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# *N*,*N*′-[(2*E*,3*E*)-Butane-2,3-diylidene]bis[4-fluoro-2-(1-phenylethyl)aniline]

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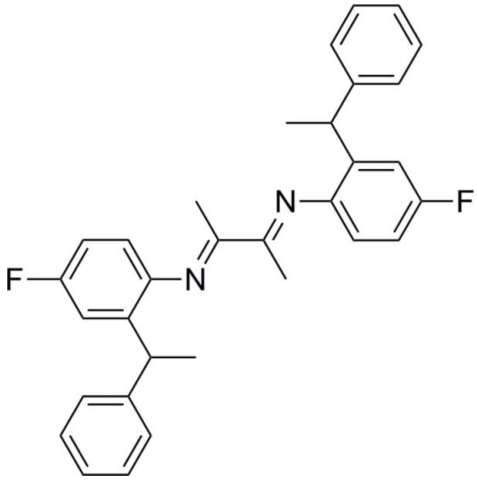
Key indicators: single-crystal X-ray study; $T$ = 295 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.040; $wR$ factor = 0.118; data-to-parameter ratio = 15.1.

The title molecule, $C_{32}H_{30}F_2N_2$, a product of the condensation reaction of butane-2,3-dione and 4-fluoro-2-(1-phenylethyl)-aniline, is located about an inversion centre. In the asymmetric unit, the dihedral angle between the planes of the benzene and phenyl rings is 84.27 (5)°. Neither hydrogen bonding nor aromatic stacking is observed in the crystal structure.

## Related literature

For the synthesis of $\alpha$-diimine ligands, see: Grasa *et al.* (2001); Williams *et al.* (2008); Hanhan *et al.* (2012); Partyka (2011); Yuan *et al.* (2012). For related structures, see: Zou *et al.* (2008); Lohr *et al.* (2011).




## Experimental

### Crystal data

$C_{32}H_{30}F_2N_2$
$M_r$ = 480.58
Monoclinic, $P2_1/n$
$a$ = 11.5335 (11) Å
$b$ = 9.5024 (12) Å
$c$ = 12.1318 (14) Å
$\beta$ = 91.660 (11)°
$V$ = 1329.0 (3) Å$^3$
$Z$ = 2
Cu $K\alpha$ radiation
$\mu$ = 0.64 mm$^{-1}$
$T$ = 295 K
0.35 × 0.28 × 0.26 mm

### Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min}$ = 0.808, $T_{max}$ = 0.852
5982 measured reflections
2507 independent reflections
2132 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.019

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.118
$S$ = 1.07
2507 reflections
166 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.18 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.15 e Å$^{-3}$

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: RK2419).

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# supporting information

*Acta Cryst.* (2014). E**70**, o275 [doi:10.1107/S1600536814002657]

## *N*,*N*′-[(2*E*,3*E*)-Butane-2,3-diylidene]bis[4-fluoro-2-(1-phenylethyl)aniline]

**Juanjuan Wei, Houde She, Lijun Shi and Ziqiang Lei**

### S1. Comment

An *α*-diimine ligands with different electronic property, rigidity and steric hindrance has been widely synthesized due to their significant applications in catalysis, coordination chemistry and carbene chemistry (Grasa *et al.*, 2001; Williams *et al.*, 2008; Hanhan *et al.*, 2012; Partyka, 2011; Yuan *et al.*, 2012). As part of our research efforts focused on developing ligands and organic catalysts, a novel series of imine derivatives were synthesized. Herein, we report the preparation and crystal structure of the title compound (Fig. 1).

The title molecule, is a symmetrical structure, and the central butanediimine moiety (N═C(*Me*)–C(*Me*)═N) is planar. The dihedral angles between the benzene ring C8-C13 and benzene ring C1-C6 is 84.27 (5)°. The molecular dimensions in the title compound agree very well with the corresponding one reported in a few closely related compounds (Zou *et al.*, 2008; Lohr *et al.* 2011).

