| C7 | 0.0552 (10) | 0.0554 (10) | 0.0468 (9) | 0.0004 (8) | 0.0216 (8) | −0.0019 (7) |
| C8 | 0.0562 (11) | 0.0774 (13) | 0.0483 (10) | 0.0011 (9) | 0.0224 (8) | 0.0005 (8) |
| C9 | 0.0541 (10) | 0.0655 (12) | 0.0545 (10) | −0.0016 (8) | 0.0245 (8) | −0.0001 (8) |
| C10 | 0.0660 (12) | 0.0894 (15) | 0.0636 (12) | 0.0022 (10) | 0.0301 (10) | −0.0071 (10) |
| C11 | 0.0787 (15) | 0.0872 (16) | 0.0902 (15) | 0.0045 (12) | 0.0481 (13) | −0.0083 (12) |
| C12 | 0.0601 (13) | 0.0776 (15) | 0.1070 (18) | 0.0068 (11) | 0.0335 (13) | 0.0089 (12) |
| C13 | 0.0610 (13) | 0.0981 (18) | 0.0811 (14) | 0.0040 (11) | 0.0138 (11) | 0.0091 (12) |
| C14 | 0.0657 (13) | 0.0950 (16) | 0.0576 (11) | 0.0047 (11) | 0.0197 (10) | 0.0009 (10) |
| C15 | 0.0483 (9) | 0.0676 (12) | 0.0453 (9) | 0.0019 (8) | 0.0180 (7) | −0.0003 (8) |
| C16 | 0.0888 (15) | 0.0769 (14) | 0.0508 (10) | 0.0136 (11) | 0.0248 (10) | 0.0000 (9) |
| C17 | 0.0972 (17) | 0.1058 (19) | 0.0559 (12) | 0.0201 (14) | 0.0286 (11) | −0.0127 (12) |
| C18 | 0.0656 (13) | 0.142 (2) | 0.0486 (11) | −0.0003 (13) | 0.0267 (10) | 0.0035 (13) |
| C19 | 0.0954 (17) | 0.113 (2) | 0.0636 (13) | −0.0207 (14) | 0.0274 (12) | 0.0217 (13) |
| C20 | 0.0877 (15) | 0.0799 (15) | 0.0613 (12) | −0.0139 (11) | 0.0276 (10) | 0.0036 (10) |
| C21 | 0.0567 (13) | 0.134 (2) | 0.0743 (14) | 0.0100 (13) | 0.0106 (10) | −0.0093 (13) |
| O4A | 0.0932 (13) | 0.156 (7) | 0.0592 (9) | 0.019 (6) | 0.0347 (9) | −0.010 (3) |
| N4A | 0.0719 (13) | 0.064 (3) | 0.0525 (11) | −0.004 (3) | 0.0242 (10) | −0.004 (2) |
| C22A | 0.0719 (17) | 0.115 (3) | 0.0520 (14) | 0.0056 (19) | 0.0260 (13) | 0.0029 (17) |
| C23A | 0.146 (5) | 0.099 (3) | 0.099 (4) | 0.018 (3) | 0.048 (3) | 0.018 (3) |
| C24A | 0.122 (3) | 0.103 (3) | 0.073 (2) | −0.008 (2) | 0.045 (2) | −0.022 (2) |
| O4B | 0.0932 (13) | 0.156 (7) | 0.0592 (9) | 0.019 (6) | 0.0347 (9) | −0.010 (3) |
| N4B | 0.0719 (13) | 0.064 (3) | 0.0525 (11) | −0.004 (3) | 0.0242 (10) | −0.004 (2) |
| C22B | 0.0719 (17) | 0.115 (3) | 0.0520 (14) | 0.0056 (19) | 0.0260 (13) | 0.0029 (17) |
