# organic compounds

# 2,3,10,11-Tetramethoxy-6,7,14,15-tetrahydro-6,14-methanocycloocta-[1,2-b;5,6-b′]diquinoline

## Jason Ashmore, Roger Bishop,* Donald C. Craig and Marcia L. Scudder

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The racemic title compound, $C_{27}H_{26}N_2O_4$, crystallizes with its central carbon bridge on a twofold axis. It forms parallel chains of molecules utilizing aryl offset face–face interactions with an interplanar distance of about 3.5 Å. These chains associate further by means of pairs of $O-CH_2-H\cdots\pi$ (with H–ring distances ranging from 2.69 to 2.95 Å) and $O-CH_2-H\cdots N$ motifs. The methoxy groups in this structure are coplanar with the aromatic rings to which they are attached. This is recognized as being common behaviour amongst aromatic methoxy compounds.

## Related literature

Condensation of two equivalents of a 2-aminobenzaldehyde derivative with one of bicyclo[3.3.1]nonane-2,6-dione provides a V-shaped diquinoline adduct by means of the Friedländer condensation (Cheng & Yan, 1982). Substituted molecules of this general structural type frequently act as lattice inclusion hosts (Bishop, 2006). For related literature, see: Allen (2002); Desiraju & Gavezzotti (1989); Marjo et al. (1997); Pendrak et al. (1995); Schaefer & Honig (1968).
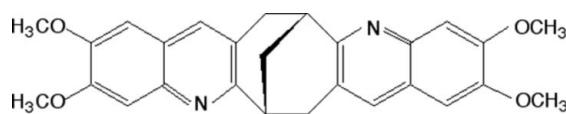


## Experimental

### Crystal data

| | |
|---|---|
| $C_{27}H_{26}N_2O_4$ | $a$ = 14.137 (7) Å |
| $M_r$ = 442.5 | $b$ = 9.533 (6) Å |
| Monoclinic, $C2/c$ | $c$ = 16.551 (7) Å |
| $\beta$ = 100.79 (3)° | $\mu$ = 0.09 mm$^{-1}$ |
| $V$ = 2191 (2) Å$^3$ | $T$ = 294 K |
| $Z$ = 4 | 0.12 mm (radius) |
| Mo $K\alpha$ radiation | |

### Data collection

| | |
|---|---|
| Enraf–Nonius CAD-4 diffractometer | 803 reflections with $I > 2\sigma(I)$ |
| Absorption correction: none | $R_{int}$ = 0.062 |
| 1999 measured reflections | 1 standard reflection |
| 1926 independent reflections | frequency: 30 min |
| | intensity decay: none |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.050 | 150 parameters |
| $wR(F^2)$ = 0.053 | H-atom parameters not refined |
| $S$ = 1.41 | $\Delta\rho_{max}$ = 0.56 e Å$^{-3}$ |
| 803 reflections | $\Delta\rho_{min}$ = $-0.48$ e Å$^{-3}$ |

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|---|---|---|---|
| C14—H3C14$\cdots$N1$^i$ | 1.00 | 2.88 | 3.723 (5) | 142 |
| C14—H3C14$\cdots$N1$^{ii}$ | 1.00 | 2.96 | 3.348 (5) | 104 |

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

Data collection: *CAD-4 Software* (Schagen *et al.*, 1989); cell refinement: *CAD-4 Software*; data reduction: Local program; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *RAELS* (Rae, 2000); molecular graphics: *ORTEPII* (Johnson, 1976) and *CrystalMaker* (Crystal-Maker, 2005); software used to prepare material for publication: Local programs.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LN2008).

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# 2,3,10,11-Tetramethoxy-6,7,14,15-tetrahydro-6,14-methanocycloocta[1,2-b;5,6-b′]diquinoline

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### S1. Comment

The asymmetric unit of the title compound, (1), contains half a molecule, with the central bridging carbon atom located on a twofold axis (Fig. 1).

