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# Methyl 4-anilino-3-nitrobenzoate

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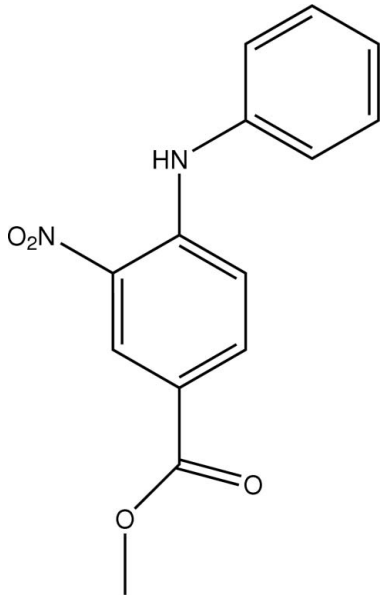
Key indicators: single-crystal X-ray study; $T$ = 294 K; mean $\sigma$(C–C) = 0.005 Å; $R$ factor = 0.066; $wR$ factor = 0.178; data-to-parameter ratio = 13.5.

In the molecule of the title compound, $C_{14}H_{12}N_2O_4$, the aromatic rings are oriented at a dihedral angle of 51.50 (4)°. An intramolecular N—H···O interaction results in the formation of a six-membered ring having an envelope conformation. In the crystal structure, intermolecular N—H···O interactions link the molecules into centrosymmetric dimers. $\pi$–$\pi$ contacts between the benzene rings [centroid–centroid distance = 3.708 (1) Å] may further stabilize the structure.

## Related literature

For bond-length data, see: Allen *et al.* (1987). For the synthesis, see: Schelz (1978).




## Experimental

### Crystal data

$C_{14}H_{12}N_2O_4$
$M_r$ = 272.26
Monoclinic, $P2_1/c$
$a$ = 11.641 (2) Å
$b$ = 16.349 (3) Å
$c$ = 7.2490 (14) Å
$\beta$ = 107.50 (3)°
$V$ = 1315.8 (5) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.10 mm$^{-1}$
$T$ = 294 K
0.30 × 0.20 × 0.10 mm

### Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: $\psi$ scan (North *et al.*, 1968)
$T_{min}$ = 0.970, $T_{max}$ = 0.990
2569 measured reflections
2367 independent reflections
1335 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.026
3 standard reflections
frequency: 120 min
intensity decay: 1%

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.178
$S$ = 1.00
2367 reflections
175 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.33 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.44 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1$A$···O1 | 0.86 | 2.01 | 2.650 (4) | 130 |
| N1—H1$A$···O1$^{i}$ | 0.86 | 2.53 | 3.314 (4) | 152 |

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

The authors thank the Center of Testing and Analysis, Nanjing University, for support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2689).

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# supporting information

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## Methyl 4-anilino-3-nitrobenzoate

**Hao-Yuan Li, Yong-Zhong Wu, Bo-Nian Liu, Shi-Gui Tang and Cheng Guo**

### S1. Comment

Some derivatives of benzoic acid are important chemical materials. We report herein the crystal structure of the title compound.

In the molecule of the title compound (Fig 1), the bond lengths (Allen *et al.*, 1987) and angles are within normal ranges. Rings A (C1-C6) and B (C7-C12) are, of course, planar and they are oriented at a dihedral angle of A/B = 51.50 (4)°. Intramolecular N-H···O interaction (Table 1) results in the formation of a six-membered ring C (O1/N1/N2/C7/C12/H1A) having envelope conformation with atom O1 displaced by 0.125 (4) Å from the plane of the other ring atoms.

In the crystal structure, intra- and intermolecular N-H···O interactions (Table 1) link the molecules into centrosymmetric dimers (Fig. 2), in which they may be effective in the stabilization of the structure. The $\pi$–$\pi$ contact between the benzene rings, Cg2—Cg2$^{i}$ [symmetry code: (i) x, 1/2 - y, z - 1/2, where Cg2 is centroid of the ring B (C7-C12)] may further stabilize the structure, with centroid-centroid distance of 3.708 (1) Å.

### S2. Experimental

For the preparation of the title compound, methyl 4-chloro-3-nitrobenzoate (5.0 g, 23 mmol) was heated in distilled aniline (10 ml) for 18 h at 393 K. After the reaction was completed, ethanol (50 ml) was added, at room temperature. The yellow precipitate was washed with cold ethanol (2 × 20 ml), and then dried (yield; 4.7 g). Crystals suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution.

