# organic compounds

# Dimethyl 2-(methylaminomethylene)-malonate

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In the title compound, $C_7H_{11}NO_4$, which is an example of a push–pull alkene, a network of N—H⋯O and C—H⋯O interactions helps to establish the crystal structure. The investigated crystal turned out to be a non-merohedral twin with a ratio of twin components of 0.442 (3):0.558 (3). Two pairs of independent molecules ($Z'$ = 4) are linked by intermolecular N—H⋯O hydrogen bonds, forming independent chains; the chains are connected *via* intermolecular C—H⋯O contacts, building a three-dimensional network.

## Related literature

For related literature, see: Bouzard (1990); Cook (1969); Dyke (1973); Freeman (1981); Gróf *et al.* (2008); Kálmán & Argay (1998); Bolte (2004).
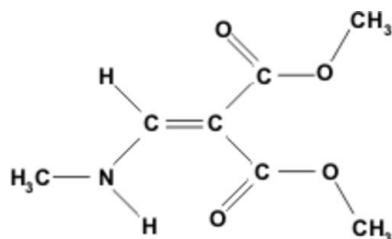
## Experimental

### Crystal data

| | |
|---|---|
| $C_7H_{11}NO_4$ | $\gamma$ = 94.02 (3)° |
| $M_r$ = 173.17 | $V$ = 1618.1 (6) Å³ |
| Triclinic, $P\overline{1}$ | $Z$ = 8 |
| $a$ = 11.165 (2) Å | Mo $K\alpha$ radiation |
| $b$ = 12.073 (2) Å | $\mu$ = 0.12 mm⁻¹ |
| $c$ = 13.211 (3) Å | $T$ = 100 K |
| $\alpha$ = 113.70 (3)° | 0.43 × 0.15 × 0.08 mm |
| $\beta$ = 93.71 (3)° | |

### Data collection

| | |
|---|---|
| Oxford Diffraction GEMINI R diffractometer | Diffraction, 2006) |
| | $T_{min}$ = 0.968, $T_{max}$ = 0.996 |
| Absorption correction: analytical (*CrysAlis RED*; Oxford | 9295 measured reflections |
| | 9295 independent reflections |
| | 3920 reflections with $I > 2\sigma(I)$ |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.091 | 96 restraints |
| $wR(F^2)$ = 0.257 | H-atom parameters constrained |
| $S$ = 0.90 | $\Delta\rho_{max}$ = 1.13 e Å⁻³ |
| 9295 reflections | $\Delta\rho_{min}$ = −0.54 e Å⁻³ |
| 446 parameters | |

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

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| N1—H1⋯O1 | 0.86 | 2.08 | 2.689 (4) | 127 |
| N1—H1⋯O10 | 0.86 | 2.42 | 2.990 (4) | 125 |
| N2—H2⋯O5 | 0.86 | 2.08 | 2.687 (4) | 127 |
| N2—H2⋯O14$^i$ | 0.86 | 2.30 | 2.893 (5) | 127 |
| N3—H3⋯O9 | 0.86 | 2.06 | 2.684 (4) | 129 |
| N3—H3⋯O2$^i$ | 0.86 | 2.32 | 2.912 (5) | 126 |
| N4—H4⋯O13 | 0.86 | 2.08 | 2.698 (5) | 128 |
| N4—H4⋯O6 | 0.86 | 2.40 | 2.957 (5) | 123 |
| C4—H4$A$⋯O2 | 0.93 | 2.27 | 2.683 (7) | 106 |
| C6—H6$A$⋯O14 | 0.96 | 2.50 | 3.449 (7) | 169 |
| C11—H11$A$⋯O6 | 0.93 | 2.29 | 2.706 (6) | 107 |
| C11—H11$A$⋯O13 | 0.93 | 2.60 | 3.487 (6) | 159 |
| C14—H14$A$⋯O13 | 0.96 | 2.59 | 3.507 (6) | 161 |
| C18—H18$A$⋯O1 | 0.93 | 2.58 | 3.470 (6) | 160 |
| C18—H18$A$⋯O10 | 0.93 | 2.27 | 2.679 (6) | 106 |
| C25—H25$A$⋯O14 | 0.93 | 2.28 | 2.691 (6) | 106 |
| C27—H27$A$⋯O2$^i$ | 0.96 | 2.59 | 3.340 (7) | 135 |
| C28—H28$C$⋯O6 | 0.96 | 2.60 | 3.024 (6) | 107 |

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2088).

## References

Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.

Bolte, M. (2004). *J. Appl. Cryst.* **37**, 162–165.

Bouzard, D. (1990). *Recent Progress in the Chemical Synthesis of Antibiotics*, p. 249. München: Springer-Verlag.

Brandenburg, K. (1998). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Cook, A. G. (1969). *Enamines: Syntheses, Structure and Reactions*. New York: Marcel Dekker.

Dyke, S. F. (1973). *The Chemistry of Enamines*. London: Cambridge University Press.

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Freeman, F. (1981). *LONZA Reaction of Malononitrile Derivatives*, p. 925. Stuttgart: Georg Thieme Verlag.

Gróf, M., Kožíšek, J., Milata, V. & Gatial, A. (2008). *Acta Cryst.* E**64**, o998.

Kálmán, A. & Argay, Gy. (1998). *Acta Cryst.* B**54**, 877–888.

Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.

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

# Dimethyl 2-(methylaminomethylene)malonate

**Martin Gróf, Jozef Kožíšek, Viktor Milata and Anton Gatial**

### S1. Comment

The title compound, $C_7 H_{11} N O_4$, belongs to the so-called push-pull olefins. Push-pull alkenes are substituted ethylenes containing electron-donor groups (D) at one end and electron-acceptor groups (A) at the other end of the general formula $D^1D^2C=CA^1A^2$. These compounds very often contain alkoxy, amino, alkylamino, dialkylamino or (hetero)aryl groups as electron-donor groups and cyano, acetyl, alkylester, methylsulfonyl or $NO_2$ groups as electron-acceptor groups. They are useful as starting reactants or intermediates for a lot of pharmaceutical, polymer and other syntheses (Cook, 1969; Dyke, 1973). Mainly enamines are frequently used as reactants or intermediates in chemical syntheses of drugs, polymers and dyes (Bouzard, 1990). But also alkoxymethylenes are often used in organic synthesis (Freeman, 1981).

