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# 5-Nitro-2,3-bis(thiophen-2-yl)quinoxaline

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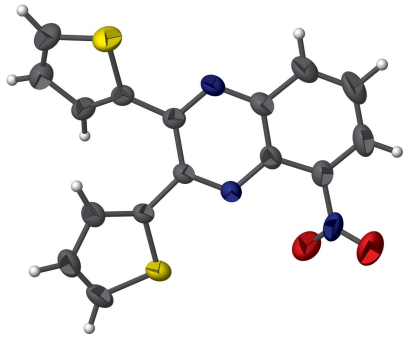
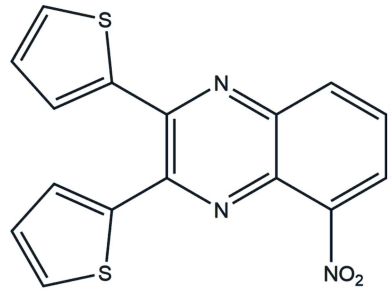
**Structural data**: full structural data are available from iucrdata.iucr.org

The title compound, $C_{16}H_9N_3O_2S_2$, was synthesized *via* a condensation reaction in refluxing acetic acid. The dihedral angles between the mean plane of the quinoxaline unit and the thienyl rings are 35.16 (5)° and 24.94 (3)°.

**3D view**



**Chemical scheme**




## Structure description

5-Nitro-2,3-bis(thiophen-2-yl)quinoxaline crystallizes in space group $P2_1$. All bond lengths and angles are within expected values. The nitro group makes a angle of 43.07 (6)° with respect to the mean plane of the quinoxaline unit. This angle is comparable to the angles of 44.96 and 50.93° observed for the two molecules in the asymmetric unit in the published crystal structure of 5-nitro-2,3-bis(2-pyridyl)quinoxaline (Du & Zhao, 2003) and with the 44.12° determined in a corresponding silver complex with the pyridyl ligand (Liu & Du, 2002). The thienyl rings make angles of 35.16 (5) and 24.94 (3)°, for rings with S1 and S2 respectively, with the mean plane of the quinoxaline unit. Both the heterocyclic thienyl ring sulfur atoms reside in close proximity to the quinoxaline N atoms. When describing the structure of 5-nitro-2,3-bis(2-pyridyl)quinoxaline, Du & Zhao (2003) labeled this orientation of the heterocyclic ring to the quinoxaline unit as a *trans–trans* arrangement. There are no intermolecular interactions of consequence. An *ORTEP* view is shown in Fig. 1 and a view of the unit cell along (010) is shown in Fig. 2.

## Synthesis and crystallization

2-Thiophenecarboxaldehyde was condensed to 2,2′-thenoin (Crundwell *et al.*, 2002) followed by oxidation to 2,2′-thenil (Crundwell *et al.*, 2003). The nitrophenylenediamines were used as purchased from Sigma–Aldrich.

In a 100 ml round-bottom flask, 2.22 g of 2,2′-thenil (10.0 mmol) and 1.52 g of 3-nitro-1,2-phenylenediamine were added to 50 ml of concentrated acetic acid. The solution was

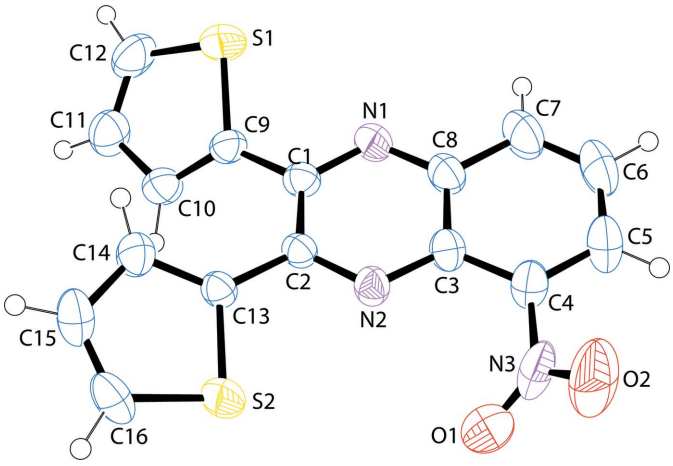



**Figure 1**
A view of 5-nitro-2,3-bis(thiophen-2-yl)quinoxaline (Farrugia, 2012). Displacement ellipsoids are drawn at the 50% probability level.