### S3. Refinement

H atoms were positioned geometrically, with N-H = 0.86 Å (for NH) and C-H = 0.93 and 0.96 Å for aromatic and methyl H, respectively, and constrained to ride on their parent atoms, with $U_{iso}$(H) = x$U_{eq}$(C,N), where x = 1.5 for methyl H and x = 1.2 for all other H atoms.

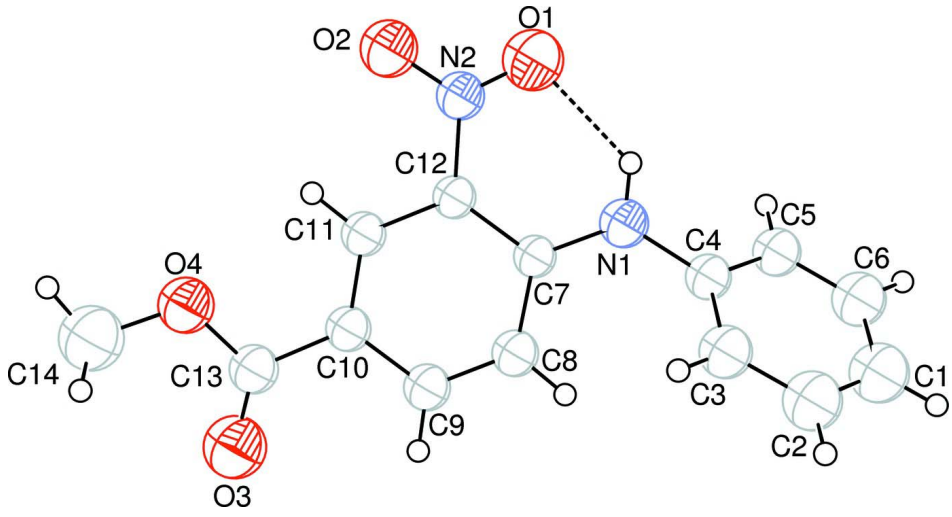


**Figure 1**

The molecular structure of the title molecule, with the atom-numbering scheme. Hydrogen bond is shown as dashed line.

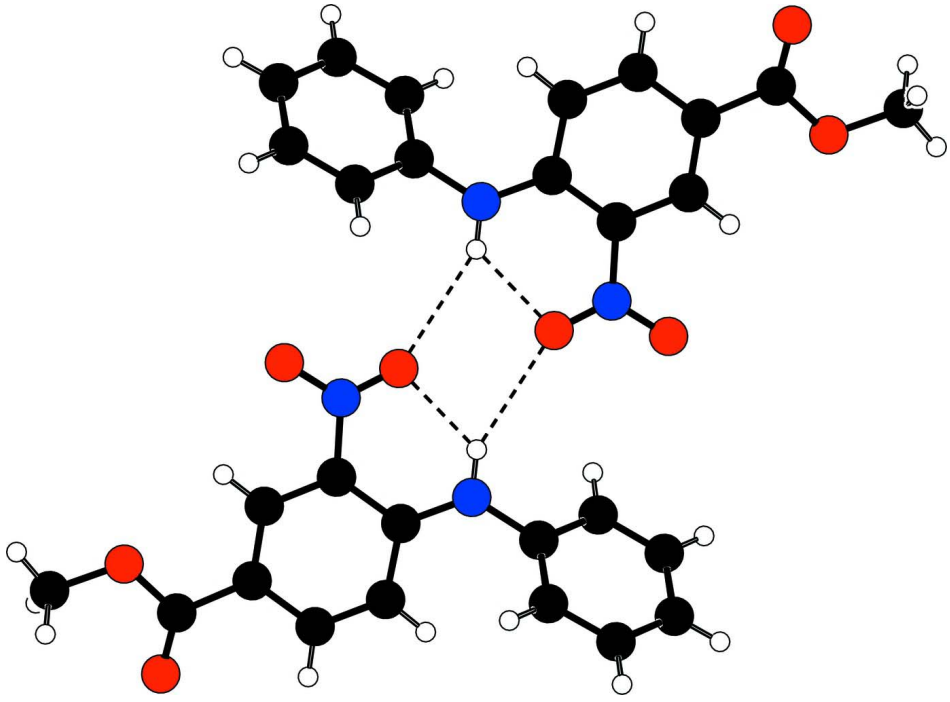

**Figure 2**

A partial packing diagram of the title compound. Hydrogen bonds are shown as dashed lines.