### S2. Experimental

Formic acid (1.0 ml) was added to a stirred solution of 4-fluoro-2-(1-phenylethyl)aniline (1.5 mmol) and 2,3-butanedione (0.7 mmol) in 20 ml anhydrous methanol (20 ml). The mixture was stirred at 323 K for 24 h, then cooled, and the precipitate was separated by filtration. The solid was recrystallized from ethanol/dichloromethane (*v*/*v* = 12:1), washed with cold ethanol and dried under vacuum to give the title compound (Fig. 2). Yield is 82%. Crystals suitable for X-ray diffraction were grown in cyclohexane/dichloromethane (*v*/*v* = 1:2) solution at room temperature by the slow evaporation method. $^{1}$H NMR (400 MHz, $CDCl_3$): *δ* (p.p.m.) 7.19(t, *J* = 7.4 Hz, 4H), 7.09-7.13 (m, 4H), 7.01-7.05(m, 4H), 6.93 (dt, *J* = 8.4, 2.9 Hz, 2H), 6.47 (dd, *J* = 8.6, 5.3 Hz, 2H), 4.08 (q, *J* = 6.8 Hz, 2H), 1.62 (s, 6H), 1.56 (d, *J* = 7.2 Hz, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* (p.p.m.) 168.54, 161.22, 158.82, 145.58, 144.69, 137.34, 128.31, 127.57, 126.06, 118.94, 113.58, 40.17, 21.42, 20.86.

### S3. Refinement

All hydrogen atoms were placed in calculated positions with C–H distances of 0.93Å, 0.96Å and 0.98Å for aryl, methyl and methine H atoms. They were included in the refinement in a riding model approximation, respectively with $U_{iso}$ = 1.2$U_{eq}$(C) for aryl and methine H, and $U_{iso}$ = 1.5$U_{eq}$(C) for methyl H.

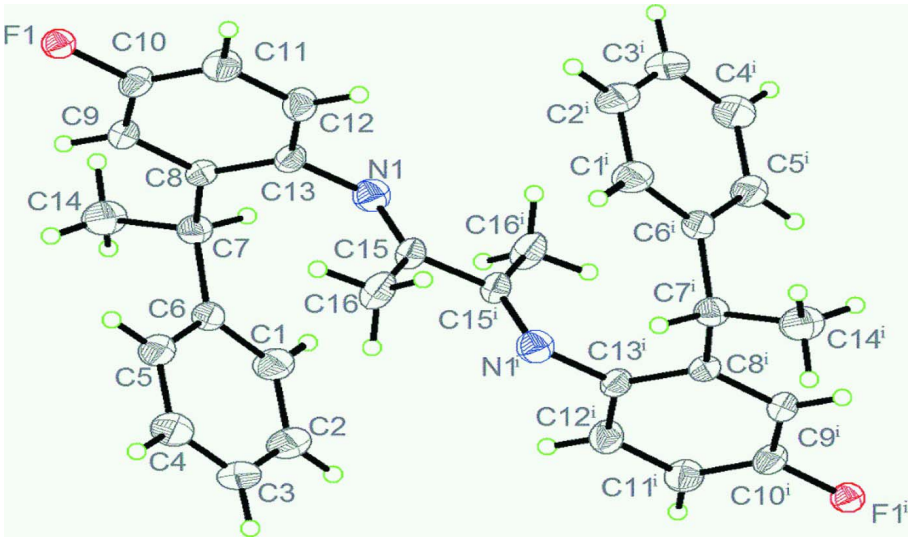


**Figure 1**

The molecular structure of title molecule with the atom numbering scheme. Displacement ellipsoids are drawn at 30% probability level. Symmetry code: (i) -*x*+1, -*y*+1, -*z*+1.

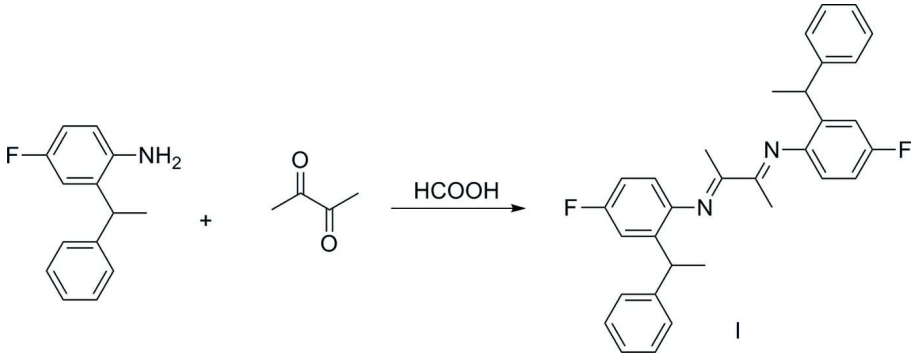


**Figure 2**

A condensation reaction of 2,3-butanedione and 4-fluoro-2-(1-phenylethyl)aniline.