refluxed with stirring for 18 h. The solution was cooled to room temperature and neutralized with 6 *M* NaOH. The solution was again cooled then filtered. The resulting solid was filtered and washed with cold water then dried. The yield of the yellow product was 2.80 g (83%), m.p. 445 K. Crystals were obtained by recrystallization from ethanol solution. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.17 (*m*, 2H), 7.42 (*dd*, 1H), 7.49 (*dd*, 1H), 7.80 (*m*, 2H), 7.97 (*t*, 1H), 8.30 (*m*, 2H); $^{13}$C NMR ($CDCl_3$, 300 MHz): $\delta$ = 124.4, 127.7, 127.8, 128.8, 130.2, 130.3, 130.5, 131.0, 132.1, 132.8, 140.1, 140.5, 141.0, 147.0, 148.0, 148.1.

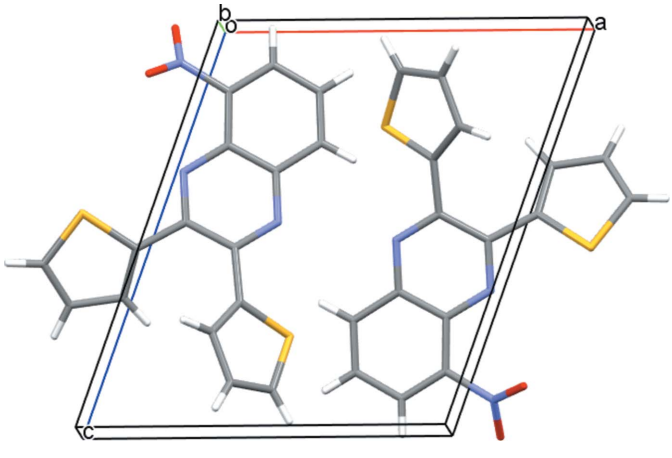



**Figure 2**
A view of the unit cell of 5-nitro-2,3-bis(thiophen-2-yl)quinoxaline along (010).

**Table 1**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_{16}H_9N_3O_2S_2$ |
| $M_r$ | 339.38 |
| Crystal system, space group | Monoclinic, $P2_1$ |
| Temperature (K) | 293 |
| *a*, *b*, *c* (Å) | 9.6598 (4), 7.4249 (3), 11.2457 (6) |
| $\beta$ (°) | 109.745 (5) |
| $V$ (Å$^3$) | 759.15 (6) |
| $Z$ | 2 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.36 |
| Crystal size (mm) | 0.42 × 0.34 × 0.21 |
| | |
| Data collection | |
| Diffractometer | Oxford Diffraction Xcalibur, Sapphire3 |
| Absorption correction | Multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009) |
| $T_{min}$, $T_{max}$ | 0.865, 1.000 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 12526, 6073, 3455 |
| $R_{int}$ | 0.021 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.802 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.038, 0.076, 0.81 |
| No. of reflections | 6073 |
| No. of parameters | 208 |
| No. of restraints | 1 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.43, −0.15 |
| Absolute structure | Flack (1983) |
| Absolute structure parameter | 0.02 (4) |

Computer programs: *CrysAlis CCD* and *CrysAlis RED* (Oxford Diffraction, 2009), *SHELXS2014* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012) and *OLEX2* (Bourhis *et al.*, 2015).

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

## Funding information

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## References

Bourhis, L. J., Dolomanov, O. V., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2015). *Acta Cryst.* A**71**, 59–75.
Crundwell, G., Sullivan, J., Pelto, R. & Kantardjieff, K. (2003). *J. Chem. Cryst*, **33**, 239–244.
Crundwell, G., Meskill, T., Sayers, D. & Kantardjieff, K. (2002). *Acta Cryst.* E**58**, o666–o667.
Du, M. & Zhao, X.-J. (2003). *Acta Cryst.* C**59**, o403–o405.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Liu, H. & Du, M. (2002). *J. Mol. Struct.* **607**, 143–148.
Oxford Diffraction (2009). *CrysAlis CCD*, *CrysAlis RED* and *CrysAlis PRO*. Oxford Diffraction, Yarnton, England.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

# full crystallographic data

*IUCrData* (2020). **5**, x200196 [https://doi.org/10.1107/S2414314620001960]

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### 5-Nitro-2,3-bis(thiophen-2-yl)quinoxaline