| C23B | 0.146 (5) | 0.099 (3) | 0.099 (4) | 0.018 (3) | 0.048 (3) | 0.018 (3) |
| C24B | 0.122 (3) | 0.103 (3) | 0.073 (2) | −0.008 (2) | 0.045 (2) | −0.022 (2) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C1 | 1.3579 (19) | C15—C20 | 1.376 (3) |
| O1—H1 | 0.8851 | C16—C17 | 1.376 (3) |
| O2—C3 | 1.367 (2) | C16—H16 | 0.9300 |
| O2—C21 | 1.418 (2) | C17—C18 | 1.368 (3) |
| O3—C8 | 1.210 (2) | C17—H17 | 0.9300 |
| N1—C7 | 1.290 (2) | C18—C19 | 1.359 (4) |
| N1—N2 | 1.364 (2) | C18—H18 | 0.9300 |
| N2—C8 | 1.377 (2) | C19—C20 | 1.376 (3) |
| N2—H2′ | 0.8683 | C19—H19 | 0.9300 |
| N3—C8 | 1.355 (2) | C20—H20 | 0.9300 |
| N3—C9 | 1.406 (2) | C21—H21A | 0.9600 |
| N3—H3′ | 0.8495 | C21—H21B | 0.9600 |
| C1—C2 | 1.378 (3) | C21—H21C | 0.9600 |
| C1—C6 | 1.413 (2) | O4A—C22A | 1.265 (10) |
| C2—C3 | 1.379 (2) | N4A—C22A | 1.295 (4) |
| C2—H2 | 0.9300 | N4A—C23A | 1.424 (6) |
| C3—C4 | 1.383 (2) | N4A—C24A | 1.455 (5) |
| C4—C5 | 1.379 (3) | C22A—H22A | 0.9300 |
| C4—H4 | 0.9300 | C23A—H23A | 0.9600 |
| C5—C6 | 1.389 (2) | C23A—H23B | 0.9600 |
| C5—H5 | 0.9300 | C23A—H23C | 0.9600 |
| C6—C7 | 1.465 (2) | C24A—H24A | 0.9600 |
| C7—C15 | 1.498 (2) | C24A—H24B | 0.9600 |
| C9—C14 | 1.378 (3) | C24A—H24C | 0.9600 |
| C9—C10 | 1.379 (2) | O4B—C22B | 1.274 (11) |
| C10—C11 | 1.380 (3) | N4B—C22B | 1.295 (10) |
| C10—H10 | 0.9300 | N4B—C24B | 1.432 (10) |
| C11—C12 | 1.369 (3) | N4B—C23B | 1.442 (11) |
| C11—H11 | 0.9300 | C22B—H22B | 0.9300 |
| C12—C13 | 1.362 (3) | C23B—H23D | 0.9600 |
| C12—H12 | 0.9300 | C23B—H23E | 0.9600 |
| C13—C14 | 1.374 (3) | C23B—H23F | 0.9600 |
| C13—H13 | 0.9300 | C24B—H24D | 0.9600 |
| C14—H14 | 0.9300 | C24B—H24E | 0.9600 |
| C15—C16 | 1.370 (3) | C24B—H24F | 0.9600 |
| | | | |
| C1—O1—H1 | 108.1 | C9—C14—H14 | 119.3 |
| C3—O2—C21 | 117.70 (15) | C16—C15—C20 | 119.64 (17) |
| C7—N1—N2 | 119.74 (14) | C16—C15—C7 | 120.25 (16) |
| N1—N2—C8 | 117.46 (14) | C20—C15—C7 | 120.11 (17) |
| N1—N2—H2′ | 119.3 | C15—C16—C17 | 120.4 (2) |
| C8—N2—H2′ | 122.4 | C15—C16—H16 | 119.8 |
| C8—N3—C9 | 127.79 (14) | C17—C16—H16 | 119.8 |
| C8—N3—H3′ | 114.5 | C18—C17—C16 | 119.8 (2) |