**N,N′-[(2*E*,3*E*)-Butane-2,3-diylidene]bis[4-fluoro-2-(1-phenylethyl)aniline]**

*Crystal data*

$C_{32}H_{30}F_2N_2$
$M_r = 480.58$
Monoclinic, $P2_1/n$
$a = 11.5335$ (11) Å
$b = 9.5024$ (12) Å
$c = 12.1318$ (14) Å
$\beta = 91.660$ (11)°
$V = 1329.0$ (3) Å$^3$
$Z = 2$
$F(000) = 508$
$D_x = 1.201$ Mg m$^{-3}$
Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Cell parameters from 2620 reflections
$\theta = 5.2$–70.8°
$\mu = 0.64$ mm$^{-1}$
$T = 295$ K
Block, clear light yellow
0.35 × 0.28 × 0.26 mm

*Data collection*

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min}$ = 0.808, $T_{max}$ = 0.852
5982 measured reflections
2507 independent reflections
2132 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.019
$\theta_{max}$ = 70.5°, $\theta_{min}$ = 5.2°
$h = -14 \rightarrow 12$
$k = -11 \rightarrow 10$
$l = -14 \rightarrow 14$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.118
$S$ = 1.07
2507 reflections
166 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
$w = 1/[\sigma^2(F_o^2) + (0.056P)^2 + 0.1881P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.15 e Å$^{-3}$
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0100 (10)

*Special details*

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

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| N1 | 0.37261 (9) | 0.49441 (12) | 0.57384 (9) | 0.0406 (3) |
| F1 | −0.02542 (7) | 0.78857 (12) | 0.66670 (9) | 0.0687 (3) |
| C1 | 0.57482 (13) | 0.64883 (19) | 0.75155 (16) | 0.0602 (4) |
| H1 | 0.5841 | 0.5539 | 0.7683 | 0.072* |
| C2 | 0.67019 (14) | 0.7270 (2) | 0.72255 (19) | 0.0747 (6) |
| H2 | 0.7426 | 0.6844 | 0.7197 | 0.090* |
| C3 | 0.65862 (15) | 0.8671 (2) | 0.69791 (18) | 0.0743 (6) |
| H3 | 0.7224 | 0.9194 | 0.6769 | 0.089* |
| C4 | 0.55119 (15) | 0.9295 (2) | 0.70466 (16) | 0.0687 (5) |
| H4 | 0.5430 | 1.0251 | 0.6899 | 0.082* |
| C5 | 0.45519 (13) | 0.85116 (16) | 0.73331 (14) | 0.0543 (4) |
| H5 | 0.3832 | 0.8946 | 0.7371 | 0.065* |
| C6 | 0.46540 (11) | 0.70923 (15) | 0.75624 (11) | 0.0420 (3) |
| C7 | 0.36098 (11) | 0.61988 (15) | 0.78526 (11) | 0.0419 (3) |
| H7 | 0.3860 | 0.5215 | 0.7814 | 0.050* |