Molecules of (1) form parallel chains along the *ac* diagonal (Fig. 2), associating by means of *exo,exo*-facial aryl offset face-face (OFF) interactions (Desiraju & Gavezzotti, 1989). The distance between the aromatic planes is about 3.5 Å. Complementary to the $\pi \cdots \pi$ interaction are a pair of associations between a methoxy group and a quinoline N atom (O—$CH_2$—H⋯N; d = 2.88 Å), and a pair between an aliphatic methylene and a methoxy group (C—H⋯O—$CH_3$, d = 2.84 Å). Adjacent chains interact in two ways: by means of a double centrosymmetric O—$CH_2$—H⋯$\pi$ interaction (utilizing the 3-methoxy group, with shortest C⋯C contacts of 3.57 and 3.82 Å) and an O—$CH_2$—H⋯N interaction (utilizing the 10-methoxy group with C⋯N of 3.35 Å).

It is noteworthy that the methoxy groups in this structure are co-planar with the aromatic rings to which they are attached. The Cambridge Structural Database (Allen *et al.*, 2002) reveals that this situation is commonplace amongst related compounds. The steric effects resulting from this co-planarity would be sufficient cause for the absence of centrosymmetric dimers utilizing the edge-edge aryl C—H⋯N supramolecular synthon which are found in the parent the non-methoxy diquinoline adduct (Marjo *et al.*, 1997).

### S2. Experimental

2-Amino-4,5-dimethoxybenzaldehyde (Pendrak *et al.*, 1995) (1.20 g, 6.62 mmol) and bicyclo[3.3.1]nonane-2,6-dione (Schaefer & Honig, 1968) (0.38 g, 2.50 mol) were dissolved in hot ethanol (20 ml) and a solution of sodium hydroxide (0.49 g, 12.25 mmol) in ethanol (10 ml) was added. The mixture was refluxed for 5 h, allowed to cool, then kept at 273 K for 5 h. Filtration gave the product 1 (0.51 g, 46%) of m.p. 548–549 K. $^{13}$C NMR (75.5 MHz, $CDCl_3$) $\delta$: 29.5 ($CH_2$), 36.6 (CH), 38.2 ($CH_2$), 56.2 ($CH_3$), 56.4 ($CH_3$), 104.6 (CH), 107.4 (CH), 123.3 (C), 126.8 (C), 134.7 (CH), 144.3 (C), 149.7 (C), 152.3 (C), 159.2 (C); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$: 2.49 (br s, 2H), 3.25 & 3.32 (d, 2H, $J_{AB}$ 16.6 Hz), 3.42 & 3.49 (dd, 2H, $J_{AB}$ 16.6, $J_{BX}$ 5.3 Hz), 3.70 (d, 2H, $J$ 2.6 Hz), 3.91 (s, 6H), 3.99 (s, 6H), 6.79 (s, 2H), 7.32 (s, 2H), 7.50 (s, 2H). X-ray quality crystals were obtained from ethyl acetate solution.

### S3. Refinement

All hydrogen atoms were placed geometrically with C—H = 1.0 Å and $U_{iso}$(H) = $U_{eq}$(C).
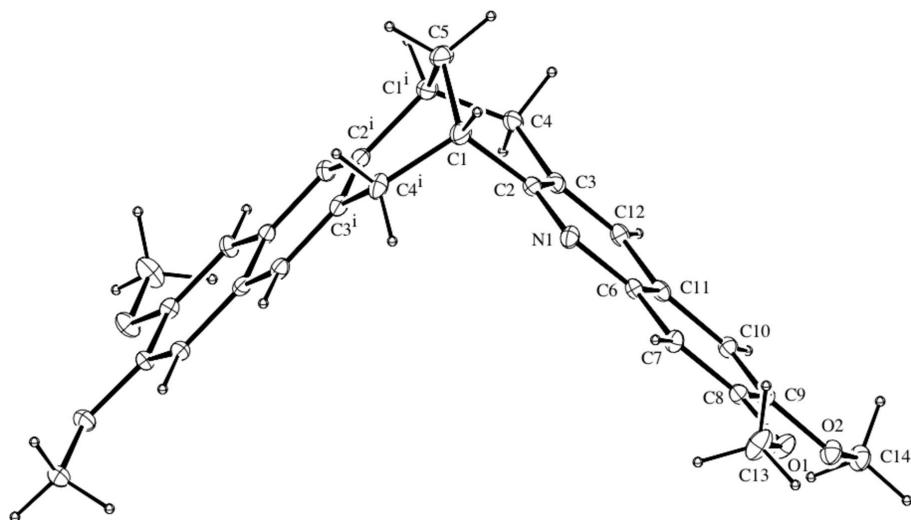
**Figure 1**