Chemical and physical properties of the title related structures were recently discussed (Gróf *et al.*, 2008 and literature cited therein).

The study of a similar compound, dimethyl 2-(aminomethylene)malonate, (Gróf *et al.*, 2008) revealed that this structure exists in the solid phase as EZ conformer (E denotes away from C=C double bond orientation of the carbonyl oxygen in *trans* position; Z denotes towards to C=C double bond orientation of the carbonyl oxygen in *cis* position). The title compound exists in the solid phase as ZZa conformer (a denotes anti orientation of the methylamino group, *e.g.* away from the C=C double bond orientation).

The molecules I and II, and molecules III and IV of the title compound (Fig.1) show pseudo translation (Kálmán & Argay, (1998).

### S2. Experimental

To dimethyl 3-methoxymethylenemalonate (1.74 g, 10 mmol) in methanol (10 ml), an aqueous solution of methylamine (12 mmol) was added dropwise (amount according to concentration and density) over a period of 30 min with stirring. The slightly warmed mixture was stirred overnight at room temperature. The reaction mixture was then briefly heated to reflux (ca. 20 min). After ensuring that no starting derivative remained (thin-layer chromatography; Silufol 254, Kavalier Czechoslovakia; eluent chloroform-methanol 10:1 *v/v*, detection UV light 254 nm), the reaction mixture was evaporated on a vacuum evaporator and chromatographed on silica gel (eluent dichloromethane-methanol 10:1 *v/v*). Obtained product was recrystallized from minimal amount of chloroform and n-hexane mixture in refrigerator.

The solid phase mid-IR vibrational spectrum was recorded with a Nicolet model NEXUS 470 FTIR spectrometer at room temperature. The measurement was performed after mixing the powdered sample with KBr into a pellet.

The mid-IR vibrational frequencies of dimethyl 2-(methylaminomethylene)malonate are (in $cm^{-1}$): 3301 m; 3199 w, sh, b; 3092 vw; 3052 vw; 3039 vw; 3013 w; 2999 w; 2951 m; 2924 w, sh; 2905 vw, sh; 1701 vw, sh; 1680 v s; 1651 vw, sh; 1631 v s; 1612 w, sh; 1541 vw; 1478 w; 1450 m; 1430 m; 1405 m; 1360 s; 1330 vw, sh; 1322 m; 1281 s; 1225 s; 1187 m; 1151 s; 1082 m; 1042 w; 1018 m; 998 w; 942 vw; 837 vw, sh; 820 s; 808 s; 768 m; 759 vw, sh; 671 m; 579 w, b; 459 vw; 446 vw; 413 m.

## S3. Refinement

Olefinic and amino H atoms were positioned geometrically and allowed to ride on their corresponding parent atoms at distances of 0.93 and 0.86 Å, respectively, with $U_{iso}(H) = 1.2U_{eq}(C,N)$. Methyl H atoms were located in a difference Fourier map and included in the model as a rigid rotating group, with C—H distance of 0.96 Å and with $U_{iso}(H) = 1.5U_{eq}(C)$.

The investigated crystal was a non-merohedral twin. Two orientation matrices could be determined and the twin law was derived using the program TWINLAW (Bolte, 2004):

h(twin) = (1.00 * h) + (0.00 * k) + (0.00 * l)

k(twin) = (-0.15 * h) + (-1.00 * k) + (0.00 * l)

l(twin) = (-0.16 * h) + (0.00 * k) + (-1.00 *l).

For the refinement the reflection data file was modified using the program HKLF5 (Bolte, 2004). The contribution of the minor twin component refined to 0.442 (3).
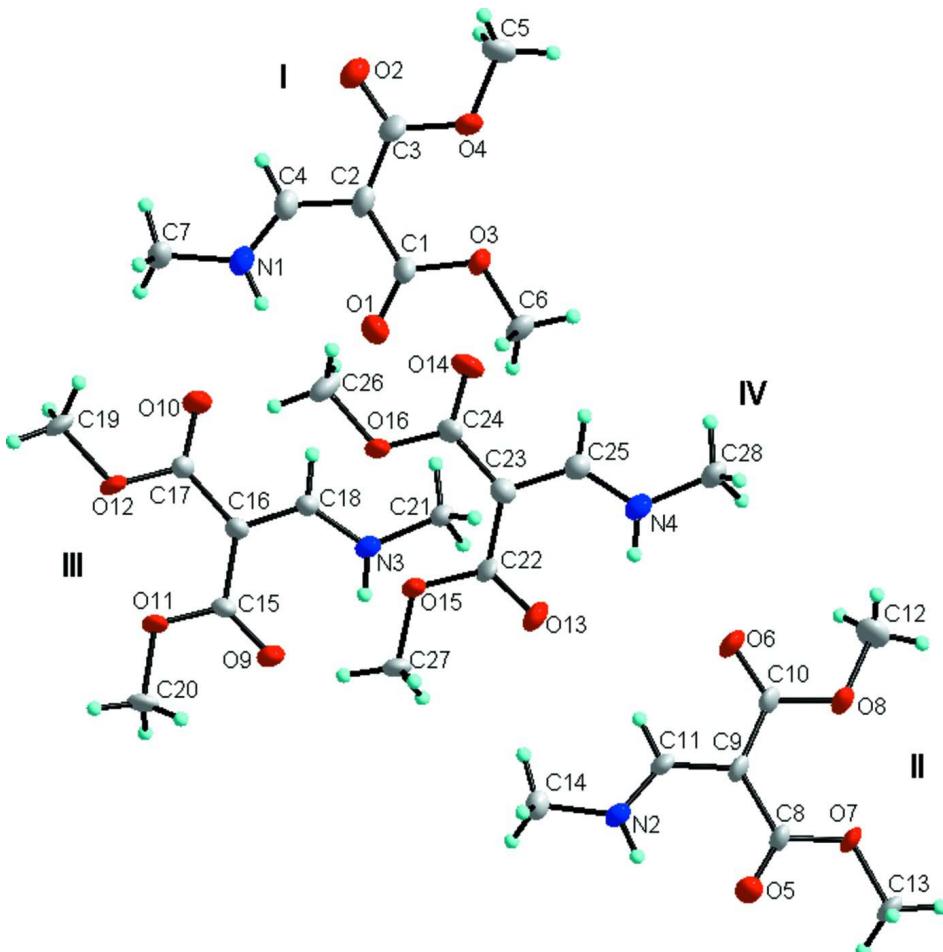
**Figure 1**