| C9—N3—H3′ | 117.2 | C18—C17—H17 | 120.1 |
| O1—C1—C2 | 117.44 (14) | C16—C17—H17 | 120.1 |
| O1—C1—C6 | 122.02 (16) | C19—C18—C17 | 119.97 (19) |
| C2—C1—C6 | 120.54 (15) | C19—C18—H18 | 120.0 |

| | | | |
|---|---|---|---|
| C1—C2—C3 | 120.95 (15) | C17—C18—H18 | 120.0 |
| C1—C2—H2 | 119.5 | C18—C19—C20 | 120.8 (2) |
| C3—C2—H2 | 119.5 | C18—C19—H19 | 119.6 |
| O2—C3—C2 | 115.74 (15) | C20—C19—H19 | 119.6 |
| O2—C3—C4 | 124.42 (16) | C15—C20—C19 | 119.4 (2) |
| C2—C3—C4 | 119.85 (17) | C15—C20—H20 | 120.3 |
| C5—C4—C3 | 119.02 (16) | C19—C20—H20 | 120.3 |
| C5—C4—H4 | 120.5 | O2—C21—H21A | 109.5 |
| C3—C4—H4 | 120.5 | O2—C21—H21B | 109.5 |
| C4—C5—C6 | 122.93 (15) | H21A—C21—H21B | 109.5 |
| C4—C5—H5 | 118.5 | O2—C21—H21C | 109.5 |
| C6—C5—H5 | 118.5 | H21A—C21—H21C | 109.5 |
| C5—C6—C1 | 116.71 (16) | H21B—C21—H21C | 109.5 |
| C5—C6—C7 | 120.84 (14) | C22A—N4A—C23A | 122.5 (4) |
| C1—C6—C7 | 122.44 (15) | C22A—N4A—C24A | 121.3 (3) |
| N1—C7—C6 | 117.22 (14) | C23A—N4A—C24A | 115.8 (4) |
| N1—C7—C15 | 122.50 (15) | O4A—C22A—N4A | 123.1 (5) |
| C6—C7—C15 | 120.28 (14) | O4A—C22A—H22A | 118.4 |
| O3—C8—N3 | 125.60 (16) | N4A—C22A—H22A | 118.4 |
| O3—C8—N2 | 122.28 (17) | C22B—N4B—C24B | 120.9 (10) |
| N3—C8—N2 | 112.12 (14) | C22B—N4B—C23B | 121.1 (9) |
| C14—C9—C10 | 118.51 (17) | C24B—N4B—C23B | 118.0 (9) |
| C14—C9—N3 | 117.47 (15) | O4B—C22B—N4B | 119.8 (14) |
| C10—C9—N3 | 124.01 (17) | O4B—C22B—H22B | 120.1 |
| C9—C10—C11 | 119.4 (2) | N4B—C22B—H22B | 120.1 |
| C9—C10—H10 | 120.3 | N4B—C23B—H23D | 109.5 |
| C11—C10—H10 | 120.3 | N4B—C23B—H23E | 109.5 |
| C12—C11—C10 | 121.66 (19) | H23D—C23B—H23E | 109.5 |
| C12—C11—H11 | 119.2 | N4B—C23B—H23F | 109.5 |
| C10—C11—H11 | 119.2 | H23D—C23B—H23F | 109.5 |
| C13—C12—C11 | 118.96 (19) | H23E—C23B—H23F | 109.5 |
| C13—C12—H12 | 120.5 | N4B—C24B—H24D | 109.5 |
| C11—C12—H12 | 120.5 | N4B—C24B—H24E | 109.5 |
| C12—C13—C14 | 120.1 (2) | H24D—C24B—H24E | 109.5 |
| C12—C13—H13 | 120.0 | N4B—C24B—H24F | 109.5 |
| C14—C13—H13 | 120.0 | H24D—C24B—H24F | 109.5 |
| C13—C14—C9 | 121.45 (18) | H24E—C24B—H24F | 109.5 |