*Crystal data*

$C_{16}H_9N_3O_2S_2$
$M_r$ = 339.38
Monoclinic, $P2_1$
$a$ = 9.6598 (4) Å
$b$ = 7.4249 (3) Å
$c$ = 11.2457 (6) Å
$\beta$ = 109.745 (5)°
$V$ = 759.15 (6) Å$^3$
$Z$ = 2
$F(000)$ = 348
$D_x$ = 1.485 Mg m$^{-3}$
Melting point: 445 K
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 4761 reflections
$\theta$ = 4.2–34.7°
$\mu$ = 0.36 mm$^{-1}$
$T$ = 293 K
Block, yellow
0.42 × 0.34 × 0.21 mm

*Data collection*

Oxford Diffraction Xcalibur, Sapphire3 diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.1790 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (CrysAlis PRO; Oxford Diffraction, 2009)
$T_{min}$ = 0.865, $T_{max}$ = 1.000
12526 measured reflections
6073 independent reflections
3455 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.021
$\theta_{max}$ = 34.7°, $\theta_{min}$ = 4.2°
$h$ = −14→15
$k$ = −11→11
$l$ = −17→17

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.076
$S$ = 0.81
6073 reflections
208 parameters
1 restraint
Primary atom site location: iterative
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.43 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.15 e Å$^{-3}$
Absolute structure: Flack (1983)
Absolute structure parameter: 0.02 (4)