The atom-numbering scheme of dimethyl 2-(methylaminomethylene)malonate. Displacement ellipsoids are drawn at the 60% probability level.
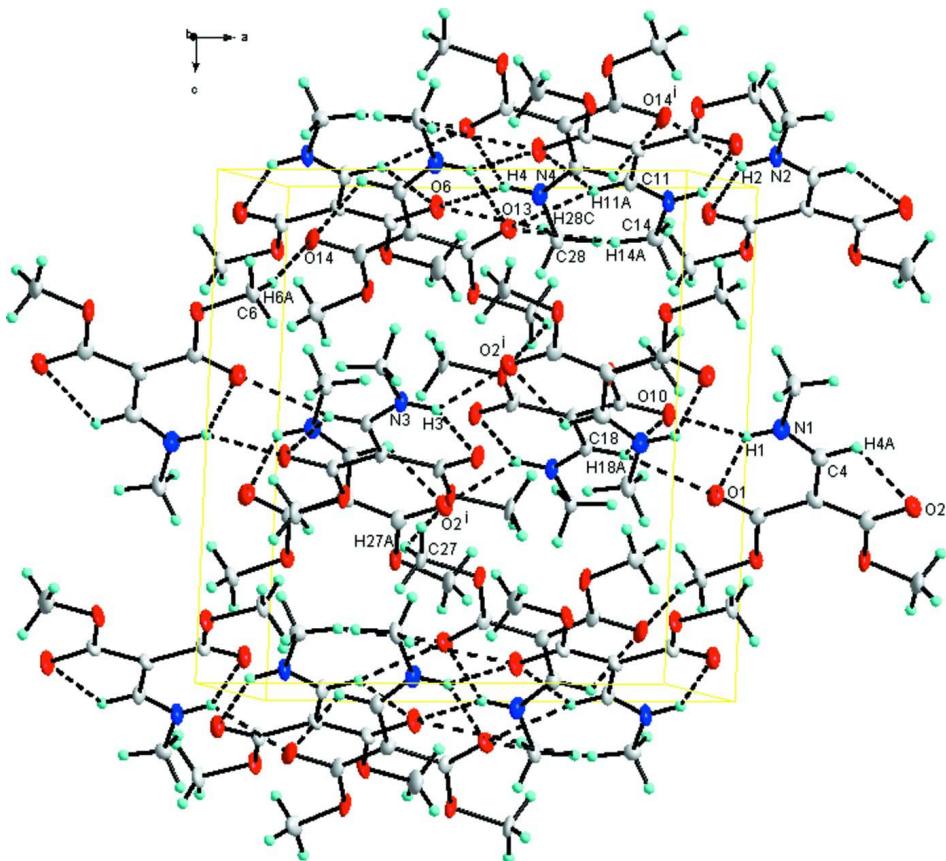
**Figure 2**

Packing diagram of dimethyl 2-(methylaminomethylene)malonate. Hydrogen-bond interactions are indicated by dashed lines.

**Dimethyl 2-(methylaminomethylene)malonate**

*Crystal data*

| | |
|---|---|
| $C_7H_{11}NO_4$ | $Z = 8$ |
| $M_r = 173.17$ | $F(000) = 736$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.422$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 11.165$ (2) Å | Cell parameters from 2135 reflections |
| $b = 12.073$ (2) Å | $\theta = 3.3–29.5°$ |
| $c = 13.211$ (3) Å | $\mu = 0.12$ mm$^{-1}$ |
| $\alpha = 113.70$ (3)° | $T = 100$ K |
| $\beta = 93.71$ (3)° | Block, yellow |
| $\gamma = 94.02$ (3)° | $0.43 \times 0.15 \times 0.08$ mm |
| $V = 1618.1$ (6) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Oxford Diffraction GEMINI R diffractometer | Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2006) |
| Radiation source: fine-focus sealed tube | $T_{min} = 0.968$, $T_{max} = 0.996$ |
| Graphite monochromator | 9295 measured reflections |
| Rotation method data acquisition using $\omega$ and $\varphi$ scans | 9295 independent reflections |
| | 3920 reflections with $I > 2\sigma(I)$ |

$R_{int} = 0.000$

$\theta_{max} = 25.4°, \theta_{min} = 4.1°$

$h = -13 \rightarrow 13$

$k = -14 \rightarrow 14$

$l = -15 \rightarrow 15$

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.092$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.257$ | |
| $S = 0.90$ | H-atom parameters constrained |
| 9295 reflections | $w = 1/[\sigma^2(F_o^2) + (0.1527P)^2]$ |
| 446 parameters | where $P = (F_o^2 + 2F_c^2)/3$ |
| 96 restraints | $(\Delta/\sigma)_{max} = 0.067$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{max} = 1.13$ e Å$^{-3}$ |
| | $\Delta\rho_{min} = -0.54$ e Å$^{-3}$ |

*Special details*

**Experimental**. face-indexed (*CrysAlis RED*; Oxford Diffraction, 2006). 96 rigid bond restaints (DELU) were used in the refinement because the data to parameter ratio is low due to four independent molecules in the twinned structure.