| | | | | |
|---|---|---|---|---|
| C8 | 0.26187 (10) | 0.63660 (13) | 0.70095 (10) | 0.0361 (3) |
| C9 | 0.16094 (11) | 0.71082 (15) | 0.72229 (11) | 0.0422 (3) |
| H9 | 0.1525 | 0.7555 | 0.7898 | 0.051* |
| C10 | 0.07376 (11) | 0.71744 (15) | 0.64271 (13) | 0.0468 (3) |
| C11 | 0.08083 (12) | 0.65451 (17) | 0.54169 (13) | 0.0518 (4) |
| H11 | 0.0199 | 0.6601 | 0.4899 | 0.062* |
| C12 | 0.18142 (12) | 0.58231 (17) | 0.51907 (11) | 0.0488 (4) |
| H12 | 0.1885 | 0.5385 | 0.4510 | 0.059* |
| C13 | 0.27209 (11) | 0.57440 (14) | 0.59672 (10) | 0.0379 (3) |
| C14 | 0.32418 (14) | 0.6453 (2) | 0.90437 (13) | 0.0628 (5) |
| H14A | 0.3068 | 0.7433 | 0.9142 | 0.094* |
| H14B | 0.3862 | 0.6185 | 0.9545 | 0.094* |
| H14C | 0.2566 | 0.5902 | 0.9188 | 0.094* |
| C15 | 0.44839 (10) | 0.54573 (14) | 0.51063 (10) | 0.0399 (3) |
| C16 | 0.44521 (14) | 0.68862 (16) | 0.45826 (14) | 0.0558 (4) |
| H16A | 0.3815 | 0.7414 | 0.4862 | 0.084* |
| H16B | 0.4356 | 0.6788 | 0.3798 | 0.084* |
| H16C | 0.5165 | 0.7371 | 0.4753 | 0.084* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| N1 | 0.0385 (6) | 0.0450 (6) | 0.0388 (6) | 0.0027 (5) | 0.0096 (4) | −0.0018 (5) |
| F1 | 0.0418 (5) | 0.0843 (7) | 0.0801 (7) | 0.0223 (4) | 0.0027 (4) | −0.0130 (5) |
| C1 | 0.0394 (7) | 0.0582 (10) | 0.0828 (11) | 0.0038 (7) | −0.0031 (7) | −0.0062 (8) |
| C2 | 0.0369 (8) | 0.0801 (13) | 0.1072 (16) | −0.0020 (8) | 0.0043 (9) | −0.0174 (11) |
| C3 | 0.0512 (9) | 0.0828 (13) | 0.0896 (13) | −0.0260 (9) | 0.0173 (9) | −0.0201 (11) |
| C4 | 0.0681 (11) | 0.0520 (10) | 0.0868 (13) | −0.0131 (8) | 0.0148 (10) | −0.0048 (8) |
| C5 | 0.0465 (8) | 0.0472 (8) | 0.0698 (10) | 0.0001 (6) | 0.0093 (7) | −0.0048 (7) |
| C6 | 0.0372 (6) | 0.0461 (8) | 0.0427 (7) | −0.0009 (5) | −0.0001 (5) | −0.0071 (6) |
| C7 | 0.0396 (7) | 0.0438 (7) | 0.0423 (7) | −0.0011 (5) | 0.0004 (5) | 0.0002 (6) |
| C8 | 0.0328 (6) | 0.0381 (7) | 0.0377 (6) | −0.0033 (5) | 0.0066 (5) | −0.0001 (5) |
| C9 | 0.0387 (6) | 0.0454 (7) | 0.0431 (7) | 0.0000 (5) | 0.0085 (5) | −0.0065 (5) |
| C10 | 0.0341 (6) | 0.0484 (8) | 0.0583 (8) | 0.0063 (5) | 0.0066 (6) | −0.0022 (6) |
| C11 | 0.0407 (7) | 0.0626 (9) | 0.0515 (8) | 0.0045 (6) | −0.0070 (6) | −0.0020 (7) |
| C12 | 0.0481 (8) | 0.0597 (9) | 0.0386 (7) | 0.0038 (6) | 0.0011 (6) | −0.0071 (6) |
| C13 | 0.0353 (6) | 0.0406 (7) | 0.0383 (6) | 0.0003 (5) | 0.0087 (5) | 0.0010 (5) |
| C14 | 0.0585 (9) | 0.0879 (13) | 0.0420 (8) | −0.0129 (9) | 0.0003 (7) | 0.0006 (8) |
| C15 | 0.0411 (7) | 0.0427 (7) | 0.0363 (6) | 0.0042 (6) | 0.0088 (5) | −0.0019 (5) |
| C16 | 0.0559 (8) | 0.0505 (9) | 0.0623 (9) | 0.0119 (7) | 0.0237 (7) | 0.0108 (7) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| N1—C15 | 1.2761 (16) | C8—C9 | 1.3917 (17) |
| N1—C13 | 1.4204 (15) | C8—C13 | 1.4039 (17) |
| F1—C10 | 1.3673 (15) | C9—C10 | 1.375 (2) |
| C1—C2 | 1.382 (2) | C9—H9 | 0.9300 |
| C1—C6 | 1.3890 (19) | C10—C11 | 1.368 (2) |

| | | | |
|---|---|---|---|
| C1—H1 | 0.9300 | C11—C12 | 1.382 (2) |
| C2—C3 | 1.370 (3) | C11—H11 | 0.9300 |
| C2—H2 | 0.9300 | C12—C13 | 1.3892 (19) |
| C3—C4 | 1.378 (3) | C12—H12 | 0.9300 |
| C3—H3 | 0.9300 | C14—H14A | 0.9600 |
| C4—C5 | 1.387 (2) | C14—H14B | 0.9600 |
| C4—H4 | 0.9300 | C14—H14C | 0.9600 |
| C5—C6 | 1.381 (2) | C15—C16 | 1.4992 (19) |
| C5—H5 | 0.9300 | C15—C15$^{i}$ | 1.502 (2) |
| C6—C7 | 1.5231 (18) | C16—H16A | 0.9600 |
| C7—C8 | 1.5200 (18) | C16—H16B | 0.9600 |
| C7—C14 | 1.537 (2) | C16—H16C | 0.9600 |
| C7—H7 | 0.9800 | | |