### Methyl 4-anilino-3-nitrobenzoate

*Crystal data*

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Monoclinic, $P2_1/c$
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$a = 11.641\ (2)$ Å
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$\beta = 107.50\ (3)°$
$V = 1315.8\ (5)$ Å$^3$
$Z = 4$

$F(000) = 568$
$D_x = 1.374$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10–12°$
$\mu = 0.10$ mm$^{-1}$
$T = 294$ K
Block, colorless
0.30 × 0.20 × 0.10 mm

*Data collection*

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega/2\theta$ scans
Absorption correction: $\psi$ scan (North *et al.*, 1968)
$T_{min} = 0.970$, $T_{max} = 0.990$
2569 measured reflections
2367 independent reflections
1335 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 25.2°$, $\theta_{min} = 1.8°$
$h = -13 \rightarrow 13$
$k = -19 \rightarrow 0$
$l = 0 \rightarrow 8$
3 standard reflections every 120 min
intensity decay: 1%

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.178$
$S = 1.00$
2367 reflections
175 parameters
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
$w = 1/[\sigma^2(F_o^2) + (0.08P)^2 + 0.4P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.33$ e Å$^{-3}$
$\Delta\rho_{min} = -0.44$ e Å$^{-3}$

*Special details*

**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$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.0837 (2) | 0.05896 (17) | 0.1085 (4) | 0.078 |
| O2 | 0.2328 (2) | 0.11328 (16) | 0.2971 (4) | 0.0677 (9) |
| O3 | 0.1608 (3) | 0.48217 (18) | 0.1788 (5) | 0.0848 (10) |
| O4 | 0.2843 (2) | 0.39247 (16) | 0.3690 (4) | 0.0648 (8) |
| N1 | −0.1155 (2) | 0.14101 (18) | −0.0669 (4) | 0.0501 (8) |
| H1A | −0.0836 | 0.0932 | −0.0446 | 0.060* |
| N2 | 0.1335 (3) | 0.11733 (17) | 0.1801 (5) | 0.0479 (8) |
| C1 | −0.4811 (4) | 0.1408 (3) | −0.3820 (7) | 0.0754 (14) |
| H1B | −0.5621 | 0.1397 | −0.4538 | 0.091* |
| C2 | −0.4423 (4) | 0.1887 (3) | −0.2185 (7) | 0.0721 (13) |
| H2A | −0.4973 | 0.2200 | −0.1789 | 0.087* |