Molecular structure of (1), with ellipsoids drawn at 30% probability level. Symmetry code: (i) $1 - x$, $y$, $3/2 - z$.
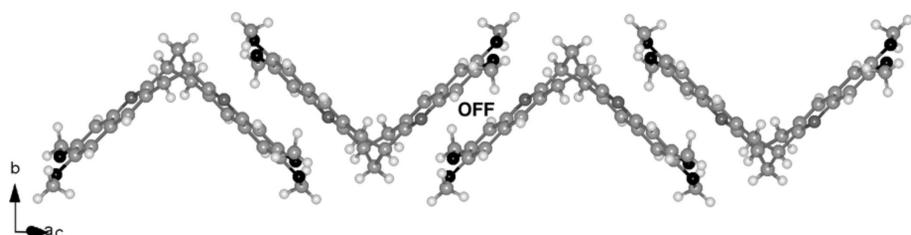


**Figure 2**

The chain of molecules of (1) with centrosymmetric OFF interactions between *exo*-surfaces of the aromatic wings. Adjacent molecules are of the opposite chirality.
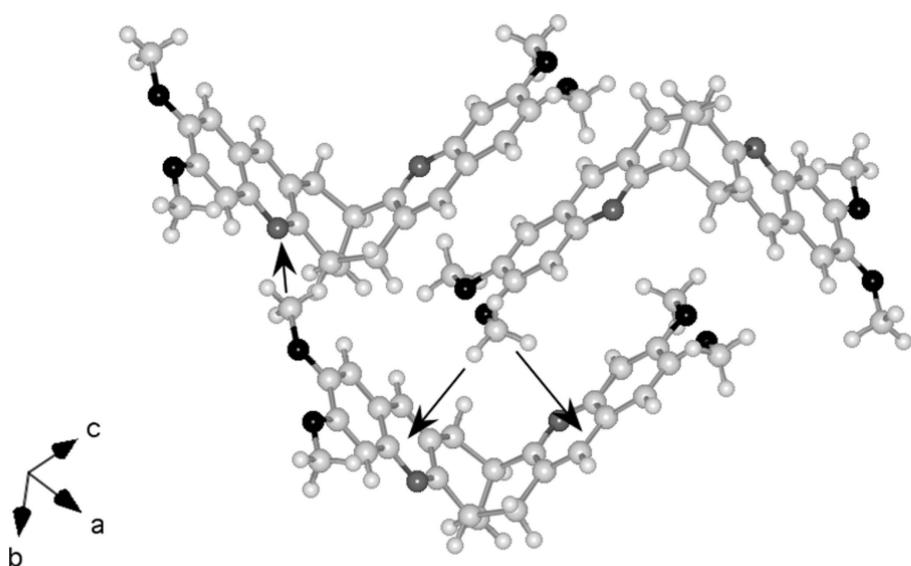


**Figure 3**

The chain (top) interacts with adjacent chains in two ways: a double CH$_3$···$\pi$ interaction (pair of arrows at the bottom of the figure) and a CH$_3$···N interaction (at the left of the figure).