**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)*

| | $x$ | $y$ | $z$ | $U_{iso}*/U_{eq}$ |
|---|---|---|---|---|
| C1 | 1.0504 (4) | 0.1221 (5) | 0.6433 (4) | 0.0202 (11) |
| C2 | 1.1715 (5) | 0.1334 (5) | 0.6103 (4) | 0.0234 (11) |
| C3 | 1.2819 (5) | 0.1043 (5) | 0.6504 (4) | 0.0238 (11) |
| C4 | 1.1851 (5) | 0.1766 (5) | 0.5297 (4) | 0.0274 (12) |
| H4A | 1.2634 | 0.1815 | 0.5106 | 0.033* |
| C5 | 1.3825 (4) | 0.0278 (5) | 0.7690 (4) | 0.0327 (14) |
| H5C | 1.3656 | −0.0079 | 0.8203 | 0.039* |
| H5B | 1.4350 | 0.1019 | 0.8066 | 0.039* |
| H5A | 1.4210 | −0.0279 | 0.7090 | 0.039* |
| C6 | 0.9264 (4) | 0.0767 (5) | 0.7613 (4) | 0.0241 (12) |
| H6C | 0.9311 | 0.0528 | 0.8224 | 0.029* |
| H6B | 0.8723 | 0.0182 | 0.7012 | 0.029* |
| H6A | 0.8970 | 0.1552 | 0.7848 | 0.029* |
| C7 | 1.1353 (4) | 0.2577 (5) | 0.3932 (4) | 0.0298 (13) |
| H7C | 1.1168 | 0.3404 | 0.4176 | 0.036* |
| H7B | 1.0889 | 0.2087 | 0.3236 | 0.036* |
| H7A | 1.2198 | 0.2546 | 0.3840 | 0.036* |
| O1 | 0.9618 (3) | 0.1470 (3) | 0.6036 (3) | 0.0317 (9) |
| O2 | 1.3803 (3) | 0.1235 (3) | 0.6240 (3) | 0.0294 (9) |
| O3 | 1.0441 (3) | 0.0828 (3) | 0.7250 (3) | 0.0257 (8) |

| O4 | 1.2710 (3) | 0.0540 (3) | 0.7254 (3) | 0.0303 (9) |
| N1 | 1.1056 (4) | 0.2113 (4) | 0.4763 (3) | 0.0290 (11) |
| H1 | 1.0317 | 0.2069 | 0.4902 | 0.035* |
| C8 | 0.0163 (4) | 0.1936 (5) | 1.0767 (4) | 0.0227 (11) |
| C9 | 0.1389 (4) | 0.2097 (5) | 1.0475 (4) | 0.0198 (10) |
| C10 | 0.2442 (4) | 0.1583 (5) | 1.0733 (4) | 0.0234 (11) |
| C11 | 0.1614 (4) | 0.2782 (5) | 0.9871 (4) | 0.0224 (11) |
| H11A | 0.2405 | 0.2835 | 0.9699 | 0.027* |
| C12 | 0.3325 (4) | 0.0431 (6) | 1.1587 (4) | 0.0374 (14) |
| H12C | 0.3077 | −0.0189 | 1.1835 | 0.045* |
| H12B | 0.3855 | 0.1061 | 1.2165 | 0.045* |
| H12A | 0.3742 | 0.0082 | 1.0936 | 0.045* |
| C13 | −0.1214 (4) | 0.1026 (5) | 1.1526 (4) | 0.0261 (13) |
| H13C | −0.1269 | 0.0428 | 1.1833 | 0.031* |
| H13B | −0.1767 | 0.0763 | 1.0866 | 0.031* |
| H13A | −0.1415 | 0.1788 | 1.2061 | 0.031* |
| C14 | 0.1222 (4) | 0.3979 (5) | 0.8809 (4) | 0.0231 (12) |
| H14C | 0.1054 | 0.4812 | 0.9146 | 0.028* |
| H14B | 0.0770 | 0.3583 | 0.8092 | 0.028* |
| H14A | 0.2068 | 0.3949 | 0.8728 | 0.028* |
| O5 | −0.0631 (3) | 0.2510 (3) | 1.0591 (3) | 0.0302 (9) |
| O6 | 0.3444 (3) | 0.1722 (3) | 1.0442 (3) | 0.0350 (10) |
| O7 | −0.0002 (3) | 0.1176 (3) | 1.1253 (3) | 0.0272 (9) |
| O8 | 0.2281 (3) | 0.0937 (3) | 1.1328 (3) | 0.0290 (9) |
| N2 | 0.0879 (3) | 0.3365 (4) | 0.9506 (3) | 0.0262 (10) |
| H2 | 0.0153 | 0.3386 | 0.9690 | 0.031* |
| C15 | 0.5457 (4) | 0.3104 (5) | 0.4300 (4) | 0.0228 (11) |
| C16 | 0.6700 (4) | 0.2928 (5) | 0.4565 (4) | 0.0211 (11) |
| C17 | 0.7792 (4) | 0.3434 (5) | 0.4301 (4) | 0.0233 (11) |
| C18 | 0.6930 (4) | 0.2229 (5) | 0.5142 (4) | 0.0205 (11) |
| H18A | 0.7734 | 0.2125 | 0.5271 | 0.025* |
| C19 | 0.8722 (4) | 0.4640 (5) | 0.3477 (4) | 0.0289 (13) |
| H19C | 0.8530 | 0.5219 | 0.3178 | 0.035* |
| H19B | 0.9068 | 0.3981 | 0.2930 | 0.035* |
| H19A | 0.9291 | 0.5030 | 0.4126 | 0.035* |
| C20 | 0.4082 (4) | 0.4033 (5) | 0.3540 (4) | 0.0277 (13) |
| H20C | 0.4074 | 0.4651 | 0.3257 | 0.033* |
| H20B | 0.3676 | 0.4278 | 0.4203 | 0.033* |
| H20A | 0.3677 | 0.3284 | 0.2992 | 0.033* |
| C21 | 0.6479 (4) | 0.1022 (5) | 0.6200 (4) | 0.0203 (11) |
| H21C | 0.6040 | 0.0227 | 0.5890 | 0.024* |
| H21B | 0.6293 | 0.1455 | 0.6949 | 0.024* |
| H21A | 0.7329 | 0.0947 | 0.6197 | 0.024* |
| O9 | 0.4592 (3) | 0.2600 (3) | 0.4495 (3) | 0.0293 (9) |
| O10 | 0.8808 (3) | 0.3234 (3) | 0.4529 (3) | 0.0315 (9) |
| O11 | 0.5322 (3) | 0.3861 (3) | 0.3795 (3) | 0.0255 (8) |
| O12 | 0.7640 (3) | 0.4176 (3) | 0.3774 (3) | 0.0276 (9) |
| N3 | 0.6133 (3) | 0.1691 (4) | 0.5531 (3) | 0.0231 (10) |