| | | | | |
|---|---|---|---|---|
| C3 | −0.3218 (3) | 0.1902 (3) | −0.1139 (6) | 0.0575 (11) |
| H3A | −0.2959 | 0.2222 | −0.0031 | 0.069* |
| C4 | −0.2393 (3) | 0.1441 (2) | −0.1731 (5) | 0.0440 (9) |
| C5 | −0.2794 (3) | 0.0959 (2) | −0.3384 (5) | 0.0504 (10) |
| H5A | −0.2254 | 0.0647 | −0.3808 | 0.061* |
| C6 | −0.3991 (4) | 0.0951 (3) | −0.4367 (6) | 0.0638 (12) |
| H6A | −0.4259 | 0.0621 | −0.5457 | 0.077* |
| C7 | −0.0420 (3) | 0.2050 (2) | 0.0031 (5) | 0.0378 (8) |
| C8 | −0.0795 (3) | 0.2868 (2) | −0.0439 (5) | 0.0460 (9) |
| H8A | −0.1567 | 0.2963 | −0.1260 | 0.055* |
| C9 | −0.0075 (3) | 0.3514 (2) | 0.0258 (5) | 0.0465 (9) |
| H9A | −0.0363 | 0.4039 | −0.0101 | 0.056* |
| C10 | 0.1095 (3) | 0.3414 (2) | 0.1510 (5) | 0.0431 (9) |
| C11 | 0.1507 (3) | 0.2631 (2) | 0.1962 (5) | 0.0416 (9) |
| H11A | 0.2284 | 0.2549 | 0.2777 | 0.050* |
| C12 | 0.0786 (3) | 0.1958 (2) | 0.1226 (5) | 0.0385 (8) |
| C13 | 0.1830 (4) | 0.4131 (2) | 0.2287 (6) | 0.0509 (10) |
| C14 | 0.3604 (4) | 0.4579 (3) | 0.4546 (7) | 0.0886 (16) |
| H14A | 0.4293 | 0.4372 | 0.5528 | 0.133* |
| H14B | 0.3174 | 0.4954 | 0.5116 | 0.133* |
| H14C | 0.3865 | 0.4858 | 0.3576 | 0.133* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.064 | 0.060 | 0.091 | 0.006 | −0.005 | 0.000 |
| O2 | 0.0506 (16) | 0.0573 (18) | 0.075 (2) | 0.0069 (14) | −0.0122 (15) | −0.0036 (15) |
| O3 | 0.090 (2) | 0.0424 (18) | 0.108 (3) | −0.0121 (16) | 0.009 (2) | 0.0030 (17) |
| O4 | 0.0496 (16) | 0.0559 (18) | 0.078 (2) | −0.0124 (13) | 0.0026 (15) | −0.0116 (15) |
| N1 | 0.0426 (17) | 0.0421 (17) | 0.056 (2) | −0.0071 (14) | 0.0013 (15) | −0.0022 (15) |
| N2 | 0.0406 (17) | 0.0336 (16) | 0.058 (2) | −0.0125 (13) | −0.0025 (16) | −0.0141 (14) |
| C1 | 0.045 (2) | 0.082 (3) | 0.082 (3) | −0.021 (2) | −0.007 (2) | 0.010 (3) |
| C2 | 0.044 (2) | 0.086 (3) | 0.086 (4) | −0.006 (2) | 0.017 (2) | −0.007 (3) |
| C3 | 0.044 (2) | 0.071 (3) | 0.053 (3) | −0.010 (2) | 0.0090 (19) | −0.012 (2) |
| C4 | 0.040 (2) | 0.044 (2) | 0.042 (2) | −0.0085 (17) | 0.0045 (17) | 0.0034 (17) |
| C5 | 0.053 (2) | 0.046 (2) | 0.046 (2) | −0.0152 (18) | 0.0058 (19) | −0.0013 (18) |
| C6 | 0.061 (3) | 0.071 (3) | 0.049 (3) | −0.021 (2) | 0.000 (2) | −0.001 (2) |
| C7 | 0.0369 (18) | 0.043 (2) | 0.0349 (19) | −0.0075 (16) | 0.0124 (15) | −0.0044 (16) |
| C8 | 0.039 (2) | 0.054 (2) | 0.043 (2) | −0.0007 (17) | 0.0093 (17) | 0.0032 (18) |
| C9 | 0.047 (2) | 0.038 (2) | 0.054 (2) | 0.0001 (17) | 0.0157 (18) | 0.0050 (18) |
| C10 | 0.047 (2) | 0.044 (2) | 0.042 (2) | −0.0069 (17) | 0.0171 (17) | −0.0040 (17) |
| C11 | 0.0335 (18) | 0.051 (2) | 0.039 (2) | −0.0018 (16) | 0.0094 (16) | −0.0036 (17) |
| C12 | 0.0343 (18) | 0.0368 (19) | 0.044 (2) | −0.0010 (15) | 0.0115 (16) | −0.0030 (16) |
| C13 | 0.058 (2) | 0.042 (2) | 0.057 (3) | −0.0085 (19) | 0.022 (2) | −0.0058 (19) |
| C14 | 0.068 (3) | 0.090 (4) | 0.096 (4) | −0.037 (3) | 0.006 (3) | −0.029 (3) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—N2 | 1.155 (3) | C5—C6 | 1.361 (5) |
| O2—N2 | 1.213 (3) | C5—H5A | 0.9300 |
| O3—C13 | 1.190 (5) | C6—H6A | 0.9300 |
| O4—C13 | 1.348 (4) | C7—C8 | 1.416 (5) |
| O4—C14 | 1.409 (5) | C7—C12 | 1.419 (4) |
| N1—C7 | 1.349 (4) | C8—C9 | 1.348 (5) |
| N1—C4 | 1.416 (4) | C8—H8A | 0.9300 |
| N1—H1A | 0.8600 | C9—C10 | 1.401 (5) |
| N2—C12 | 1.438 (4) | C9—H9A | 0.9300 |
| C1—C6 | 1.361 (6) | C10—C11 | 1.372 (5) |
| C1—C2 | 1.378 (6) | C10—C13 | 1.461 (5) |
| C1—H1B | 0.9300 | C11—C12 | 1.389 (4) |
| C2—C3 | 1.379 (5) | C11—H11A | 0.9300 |
| C2—H2A | 0.9300 | C14—H14A | 0.9600 |
| C3—C4 | 1.387 (5) | C14—H14B | 0.9600 |
| C3—H3A | 0.9300 | C14—H14C | 0.9600 |
| C4—C5 | 1.392 (5) | | |
| | | | |
| C13—O4—C14 | 115.7 (3) | N1—C7—C12 | 123.1 (3) |
| C7—N1—C4 | 127.1 (3) | C8—C7—C12 | 115.0 (3) |
| C7—N1—H1A | 116.5 | C9—C8—C7 | 122.6 (3) |
| C4—N1—H1A | 116.5 | C9—C8—H8A | 118.7 |
| O1—N2—O2 | 120.9 (3) | C7—C8—H8A | 118.7 |
| O1—N2—C12 | 119.2 (3) | C8—C9—C10 | 121.6 (3) |
| O2—N2—C12 | 119.9 (3) | C8—C9—H9A | 119.2 |
| C6—C1—C2 | 119.0 (4) | C10—C9—H9A | 119.2 |
| C6—C1—H1B | 120.5 | C11—C10—C9 | 117.8 (3) |
| C2—C1—H1B | 120.5 | C11—C10—C13 | 122.3 (3) |
| C1—C2—C3 | 119.9 (4) | C9—C10—C13 | 119.9 (3) |
| C1—C2—H2A | 120.1 | C10—C11—C12 | 121.3 (3) |
| C3—C2—H2A | 120.1 | C10—C11—H11A | 119.3 |
| C2—C3—C4 | 120.3 (4) | C12—C11—H11A | 119.3 |
| C2—C3—H3A | 119.8 | C11—C12—C7 | 121.5 (3) |
| C4—C3—H3A | 119.8 | C11—C12—N2 | 115.5 (3) |
| C3—C4—C5 | 119.3 (3) | C7—C12—N2 | 122.9 (3) |
| C3—C4—N1 | 122.6 (3) | O3—C13—O4 | 121.9 (4) |
| C5—C4—N1 | 118.1 (3) | O3—C13—C10 | 126.6 (4) |
| C6—C5—C4 | 118.7 (4) | O4—C13—C10 | 111.6 (3) |
| C6—C5—H5A | 120.6 | O4—C14—H14A | 109.5 |
| C4—C5—H5A | 120.6 | O4—C14—H14B | 109.5 |
| C5—C6—C1 | 122.7 (4) | H14A—C14—H14B | 109.5 |
| C5—C6—H6A | 118.7 | O4—C14—H14C | 109.5 |
| C1—C6—H6A | 118.7 | H14A—C14—H14C | 109.5 |
| N1—C7—C8 | 121.8 (3) | H14B—C14—H14C | 109.5 |
| | | | |
| C6—C1—C2—C3 | 0.3 (7) | C13—C10—C11—C12 | 179.1 (4) |