**2,3,10,11-Tetramethoxy-6,7,14,15-tetrahydro-6,14- methanocycloocta[1,2 - *b*;5,6-*b*′]diquinoline**

*Crystal data*

| | |
|---|---|
| $C_{27}H_{26}N_2O_4$ | $F(000) = 936.0$ |
| $M_r = 442.5$ | $D_x = 1.34$ Mg m$^{-3}$ |
| Monoclinic, $C2/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 14.137$ (7) Å | Cell parameters from 11 reflections |
| $b = 9.533$ (6) Å | $\theta = 10–11°$ |
| $c = 16.551$ (7) Å | $\mu = 0.09$ mm$^{-1}$ |
| $\beta = 100.79$ (3)° | $T = 294$ K |
| $V = 2191$ (2) Å$^3$ | Irregular, colourless |
| $Z = 4$ | 0.12 mm (radius) |

*Data collection*

| | |
|---|---|
| Enraf–Nonius CAD-4 diffractometer | $\theta_{max} = 25°$ |
| | $h = -16 \rightarrow 16$ |
| $\omega$–$2\theta$ scans | $k = 0 \rightarrow 11$ |
| 1999 measured reflections | $l = 0 \rightarrow 19$ |
| 1926 independent reflections | 1 standard reflections every 30 min |
| 803 reflections with $I > 2\sigma(I)$ | intensity decay: none |
| $R_{int} = 0.062$ | |

*Refinement*

| | |
|---|---|
| Refinement on $F$ | 0 restraints |
| $R[F^2 > 2\sigma(F^2)] = 0.050$ | H-atom parameters not refined |
| $wR(F^2) = 0.053$ | $w = 1/[\sigma^2(F) + 0.0004F^2]$ |
| $S = 1.41$ | $(\Delta/\sigma)_{max} = 0.001$ |
| 803 reflections | $\Delta\rho_{max} = 0.56$ e Å$^{-3}$ |
| 150 parameters | $\Delta\rho_{min} = -0.48$ e Å$^{-3}$ |

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}*/U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| O1 | 0.3447 (2) | −0.0160 (3) | 0.3564 (2) | 0.059 (1) | |
| O2 | 0.2109 (2) | −0.1040 (3) | 0.4273 (2) | 0.0559 (9) | |
| N1 | 0.4643 (2) | 0.2977 (4) | 0.5789 (2) | 0.047 (1) | |
| C1 | 0.5320 (4) | 0.4581 (5) | 0.6853 (3) | 0.055 (1) | |
| C2 | 0.4554 (3) | 0.3525 (4) | 0.6509 (3) | 0.043 (1) | |
| C3 | 0.3824 (3) | 0.3145 (5) | 0.6937 (3) | 0.045 (1) | |
| C4 | 0.3736 (3) | 0.3841 (5) | 0.7746 (3) | 0.054 (1) | |
| C5 | 0.5000 | 0.5529 (7) | 0.7500 | 0.062 (2) | |
| C6 | 0.3986 (3) | 0.1982 (4) | 0.5451 (3) | 0.041 (1) | |
| C7 | 0.4076 (3) | 0.1425 (5) | 0.4682 (2) | 0.042 (1) | |
| C8 | 0.3440 (3) | 0.0430 (5) | 0.4314 (3) | 0.043 (1) | |
| C9 | 0.2697 (3) | −0.0039 (5) | 0.4705 (3) | 0.042 (1) | |
| C10 | 0.2596 (3) | 0.0469 (4) | 0.5446 (3) | 0.044 (1) | |
| C11 | 0.3242 (3) | 0.1518 (5) | 0.5843 (2) | 0.042 (1) | |
| C12 | 0.3174 (3) | 0.2147 (5) | 0.6597 (3) | 0.045 (1) | |
| C13 | 0.4183 (4) | 0.0306 (6) | 0.3148 (3) | 0.076 (2) | |
| C14 | 0.1350 (3) | −0.1571 (5) | 0.4654 (3) | 0.061 (1) | |
| HC1 | 0.5453 | 0.5182 | 0.6392 | 0.055 | |