| | | | | |
|---|---|---|---|---|
| H3 | 0.5379 | 0.1732 | 0.5389 | 0.028* |
| C22 | 0.5158 (4) | 0.3785 (5) | 0.8567 (4) | 0.0194 (10) |
| C23 | 0.6390 (5) | 0.3641 (5) | 0.8899 (4) | 0.0239 (11) |
| C24 | 0.7487 (4) | 0.3923 (5) | 0.8491 (4) | 0.0208 (11) |
| C25 | 0.6589 (4) | 0.3189 (5) | 0.9702 (4) | 0.0240 (11) |
| H25A | 0.7389 | 0.3117 | 0.9884 | 0.029* |
| C26 | 0.8480 (4) | 0.4731 (5) | 0.7386 (4) | 0.0313 (14) |
| H26C | 0.8301 | 0.5026 | 0.6823 | 0.038* |
| H26B | 0.8883 | 0.4010 | 0.7078 | 0.038* |
| H26A | 0.8992 | 0.5344 | 0.7993 | 0.038* |
| C27 | 0.3829 (4) | 0.4259 (5) | 0.7369 (4) | 0.0283 (13) |
| H27C | 0.3840 | 0.4511 | 0.6767 | 0.034* |
| H27B | 0.3486 | 0.4854 | 0.7977 | 0.034* |
| H27A | 0.3352 | 0.3488 | 0.7126 | 0.034* |
| C28 | 0.6131 (4) | 0.2394 (5) | 1.1070 (4) | 0.0288 (13) |
| H28C | 0.5723 | 0.1594 | 1.0857 | 0.035* |
| H28B | 0.5901 | 0.2928 | 1.1776 | 0.035* |
| H28A | 0.6988 | 0.2357 | 1.1127 | 0.035* |
| O13 | 0.4292 (3) | 0.3554 (3) | 0.8977 (3) | 0.0285 (9) |
| O14 | 0.8494 (3) | 0.3706 (3) | 0.8760 (3) | 0.0303 (9) |
| O15 | 0.5064 (3) | 0.4145 (3) | 0.7733 (3) | 0.0274 (9) |
| O16 | 0.7371 (3) | 0.4453 (3) | 0.7781 (3) | 0.0281 (9) |
| N4 | 0.5799 (3) | 0.2852 (4) | 1.0234 (3) | 0.0279 (11) |
| H4 | 0.5048 | 0.2902 | 1.0087 | 0.033* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0197 (14) | 0.022 (3) | 0.023 (3) | −0.001 (2) | 0.0012 (18) | 0.015 (2) |
| C2 | 0.0238 (14) | 0.027 (3) | 0.028 (3) | 0.004 (2) | 0.010 (2) | 0.018 (2) |
| C3 | 0.0194 (13) | 0.024 (3) | 0.032 (3) | −0.005 (2) | 0.0010 (19) | 0.016 (2) |
| C4 | 0.025 (2) | 0.038 (4) | 0.028 (3) | 0.001 (2) | 0.0052 (19) | 0.021 (2) |
| C5 | 0.017 (2) | 0.051 (4) | 0.037 (3) | 0.010 (3) | 0.002 (2) | 0.024 (3) |
| C6 | 0.016 (2) | 0.029 (3) | 0.033 (3) | 0.003 (2) | 0.010 (2) | 0.017 (3) |
| C7 | 0.019 (3) | 0.047 (4) | 0.039 (3) | 0.007 (3) | 0.008 (2) | 0.032 (3) |
| O1 | 0.0238 (14) | 0.045 (3) | 0.039 (2) | 0.0054 (18) | 0.0020 (16) | 0.0304 (19) |
| O2 | 0.0227 (13) | 0.035 (2) | 0.037 (2) | 0.0020 (17) | 0.0098 (15) | 0.0208 (19) |
| O3 | 0.0162 (16) | 0.041 (2) | 0.033 (2) | 0.0036 (16) | 0.0077 (14) | 0.0271 (17) |
| O4 | 0.0117 (16) | 0.050 (3) | 0.043 (2) | 0.0040 (16) | 0.0044 (14) | 0.0333 (18) |
| N1 | 0.022 (2) | 0.040 (3) | 0.037 (3) | 0.000 (2) | 0.0054 (17) | 0.028 (2) |
| C8 | 0.0168 (15) | 0.033 (3) | 0.030 (3) | 0.004 (2) | 0.009 (2) | 0.023 (2) |
| C9 | 0.0169 (15) | 0.028 (3) | 0.021 (3) | 0.0014 (19) | 0.009 (2) | 0.015 (2) |
| C10 | 0.0171 (15) | 0.039 (3) | 0.024 (3) | 0.004 (2) | 0.009 (2) | 0.022 (2) |
| C11 | 0.012 (2) | 0.032 (3) | 0.032 (3) | −0.0026 (19) | 0.0027 (19) | 0.022 (2) |
| C12 | 0.023 (3) | 0.056 (4) | 0.048 (4) | 0.015 (3) | 0.005 (3) | 0.034 (3) |
| C13 | 0.014 (2) | 0.037 (4) | 0.038 (3) | 0.002 (2) | 0.010 (2) | 0.026 (3) |
| C14 | 0.023 (3) | 0.028 (3) | 0.023 (3) | 0.002 (2) | 0.005 (2) | 0.015 (2) |
| O5 | 0.0174 (15) | 0.045 (3) | 0.042 (2) | 0.0075 (16) | 0.0068 (16) | 0.0311 (19) |