*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 $F^2 > 2\text{sigma}(F^2)$ 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.
H atoms were included in calculated positions with C-H distances of 0.93 Å and were included in the refinement in riding motion approximation with $U_{iso}$ = 1.2 of the carrier atom.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| S1 | 0.47899 (5) | 0.46766 (7) | 0.76512 (4) | 0.06021 (14) |
| S2 | −0.19846 (4) | 0.56574 (5) | 0.45980 (4) | 0.04714 (10) |
| O1 | −0.14872 (15) | 0.6115 (2) | 0.11787 (12) | 0.0794 (4) |
| O2 | −0.12755 (18) | 0.3929 (3) | 0.00033 (12) | 0.0978 (6) |
| N1 | 0.33895 (13) | 0.50828 (18) | 0.48400 (11) | 0.0434 (3) |
| N2 | 0.03464 (12) | 0.50012 (16) | 0.35820 (10) | 0.0368 (3) |
| N3 | −0.07726 (18) | 0.4977 (3) | 0.08793 (12) | 0.0608 (4) |
| C1 | 0.24643 (14) | 0.52968 (18) | 0.54672 (12) | 0.0358 (3) |
| C2 | 0.08928 (14) | 0.51352 (17) | 0.48202 (12) | 0.0324 (3) |
| C3 | 0.13010 (16) | 0.4937 (2) | 0.29286 (13) | 0.0390 (3) |
| C4 | 0.08067 (17) | 0.4805 (2) | 0.16013 (13) | 0.0473 (4) |
| C5 | 0.1750 (2) | 0.4561 (3) | 0.09426 (17) | 0.0645 (5) |
| H5 | 0.1394 | 0.4464 | 0.0067 | 0.077* |
| C6 | 0.3257 (2) | 0.4459 (3) | 0.16079 (18) | 0.0727 (6) |
| H6 | 0.3903 | 0.4287 | 0.1164 | 0.087* |
| C7 | 0.3801 (2) | 0.4603 (3) | 0.28792 (17) | 0.0647 (5) |
| H7 | 0.4811 | 0.4537 | 0.3299 | 0.078* |
| C8 | 0.28385 (16) | 0.4853 (2) | 0.35731 (14) | 0.0435 (3) |
| C9 | 0.31323 (14) | 0.5671 (2) | 0.68209 (12) | 0.0378 (3) |
| C10 | 0.26900 (17) | 0.6793 (2) | 0.75847 (14) | 0.0447 (4) |
| H10 | 0.1831 | 0.7472 | 0.7308 | 0.054* |
| C11 | 0.36745 (19) | 0.6812 (2) | 0.88351 (15) | 0.0554 (4) |
| H11 | 0.3529 | 0.7491 | 0.9478 | 0.066* |
| C12 | 0.48426 (19) | 0.5748 (3) | 0.90005 (15) | 0.0630 (5) |
| H12 | 0.5599 | 0.5610 | 0.9769 | 0.076* |
| C13 | −0.02054 (14) | 0.50573 (18) | 0.54585 (12) | 0.0332 (3) |
| C14 | −0.01082 (17) | 0.4470 (2) | 0.66529 (14) | 0.0452 (4) |
| H14 | 0.0756 | 0.4075 | 0.7262 | 0.054* |
| C15 | −0.1486 (2) | 0.4545 (3) | 0.68296 (16) | 0.0554 (4) |
| H15 | −0.1625 | 0.4191 | 0.7574 | 0.066* |
| C16 | −0.25747 (19) | 0.5175 (2) | 0.58246 (17) | 0.0552 (5) |
| H16 | −0.3539 | 0.5329 | 0.5802 | 0.066* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.0398 (2) | 0.0812 (3) | 0.0524 (2) | 0.0186 (2) | 0.00605 (16) | 0.0062 (2) |
| S2 | 0.03174 (17) | 0.0601 (2) | 0.0503 (2) | 0.00166 (19) | 0.01476 (14) | −0.0002 (2) |
| O1 | 0.0607 (8) | 0.1124 (12) | 0.0540 (8) | 0.0145 (9) | 0.0049 (6) | −0.0004 (8) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O2 | 0.0919 (11) | 0.1455 (15) | 0.0512 (8) | −0.0414 (11) | 0.0180 (7) | −0.0355 (9) |
| N1 | 0.0313 (5) | 0.0576 (8) | 0.0441 (7) | 0.0034 (5) | 0.0163 (5) | 0.0023 (6) |
| N2 | 0.0324 (5) | 0.0459 (7) | 0.0336 (6) | −0.0032 (5) | 0.0130 (4) | −0.0010 (5) |
| N3 | 0.0650 (9) | 0.0883 (11) | 0.0270 (6) | −0.0192 (9) | 0.0130 (6) | −0.0009 (7) |
| C1 | 0.0309 (6) | 0.0381 (9) | 0.0380 (7) | 0.0006 (5) | 0.0110 (5) | 0.0010 (6) |
| C2 | 0.0299 (6) | 0.0335 (7) | 0.0359 (7) | 0.0008 (5) | 0.0137 (5) | 0.0011 (5) |
| C3 | 0.0416 (7) | 0.0408 (7) | 0.0388 (7) | −0.0044 (7) | 0.0193 (6) | −0.0011 (6) |
| C4 | 0.0517 (9) | 0.0560 (9) | 0.0362 (7) | −0.0060 (8) | 0.0172 (6) | −0.0046 (7) |
| C5 | 0.0788 (13) | 0.0810 (12) | 0.0454 (9) | −0.0026 (12) | 0.0363 (9) | −0.0057 (10) |
| C6 | 0.0749 (13) | 0.0977 (15) | 0.0651 (12) | 0.0070 (12) | 0.0494 (11) | −0.0044 (11) |
| C7 | 0.0481 (9) | 0.0942 (14) | 0.0624 (11) | 0.0057 (10) | 0.0326 (8) | −0.0038 (11) |
| C8 | 0.0393 (7) | 0.0503 (8) | 0.0463 (8) | 0.0020 (7) | 0.0214 (6) | −0.0015 (7) |
| C9 | 0.0300 (6) | 0.0451 (7) | 0.0361 (7) | 0.0024 (7) | 0.0085 (5) | 0.0068 (7) |
| C10 | 0.0380 (8) | 0.0513 (9) | 0.0404 (8) | 0.0033 (7) | 0.0074 (6) | −0.0021 (7) |
| C11 | 0.0552 (10) | 0.0658 (11) | 0.0422 (9) | −0.0047 (9) | 0.0126 (7) | −0.0075 (8) |
| C12 | 0.0515 (9) | 0.0874 (13) | 0.0394 (8) | 0.0023 (11) | 0.0014 (7) | 0.0092 (10) |
| C13 | 0.0286 (6) | 0.0369 (7) | 0.0355 (7) | −0.0008 (5) | 0.0125 (5) | −0.0013 (6) |
| C14 | 0.0446 (8) | 0.0523 (9) | 0.0424 (8) | −0.0013 (8) | 0.0195 (6) | 0.0057 (7) |
| C15 | 0.0598 (10) | 0.0686 (11) | 0.0483 (9) | −0.0147 (10) | 0.0321 (8) | −0.0071 (9) |
| C16 | 0.0420 (8) | 0.0686 (12) | 0.0664 (11) | −0.0068 (8) | 0.0331 (8) | −0.0123 (9) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| S1—C9 | 1.7234 (14) | C5—C6 | 1.396 (3) |
| S1—C12 | 1.6986 (19) | C6—H6 | 0.9300 |
| S2—C13 | 1.7219 (14) | C6—C7 | 1.351 (2) |
| S2—C16 | 1.6992 (17) | C7—H7 | 0.9300 |
| O1—N3 | 1.209 (2) | C7—C8 | 1.414 (2) |
| O2—N3 | 1.220 (2) | C9—C10 | 1.365 (2) |
| N1—C1 | 1.3218 (17) | C10—H10 | 0.9300 |
| N1—C8 | 1.3528 (19) | C10—C11 | 1.407 (2) |
| N2—C2 | 1.3155 (17) | C11—H11 | 0.9300 |
| N2—C3 | 1.3602 (17) | C11—C12 | 1.338 (2) |
| N3—C4 | 1.472 (2) | C12—H12 | 0.9300 |
| C1—C2 | 1.4498 (18) | C13—C14 | 1.3849 (19) |
| C1—C9 | 1.4653 (19) | C14—H14 | 0.9300 |
| C2—C13 | 1.4693 (18) | C14—C15 | 1.411 (2) |
| C3—C4 | 1.409 (2) | C15—H15 | 0.9300 |
| C3—C8 | 1.417 (2) | C15—C16 | 1.341 (3) |
| C4—C5 | 1.367 (2) | C16—H16 | 0.9300 |
| C5—H5 | 0.9300 | | |
| | | | |
| C12—S1—C9 | 91.46 (8) | N1—C8—C3 | 120.30 (12) |
| C16—S2—C13 | 91.95 (8) | N1—C8—C7 | 119.98 (14) |
| C1—N1—C8 | 118.73 (12) | C3—C8—C7 | 119.66 (14) |
| C2—N2—C3 | 118.14 (12) | C1—C9—S1 | 118.96 (11) |
| O1—N3—O2 | 124.17 (17) | C10—C9—S1 | 110.59 (10) |
| O1—N3—C4 | 119.36 (15) | C10—C9—C1 | 130.37 (13) |