| | | | | | |
|---|---|---|---|---|---|
| H1C4 | 0.3577 | 0.3110 | 0.8132 | 0.054 | |
| H2C4 | 0.3207 | 0.4552 | 0.7640 | 0.054 | |
| H1C5 | 0.4451 | 0.6135 | 0.7235 | 0.062 | 0.5 |
| H2C5 | 0.5549 | 0.6135 | 0.7765 | 0.062 | 0.5 |
| HC7 | 0.4605 | 0.1755 | 0.4404 | 0.042 | |
| HC10 | 0.2068 | 0.0110 | 0.5717 | 0.044 | |
| HC12 | 0.2646 | 0.1863 | 0.6889 | 0.045 | |
| H1C13 | 0.4120 | −0.0191 | 0.2609 | 0.076 | |
| H2C13 | 0.4118 | 0.1340 | 0.3051 | 0.076 | |
| H3C13 | 0.4827 | 0.0098 | 0.3492 | 0.076 | |
| H1C14 | 0.0972 | −0.2287 | 0.4287 | 0.061 | |
| H2C14 | 0.1634 | −0.2014 | 0.5193 | 0.061 | |
| H3C14 | 0.0917 | −0.0783 | 0.4748 | 0.061 | |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.058 (2) | 0.066 (2) | 0.055 (2) | −0.016 (2) | 0.018 (2) | −0.021 (2) |
| O2 | 0.050 (2) | 0.057 (2) | 0.060 (2) | −0.014 (2) | 0.007 (2) | 0.003 (2) |
| N1 | 0.049 (2) | 0.050 (3) | 0.040 (2) | −0.007 (2) | 0.000 (2) | 0.002 (2) |
| C1 | 0.067 (3) | 0.050 (3) | 0.044 (3) | −0.007 (3) | 0.000 (3) | 0.004 (3) |
| C2 | 0.049 (3) | 0.039 (3) | 0.040 (3) | 0.005 (2) | 0.001 (2) | 0.004 (3) |
| C3 | 0.046 (3) | 0.047 (3) | 0.039 (3) | 0.009 (2) | 0.001 (2) | 0.007 (2) |
| C4 | 0.060 (3) | 0.060 (3) | 0.039 (3) | 0.020 (3) | −0.001 (2) | −0.006 (3) |
| C5 | 0.089 (6) | 0.045 (5) | 0.048 (4) | 0.0000 | −0.002 (4) | 0.0000 |
| C6 | 0.039 (3) | 0.044 (3) | 0.038 (3) | 0.006 (2) | 0.002 (2) | 0.007 (2) |
| C7 | 0.036 (3) | 0.054 (3) | 0.039 (3) | −0.006 (2) | 0.010 (2) | −0.003 (3) |
| C8 | 0.042 (3) | 0.045 (3) | 0.040 (3) | 0.006 (2) | 0.007 (2) | 0.002 (3) |
| C9 | 0.036 (3) | 0.041 (3) | 0.047 (3) | −0.006 (2) | 0.001 (2) | 0.001 (3) |
| C10 | 0.038 (3) | 0.043 (3) | 0.051 (3) | −0.003 (2) | 0.006 (2) | 0.006 (2) |
| C11 | 0.042 (3) | 0.044 (3) | 0.040 (3) | 0.006 (3) | 0.007 (2) | 0.013 (3) |
| C12 | 0.043 (3) | 0.054 (3) | 0.038 (3) | 0.006 (3) | 0.007 (2) | 0.012 (2) |
| C13 | 0.074 (4) | 0.106 (5) | 0.056 (3) | −0.032 (3) | 0.029 (3) | −0.029 (3) |
| C14 | 0.050 (3) | 0.060 (3) | 0.072 (3) | −0.017 (3) | 0.004 (3) | 0.008 (3) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C8 | 1.365 (4) | C6—C7 | 1.406 (5) |
| O1—C13 | 1.421 (5) | C6—C11 | 1.407 (5) |
| O2—C9 | 1.375 (5) | C7—C8 | 1.369 (5) |
| O2—C14 | 1.434 (4) | C7—HC7 | 1.000 |
| N1—C2 | 1.328 (5) | C8—C9 | 1.406 (5) |
| N1—C6 | 1.371 (5) | C9—C10 | 1.352 (5) |
| C1—C2 | 1.510 (6) | C10—C11 | 1.428 (5) |
| C1—C4[i] | 1.545 (6) | C10—HC10 | 1.000 |
| C1—C5 | 1.532 (5) | C11—C12 | 1.405 (5) |
| C1—HC1 | 1.000 | C12—HC12 | 1.000 |
| C2—C3 | 1.405 (5) | C13—H1C13 | 1.000 |