| | | | | | |
|---|---|---|---|---|---|
| O6 | 0.0161 (14) | 0.058 (3) | 0.050 (2) | 0.0019 (18) | 0.0111 (17) | 0.041 (2) |
| O7 | 0.0144 (16) | 0.043 (2) | 0.040 (2) | 0.0013 (15) | 0.0094 (15) | 0.0329 (18) |
| O8 | 0.0155 (17) | 0.049 (3) | 0.042 (2) | 0.0103 (16) | 0.0146 (15) | 0.0355 (18) |
| N2 | 0.013 (2) | 0.039 (3) | 0.039 (3) | 0.0046 (18) | 0.0077 (18) | 0.028 (2) |
| C15 | 0.0119 (11) | 0.033 (3) | 0.030 (3) | −0.0031 (19) | −0.005 (2) | 0.022 (2) |
| C16 | 0.0128 (11) | 0.032 (3) | 0.027 (3) | 0.0031 (19) | 0.001 (2) | 0.021 (2) |
| C17 | 0.0135 (12) | 0.040 (3) | 0.026 (3) | 0.003 (2) | 0.003 (2) | 0.023 (2) |
| C18 | 0.012 (2) | 0.031 (3) | 0.025 (3) | 0.0008 (19) | 0.0000 (19) | 0.019 (2) |
| C19 | 0.012 (2) | 0.040 (4) | 0.043 (3) | −0.004 (2) | 0.005 (2) | 0.026 (3) |
| C20 | 0.0096 (19) | 0.041 (4) | 0.042 (3) | 0.003 (2) | −0.003 (2) | 0.026 (3) |
| C21 | 0.013 (3) | 0.029 (3) | 0.025 (3) | −0.001 (2) | 0.002 (2) | 0.017 (2) |
| O9 | 0.0130 (12) | 0.044 (2) | 0.042 (2) | −0.0022 (16) | −0.0003 (16) | 0.0305 (19) |
| O10 | 0.0138 (11) | 0.051 (3) | 0.044 (2) | 0.0069 (16) | 0.0047 (16) | 0.033 (2) |
| O11 | 0.0089 (15) | 0.041 (2) | 0.040 (2) | 0.0046 (14) | 0.0015 (14) | 0.0301 (18) |
| O12 | 0.0089 (16) | 0.039 (2) | 0.047 (2) | −0.0023 (14) | 0.0013 (15) | 0.0319 (18) |
| N3 | 0.013 (2) | 0.030 (3) | 0.036 (3) | 0.0008 (17) | 0.0019 (17) | 0.022 (2) |
| C22 | 0.0149 (12) | 0.021 (3) | 0.028 (3) | −0.005 (2) | 0.0005 (17) | 0.017 (2) |
| C23 | 0.0187 (12) | 0.033 (4) | 0.026 (3) | 0.002 (2) | 0.0005 (19) | 0.018 (2) |
| C24 | 0.0151 (13) | 0.023 (3) | 0.031 (3) | 0.002 (2) | −0.0005 (19) | 0.018 (2) |
| C25 | 0.017 (2) | 0.032 (3) | 0.030 (3) | 0.002 (2) | 0.0029 (18) | 0.019 (2) |
| C26 | 0.020 (2) | 0.042 (4) | 0.033 (3) | −0.007 (3) | 0.006 (2) | 0.019 (3) |
| C27 | 0.0096 (19) | 0.045 (4) | 0.040 (3) | 0.000 (2) | −0.001 (2) | 0.028 (3) |
| C28 | 0.016 (3) | 0.044 (4) | 0.040 (3) | 0.004 (2) | 0.009 (2) | 0.029 (3) |
| O13 | 0.0200 (13) | 0.040 (2) | 0.035 (2) | −0.0019 (17) | 0.0086 (15) | 0.0246 (18) |
| O14 | 0.0181 (12) | 0.040 (3) | 0.040 (2) | 0.0072 (17) | −0.0039 (15) | 0.0246 (19) |
| O15 | 0.0099 (15) | 0.048 (3) | 0.039 (2) | −0.0001 (16) | 0.0013 (14) | 0.0338 (19) |
| O16 | 0.0100 (16) | 0.047 (3) | 0.043 (2) | 0.0014 (16) | 0.0000 (14) | 0.0347 (18) |
| N4 | 0.018 (2) | 0.035 (3) | 0.041 (3) | −0.0015 (19) | 0.0029 (17) | 0.026 (2) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—O1 | 1.202 (5) | C15—O9 | 1.204 (5) |
| C1—O3 | 1.346 (5) | C15—O11 | 1.341 (6) |
| C1—C2 | 1.461 (6) | C15—C16 | 1.460 (6) |
| C2—C4 | 1.373 (6) | C16—C18 | 1.372 (6) |
| C2—C3 | 1.432 (7) | C16—C17 | 1.450 (7) |
| C3—O2 | 1.208 (5) | C17—O10 | 1.220 (5) |
| C3—O4 | 1.362 (6) | C17—O12 | 1.350 (6) |
| C4—N1 | 1.292 (6) | C18—N3 | 1.313 (6) |
| C4—H4A | 0.9300 | C18—H18A | 0.9300 |
| C5—O4 | 1.447 (5) | C19—O12 | 1.439 (5) |
| C5—H5C | 0.9600 | C19—H19C | 0.9600 |
| C5—H5B | 0.9600 | C19—H19B | 0.9600 |
| C5—H5A | 0.9600 | C19—H19A | 0.9600 |
| C6—O3 | 1.435 (5) | C20—O11 | 1.452 (5) |
| C6—H6C | 0.9600 | C20—H20C | 0.9600 |
| C6—H6B | 0.9600 | C20—H20B | 0.9600 |
| C6—H6A | 0.9600 | C20—H20A | 0.9600 |