| | | | |
|---|---|---|---|
| C15—N1—C13 | 119.34 (11) | C10—C9—H9 | 120.3 |
| C2—C1—C6 | 121.28 (17) | C8—C9—H9 | 120.3 |
| C2—C1—H1 | 119.4 | F1—C10—C11 | 118.60 (13) |
| C6—C1—H1 | 119.4 | F1—C10—C9 | 118.19 (13) |
| C3—C2—C1 | 120.33 (16) | C11—C10—C9 | 123.20 (12) |
| C3—C2—H2 | 119.8 | C10—C11—C12 | 117.84 (13) |
| C1—C2—H2 | 119.8 | C10—C11—H11 | 121.1 |
| C2—C3—C4 | 119.17 (16) | C12—C11—H11 | 121.1 |
| C2—C3—H3 | 120.4 | C11—C12—C13 | 120.79 (13) |
| C4—C3—H3 | 120.4 | C11—C12—H12 | 119.6 |
| C3—C4—C5 | 120.61 (17) | C13—C12—H12 | 119.6 |
| C3—C4—H4 | 119.7 | C12—C13—C8 | 120.45 (12) |
| C5—C4—H4 | 119.7 | C12—C13—N1 | 119.94 (12) |
| C6—C5—C4 | 120.71 (15) | C8—C13—N1 | 119.45 (11) |
| C6—C5—H5 | 119.6 | C7—C14—H14A | 109.5 |
| C4—C5—H5 | 119.6 | C7—C14—H14B | 109.5 |
| C5—C6—C1 | 117.87 (14) | H14A—C14—H14B | 109.5 |
| C5—C6—C7 | 121.83 (12) | C7—C14—H14C | 109.5 |
| C1—C6—C7 | 120.30 (13) | H14A—C14—H14C | 109.5 |
| C8—C7—C6 | 111.74 (11) | H14B—C14—H14C | 109.5 |
| C8—C7—C14 | 113.17 (12) | N1—C15—C16 | 126.30 (12) |
| C6—C7—C14 | 111.80 (12) | N1—C15—C15$^{i}$ | 116.24 (15) |
| C8—C7—H7 | 106.5 | C16—C15—C15$^{i}$ | 117.44 (14) |
| C6—C7—H7 | 106.5 | C15—C16—H16A | 109.5 |
| C14—C7—H7 | 106.5 | C15—C16—H16B | 109.5 |
| C9—C8—C13 | 118.26 (12) | H16A—C16—H16B | 109.5 |
| C9—C8—C7 | 122.99 (12) | C15—C16—H16C | 109.5 |
| C13—C8—C7 | 118.74 (11) | H16A—C16—H16C | 109.5 |
| C10—C9—C8 | 119.41 (12) | H16B—C16—H16C | 109.5 |

| | | | |
|---|---|---|---|
| C6—C1—C2—C3 | 0.2 (3) | C7—C8—C9—C10 | −178.02 (13) |
| C1—C2—C3—C4 | 1.3 (3) | C8—C9—C10—F1 | 178.66 (12) |
| C2—C3—C4—C5 | −1.6 (3) | C8—C9—C10—C11 | −0.3 (2) |
| C3—C4—C5—C6 | 0.4 (3) | F1—C10—C11—C12 | −179.60 (13) |

| | | | |
|---|---|---|---|
| C4—C5—C6—C1 | 1.1 (2) | C9—C10—C11—C12 | −0.7 (2) |
| C4—C5—C6—C7 | −178.53 (14) | C10—C11—C12—C13 | 0.0 (2) |
| C2—C1—C6—C5 | −1.4 (2) | C11—C12—C13—C8 | 1.7 (2) |
| C2—C1—C6—C7 | 178.26 (16) | C11—C12—C13—N1 | 177.16 (13) |
| C5—C6—C7—C8 | 51.52 (17) | C9—C8—C13—C12 | −2.62 (19) |
| C1—C6—C7—C8 | −128.13 (14) | C7—C8—C13—C12 | 177.29 (12) |
| C5—C6—C7—C14 | −76.48 (18) | C9—C8—C13—N1 | −178.09 (11) |
| C1—C6—C7—C14 | 103.86 (17) | C7—C8—C13—N1 | 1.83 (18) |
| C6—C7—C8—C9 | −107.17 (14) | C15—N1—C13—C12 | 77.96 (17) |
| C14—C7—C8—C9 | 20.09 (19) | C15—N1—C13—C8 | −106.56 (14) |
| C6—C7—C8—C13 | 72.91 (15) | C13—N1—C15—C16 | 2.1 (2) |
| C14—C7—C8—C13 | −159.82 (13) | C13—N1—C15—C15$^{i}$ | −179.36 (13) |
| C13—C8—C9—C10 | 1.89 (19) | | |

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.