| | | | |
|---|---|---|---|
| C3—C4 | 1.520 (5) | C13—H2C13 | 1.000 |
| C3—C12 | 1.368 (5) | C13—H3C13 | 1.000 |
| C4—H1C4 | 1.000 | C14—H1C14 | 1.000 |
| C4—H2C4 | 1.000 | C14—H2C14 | 1.000 |
| C5—H1C5 | 1.000 | C14—H3C14 | 1.000 |
| C5—H2C5 | 1.000 | | |
| | | | |
| C8—O1—C13 | 116.3 (4) | C6—C7—C8 | 120.1 (4) |
| C9—O2—C14 | 116.5 (3) | C6—C7—HC7 | 119.9 |
| C2—N1—C6 | 117.9 (4) | C8—C7—HC7 | 119.9 |
| C2—C1—C4$^i$ | 111.0 (4) | O1—C8—C7 | 125.1 (4) |
| C2—C1—C5 | 111.9 (4) | O1—C8—C9 | 114.9 (4) |
| C2—C1—HC1 | 108.6 | C7—C8—C9 | 120.0 (4) |
| C4$^i$—C1—C5 | 108.3 (3) | O2—C9—C8 | 114.4 (4) |
| C4$^i$—C1—HC1 | 108.6 | O2—C9—C10 | 124.3 (4) |
| C5—C1—HC1 | 108.6 | C8—C9—C10 | 121.3 (4) |
| N1—C2—C1 | 114.8 (4) | C9—C10—C11 | 120.0 (4) |
| N1—C2—C3 | 123.6 (4) | C9—C10—HC10 | 120.0 |
| C1—C2—C3 | 121.6 (4) | C11—C10—HC10 | 120.0 |
| C2—C3—C4 | 121.3 (4) | C6—C11—C10 | 118.5 (4) |
| C2—C3—C12 | 118.2 (4) | C6—C11—C12 | 117.2 (4) |
| C4—C3—C12 | 120.5 (4) | C10—C11—C12 | 124.3 (4) |
| C1$^i$—C4—C3 | 111.8 (4) | C3—C12—C11 | 120.7 (4) |
| C1$^i$—C4—H1C4 | 108.9 | C3—C12—HC12 | 119.7 |
| C1$^i$—C4—H2C4 | 108.9 | C11—C12—HC12 | 119.7 |
| C3—C4—H1C4 | 108.9 | O1—C13—H1C13 | 109.5 |
| C3—C4—H2C4 | 108.9 | O1—C13—H2C13 | 109.5 |
| H1C4—C4—H2C4 | 109.5 | O1—C13—H3C13 | 109.5 |
| C1—C5—C1$^i$ | 107.7 (5) | H1C13—C13—H2C13 | 109.5 |
| C1—C5—H1C5 | 109.9 | H1C13—C13—H3C13 | 109.5 |
| C1—C5—H2C5 | 109.9 | H2C13—C13—H3C13 | 109.5 |
| C1$^i$—C5—H1C5 | 109.9 | O2—C14—H1C14 | 109.5 |
| C1$^i$—C5—H2C5 | 109.9 | O2—C14—H2C14 | 109.5 |
| H1C5—C5—H2C5 | 109.5 | O2—C14—H3C14 | 109.5 |
| N1—C6—C7 | 117.5 (4) | H1C14—C14—H2C14 | 109.5 |
| N1—C6—C11 | 122.5 (4) | H1C14—C14—H3C14 | 109.5 |
| C7—C6—C11 | 120.0 (4) | H2C14—C14—H3C14 | 109.5 |

Symmetry code: (i) −$x$+1, $y$, −$z$+3/2.

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C14—H3$C$14···N1$^{ii}$ | 1.00 | 2.882 | 3.723 (5) | 142 |
| C14—H3$C$14···N1$^{iii}$ | 1.00 | 2.958 | 3.348 (5) | 104 |

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