| | | | |
|---|---|---|---|
| C7—N1 | 1.465 (6) | C21—N3 | 1.467 (6) |
| C7—H7C | 0.9600 | C21—H21C | 0.9600 |
| C7—H7B | 0.9600 | C21—H21B | 0.9600 |
| C7—H7A | 0.9600 | C21—H21A | 0.9600 |
| N1—H1 | 0.8600 | N3—H3 | 0.8600 |
| C8—O5 | 1.228 (5) | C22—O13 | 1.207 (5) |
| C8—O7 | 1.326 (6) | C22—O15 | 1.338 (5) |
| C8—C9 | 1.466 (6) | C22—C23 | 1.459 (6) |
| C9—C11 | 1.383 (6) | C23—C25 | 1.388 (7) |
| C9—C10 | 1.450 (6) | C23—C24 | 1.443 (7) |
| C10—O6 | 1.228 (5) | C24—O14 | 1.235 (5) |
| C10—O8 | 1.324 (5) | C24—O16 | 1.335 (6) |
| C11—N2 | 1.305 (6) | C25—N4 | 1.302 (6) |
| C11—H11A | 0.9300 | C25—H25A | 0.9300 |
| C12—O8 | 1.438 (5) | C26—O16 | 1.444 (5) |
| C12—H12C | 0.9600 | C26—H26C | 0.9600 |
| C12—H12B | 0.9600 | C26—H26B | 0.9600 |
| C12—H12A | 0.9600 | C26—H26A | 0.9600 |
| C13—O7 | 1.440 (5) | C27—O15 | 1.465 (5) |
| C13—H13C | 0.9600 | C27—H27C | 0.9600 |
| C13—H13B | 0.9600 | C27—H27B | 0.9600 |
| C13—H13A | 0.9600 | C27—H27A | 0.9600 |
| C14—N2 | 1.449 (6) | C28—N4 | 1.460 (6) |
| C14—H14C | 0.9600 | C28—H28C | 0.9600 |
| C14—H14B | 0.9600 | C28—H28B | 0.9600 |
| C14—H14A | 0.9600 | C28—H28A | 0.9600 |
| N2—H2 | 0.8600 | N4—H4 | 0.8600 |
| | | | |
| O1—C1—O3 | 121.1 (4) | O9—C15—O11 | 120.7 (4) |
| O1—C1—C2 | 124.2 (5) | O9—C15—C16 | 123.5 (5) |
| O3—C1—C2 | 114.7 (4) | O11—C15—C16 | 115.8 (4) |
| C4—C2—C3 | 113.4 (5) | C18—C16—C17 | 112.7 (4) |
| C4—C2—C1 | 117.9 (5) | C18—C16—C15 | 119.9 (4) |
| C3—C2—C1 | 128.7 (5) | C17—C16—C15 | 127.4 (5) |
| O2—C3—O4 | 120.0 (5) | O10—C17—O12 | 119.6 (4) |
| O2—C3—C2 | 124.8 (5) | O10—C17—C16 | 124.3 (5) |
| O4—C3—C2 | 115.2 (4) | O12—C17—C16 | 116.1 (4) |
| N1—C4—C2 | 129.8 (5) | N3—C18—C16 | 126.8 (4) |
| N1—C4—H4A | 115.1 | N3—C18—H18A | 116.6 |
| C2—C4—H4A | 115.1 | C16—C18—H18A | 116.6 |
| O4—C5—H5C | 109.5 | O12—C19—H19C | 109.5 |
| O4—C5—H5B | 109.5 | O12—C19—H19B | 109.5 |
| H5C—C5—H5B | 109.5 | H19C—C19—H19B | 109.5 |
| O4—C5—H5A | 109.5 | O12—C19—H19A | 109.5 |
| H5C—C5—H5A | 109.5 | H19C—C19—H19A | 109.5 |
| H5B—C5—H5A | 109.5 | H19B—C19—H19A | 109.5 |
| O3—C6—H6C | 109.5 | O11—C20—H20C | 109.5 |
| O3—C6—H6B | 109.5 | O11—C20—H20B | 109.5 |

| | | | |
|---|---|---|---|
| H6C—C6—H6B | 109.5 | H20C—C20—H20B | 109.5 |
| O3—C6—H6A | 109.5 | O11—C20—H20A | 109.5 |
| H6C—C6—H6A | 109.5 | H20C—C20—H20A | 109.5 |
| H6B—C6—H6A | 109.5 | H20B—C20—H20A | 109.5 |
| N1—C7—H7C | 109.5 | N3—C21—H21C | 109.5 |
| N1—C7—H7B | 109.5 | N3—C21—H21B | 109.5 |
| H7C—C7—H7B | 109.5 | H21C—C21—H21B | 109.5 |
| N1—C7—H7A | 109.5 | N3—C21—H21A | 109.5 |
| H7C—C7—H7A | 109.5 | H21C—C21—H21A | 109.5 |
| H7B—C7—H7A | 109.5 | H21B—C21—H21A | 109.5 |
| C1—O3—C6 | 115.1 (4) | C15—O11—C20 | 115.3 (4) |
| C3—O4—C5 | 115.6 (4) | C17—O12—C19 | 115.9 (4) |
| C4—N1—C7 | 123.2 (4) | C18—N3—C21 | 122.5 (4) |
| C4—N1—H1 | 118.4 | C18—N3—H3 | 118.7 |
| C7—N1—H1 | 118.4 | C21—N3—H3 | 118.7 |
| O5—C8—O7 | 123.5 (4) | O13—C22—O15 | 122.7 (4) |
| O5—C8—C9 | 120.8 (5) | O13—C22—C23 | 123.1 (5) |
| O7—C8—C9 | 115.7 (4) | O15—C22—C23 | 114.2 (4) |
| C11—C9—C10 | 113.6 (4) | C25—C23—C24 | 113.1 (5) |
| C11—C9—C8 | 119.4 (5) | C25—C23—C22 | 119.3 (5) |
| C10—C9—C8 | 127.0 (4) | C24—C23—C22 | 127.6 (5) |
| O6—C10—O8 | 119.7 (5) | O14—C24—O16 | 119.8 (4) |
| O6—C10—C9 | 124.2 (5) | O14—C24—C23 | 124.0 (5) |
| O8—C10—C9 | 116.1 (4) | O16—C24—C23 | 116.2 (4) |
| N2—C11—C9 | 129.5 (4) | N4—C25—C23 | 128.4 (5) |
| N2—C11—H11A | 115.3 | N4—C25—H25A | 115.8 |
| C9—C11—H11A | 115.3 | C23—C25—H25A | 115.8 |
| O8—C12—H12C | 109.5 | O16—C26—H26C | 109.5 |
| O8—C12—H12B | 109.5 | O16—C26—H26B | 109.5 |
| H12C—C12—H12B | 109.5 | H26C—C26—H26B | 109.5 |
| O8—C12—H12A | 109.5 | O16—C26—H26A | 109.5 |
| H12C—C12—H12A | 109.5 | H26C—C26—H26A | 109.5 |
| H12B—C12—H12A | 109.5 | H26B—C26—H26A | 109.5 |
| O7—C13—H13C | 109.5 | O15—C27—H27C | 109.5 |
| O7—C13—H13B | 109.5 | O15—C27—H27B | 109.5 |
| H13C—C13—H13B | 109.5 | H27C—C27—H27B | 109.5 |
| O7—C13—H13A | 109.5 | O15—C27—H27A | 109.5 |
| H13C—C13—H13A | 109.5 | H27C—C27—H27A | 109.5 |
| H13B—C13—H13A | 109.5 | H27B—C27—H27A | 109.5 |
| N2—C14—H14C | 109.5 | N4—C28—H28C | 109.5 |
| N2—C14—H14B | 109.5 | N4—C28—H28B | 109.5 |
| H14C—C14—H14B | 109.5 | H28C—C28—H28B | 109.5 |
| N2—C14—H14A | 109.5 | N4—C28—H28A | 109.5 |
| H14C—C14—H14A | 109.5 | H28C—C28—H28A | 109.5 |
| H14B—C14—H14A | 109.5 | H28B—C28—H28A | 109.5 |
| C8—O7—C13 | 114.7 (4) | C22—O15—C27 | 114.7 (4) |
| C10—O8—C12 | 116.1 (4) | C24—O16—C26 | 115.3 (4) |
| C11—N2—C14 | 123.4 (4) | C25—N4—C28 | 122.9 (4) |