| C13—C14—H14 | 119.3 | | |
| | | | |
| C7—N1—N2—C8 | −174.78 (16) | C8—N3—C9—C14 | −175.6 (2) |
| O1—C1—C2—C3 | 179.87 (16) | C8—N3—C9—C10 | 5.9 (3) |
| C6—C1—C2—C3 | −0.3 (3) | C14—C9—C10—C11 | 0.7 (3) |
| C21—O2—C3—C2 | −178.32 (18) | N3—C9—C10—C11 | 179.1 (2) |
| C21—O2—C3—C4 | 1.9 (3) | C9—C10—C11—C12 | −0.6 (3) |
| C1—C2—C3—O2 | −179.31 (16) | C10—C11—C12—C13 | 0.2 (4) |
| C1—C2—C3—C4 | 0.5 (3) | C11—C12—C13—C14 | 0.3 (4) |
| O2—C3—C4—C5 | 179.65 (17) | C12—C13—C14—C9 | −0.2 (4) |
| C2—C3—C4—C5 | −0.1 (3) | C10—C9—C14—C13 | −0.3 (3) |
| C3—C4—C5—C6 | −0.5 (3) | N3—C9—C14—C13 | −178.8 (2) |

| | | | |
|---|---|---|---|
| C4—C5—C6—C1 | 0.7 (3) | N1—C7—C15—C16 | −89.3 (2) |
| C4—C5—C6—C7 | −178.17 (17) | C6—C7—C15—C16 | 90.6 (2) |
| O1—C1—C6—C5 | 179.55 (16) | N1—C7—C15—C20 | 90.7 (2) |
| C2—C1—C6—C5 | −0.3 (2) | C6—C7—C15—C20 | −89.4 (2) |
| O1—C1—C6—C7 | −1.6 (3) | C20—C15—C16—C17 | 0.9 (3) |
| C2—C1—C6—C7 | 178.53 (17) | C7—C15—C16—C17 | −179.07 (18) |
| N2—N1—C7—C6 | −179.56 (15) | C15—C16—C17—C18 | −0.5 (3) |
| N2—N1—C7—C15 | 0.3 (3) | C16—C17—C18—C19 | −0.2 (4) |
| C5—C6—C7—N1 | 177.65 (16) | C17—C18—C19—C20 | 0.5 (4) |
| C1—C6—C7—N1 | −1.2 (2) | C16—C15—C20—C19 | −0.6 (3) |
| C5—C6—C7—C15 | −2.2 (3) | C7—C15—C20—C19 | 179.34 (19) |
| C1—C6—C7—C15 | 178.97 (15) | C18—C19—C20—C15 | −0.1 (3) |
| C9—N3—C8—O3 | 8.5 (3) | C23A—N4A—C22A—O4A | 5.7 (12) |
| C9—N3—C8—N2 | −171.40 (18) | C24A—N4A—C22A—O4A | 178.0 (10) |
| N1—N2—C8—O3 | −3.9 (3) | C24B—N4B—C22B—O4B | 2 (3) |
| N1—N2—C8—N3 | 175.94 (16) | C23B—N4B—C22B—O4B | −178 (2) |

*Hydrogen-bond geometry (Å, º)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| O1—H1···N1 | 0.89 | 1.78 | 2.5655 (18) | 147 |
| N2—H2′···O4*A* | 0.87 | 2.19 | 2.941 (12) | 145 |
| N2—H2′···O4*B* | 0.87 | 2.22 | 2.96 (3) | 143 |
| N3—H3′···O4*A* | 0.85 | 2.00 | 2.830 (7) | 165 |
| N3—H3′···O4*B* | 0.85 | 2.07 | 2.882 (18) | 161 |
| C24*A*—H24*C*···O3[i] | 0.96 | 2.62 | 3.400 (4) | 139 |
| C23*B*—H23*E*···O3[i] | 0.96 | 2.31 | 3.157 (13) | 147 |
| C23*B*—H23*F*···O1[i] | 0.96 | 2.59 | 3.473 (13) | 153 |

Symmetry code: (i) *x*, *y*, *z*−1.