| | | | |
|---|---|---|---|
| O2—N3—C4 | 116.47 (19) | C9—C10—H10 | 123.7 |
| N1—C1—C2 | 120.28 (12) | C9—C10—C11 | 112.66 (14) |
| N1—C1—C9 | 115.93 (12) | C11—C10—H10 | 123.7 |
| C2—C1—C9 | 123.78 (12) | C10—C11—H11 | 123.6 |
| N2—C2—C1 | 121.01 (12) | C12—C11—C10 | 112.76 (15) |
| N2—C2—C13 | 114.61 (11) | C12—C11—H11 | 123.6 |
| C1—C2—C13 | 124.37 (12) | S1—C12—H12 | 123.7 |
| N2—C3—C4 | 121.73 (13) | C11—C12—S1 | 112.51 (12) |
| N2—C3—C8 | 120.66 (13) | C11—C12—H12 | 123.7 |
| C8—C3—C4 | 117.41 (12) | C2—C13—S2 | 117.62 (10) |
| C3—C4—N3 | 119.71 (13) | C14—C13—S2 | 110.76 (10) |
| C5—C4—N3 | 117.98 (14) | C14—C13—C2 | 131.50 (13) |
| C5—C4—C3 | 122.29 (15) | C13—C14—H14 | 124.3 |
| C4—C5—H5 | 120.6 | C13—C14—C15 | 111.45 (14) |
| C4—C5—C6 | 118.83 (16) | C15—C14—H14 | 124.3 |
| C6—C5—H5 | 120.6 | C14—C15—H15 | 123.1 |
| C5—C6—H6 | 119.1 | C16—C15—C14 | 113.81 (14) |
| C7—C6—C5 | 121.71 (15) | C16—C15—H15 | 123.1 |
| C7—C6—H6 | 119.1 | S2—C16—H16 | 124.0 |
| C6—C7—H7 | 120.0 | C15—C16—S2 | 112.01 (12) |
| C6—C7—C8 | 120.09 (17) | C15—C16—H16 | 124.0 |
| C8—C7—H7 | 120.0 | | |