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|---|---|---|---|
| C11—N2—H2 | 118.3 | C25—N4—H4 | 118.6 |
| C14—N2—H2 | 118.3 | C28—N4—H4 | 118.6 |
| | | | |
| O1—C1—C2—C4 | 0.8 (8) | O9—C15—C16—C18 | −5.1 (8) |
| O3—C1—C2—C4 | −178.1 (5) | O11—C15—C16—C18 | 176.0 (5) |
| O1—C1—C2—C3 | −178.7 (5) | O9—C15—C16—C17 | 175.9 (6) |
| O3—C1—C2—C3 | 2.4 (8) | O11—C15—C16—C17 | −3.0 (7) |
| C4—C2—C3—O2 | 5.5 (8) | C18—C16—C17—O10 | 2.3 (8) |
| C1—C2—C3—O2 | −175.0 (5) | C15—C16—C17—O10 | −178.6 (5) |
| C4—C2—C3—O4 | −176.0 (5) | C18—C16—C17—O12 | −177.3 (4) |
| C1—C2—C3—O4 | 3.5 (8) | C15—C16—C17—O12 | 1.8 (8) |
| C3—C2—C4—N1 | −179.8 (5) | C17—C16—C18—N3 | 177.3 (5) |
| C1—C2—C4—N1 | 0.6 (9) | C15—C16—C18—N3 | −1.9 (8) |
| O1—C1—O3—C6 | −1.6 (7) | O9—C15—O11—C20 | 1.4 (7) |
| C2—C1—O3—C6 | 177.3 (4) | C16—C15—O11—C20 | −179.7 (4) |
| O2—C3—O4—C5 | 0.4 (7) | O10—C17—O12—C19 | 2.6 (7) |
| C2—C3—O4—C5 | −178.1 (4) | C16—C17—O12—C19 | −177.8 (4) |
| C2—C4—N1—C7 | 178.8 (5) | C16—C18—N3—C21 | −176.1 (5) |
| O5—C8—C9—C11 | −8.2 (7) | O13—C22—C23—C25 | 1.8 (8) |
| O7—C8—C9—C11 | 173.8 (5) | O15—C22—C23—C25 | −175.5 (5) |
| O5—C8—C9—C10 | 173.2 (5) | O13—C22—C23—C24 | −178.0 (5) |
| O7—C8—C9—C10 | −4.7 (7) | O15—C22—C23—C24 | 4.8 (8) |
| C11—C9—C10—O6 | −0.6 (8) | C25—C23—C24—O14 | 5.0 (8) |
| C8—C9—C10—O6 | 178.0 (5) | C22—C23—C24—O14 | −175.2 (5) |
| C11—C9—C10—O8 | 178.8 (4) | C25—C23—C24—O16 | −174.8 (4) |
| C8—C9—C10—O8 | −2.6 (8) | C22—C23—C24—O16 | 4.9 (8) |
| C10—C9—C11—N2 | −179.9 (5) | C24—C23—C25—N4 | 179.9 (5) |
| C8—C9—C11—N2 | 1.3 (8) | C22—C23—C25—N4 | 0.1 (9) |
| O5—C8—O7—C13 | 2.5 (7) | O13—C22—O15—C27 | 1.1 (7) |
| C9—C8—O7—C13 | −179.6 (4) | C23—C22—O15—C27 | 178.3 (4) |
| O6—C10—O8—C12 | −0.3 (7) | O14—C24—O16—C26 | −0.1 (7) |
| C9—C10—O8—C12 | −179.8 (4) | C23—C24—O16—C26 | 179.8 (4) |
| C9—C11—N2—C14 | −175.4 (5) | C23—C25—N4—C28 | −179.7 (5) |

*Hydrogen-bond geometry (Å, º)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| N1—H1···O1 | 0.86 | 2.08 | 2.689 (4) | 127 |
| N1—H1···O10 | 0.86 | 2.42 | 2.990 (4) | 125 |
| N2—H2···O5 | 0.86 | 2.08 | 2.687 (4) | 127 |
| N2—H2···O14[i] | 0.86 | 2.30 | 2.893 (5) | 127 |
| N3—H3···O9 | 0.86 | 2.06 | 2.684 (4) | 129 |
| N3—H3···O2[i] | 0.86 | 2.32 | 2.912 (5) | 126 |
| N4—H4···O13 | 0.86 | 2.08 | 2.698 (5) | 128 |
| N4—H4···O6 | 0.86 | 2.40 | 2.957 (5) | 123 |
| C4—H4*A*···O2 | 0.93 | 2.27 | 2.683 (7) | 106 |
| C6—H6*A*···O14 | 0.96 | 2.50 | 3.449 (7) | 169 |
| C11—H11*A*···O6 | 0.93 | 2.29 | 2.706 (6) | 107 |

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|---|---|---|---|---|
| C11—H11*A*···O13 | 0.93 | 2.60 | 3.487 (6) | 159 |
| C14—H14*A*···O13 | 0.96 | 2.59 | 3.507 (6) | 161 |
| C18—H18*A*···O1 | 0.93 | 2.58 | 3.470 (6) | 160 |
| C18—H18*A*···O10 | 0.93 | 2.27 | 2.679 (6) | 106 |
| C25—H25*A*···O14 | 0.93 | 2.28 | 2.691 (6) | 106 |
| C27—H27*A*···O2[i] | 0.96 | 2.59 | 3.340 (7) | 135 |
| C28—H28*C*···O6 | 0.96 | 2.60 | 3.024 (6) | 107 |

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