| | | | |
|---|---|---|---|
| C1—C2—C3—C4 | 0.5 (7) | C10—C11—C12—C7 | −2.3 (5) |
| C2—C3—C4—C5 | −0.5 (6) | C10—C11—C12—N2 | 179.4 (3) |
| C2—C3—C4—N1 | −177.5 (4) | N1—C7—C12—C11 | −178.3 (3) |
| C7—N1—C4—C3 | −48.9 (5) | C8—C7—C12—C11 | 3.8 (5) |
| C7—N1—C4—C5 | 134.0 (4) | N1—C7—C12—N2 | −0.1 (5) |
| C3—C4—C5—C6 | −0.3 (6) | C8—C7—C12—N2 | −178.0 (3) |
| N1—C4—C5—C6 | 176.9 (3) | O1—N2—C12—C11 | −171.9 (4) |
| C4—C5—C6—C1 | 1.2 (6) | O2—N2—C12—C11 | 5.4 (5) |
| C2—C1—C6—C5 | −1.2 (7) | O1—N2—C12—C7 | 9.8 (6) |
| C4—N1—C7—C8 | −7.9 (6) | O2—N2—C12—C7 | −172.9 (3) |
| C4—N1—C7—C12 | 174.4 (3) | C14—O4—C13—O3 | 1.2 (6) |
| N1—C7—C8—C9 | 179.6 (4) | C14—O4—C13—C10 | −179.3 (4) |
| C12—C7—C8—C9 | −2.5 (5) | C11—C10—C13—O3 | 169.8 (4) |
| C7—C8—C9—C10 | −0.3 (6) | C9—C10—C13—O3 | −10.4 (6) |
| C8—C9—C10—C11 | 2.1 (6) | C11—C10—C13—O4 | −9.8 (5) |
| C8—C9—C10—C13 | −177.8 (3) | C9—C10—C13—O4 | 170.1 (3) |
| C9—C10—C11—C12 | −0.8 (5) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1*A*···O1 | 0.86 | 2.01 | 2.650 (4) | 130 |
| N1—H1*A*···O1$^{i}$ | 0.86 | 2.53 | 3.314 (4) | 152 |

Symmetry code: (i) −*x*, −*y*, −*z*.