Formation of 1-(thiazol-2-yl)-4,5-dihydropyrazoles from simple precursors: synthesis, spectroscopic characterization and the structures of an intermediate and two products

Ninganayaka Mahesha,a Hemmige S. Yathirajan,a* Holalagudu A. Nagma Banu,b Balakrishna Kalluraya,b Ravindranath S. Rathorec* and Christopher Glidewelld

aDepartment of Studies in Chemistry, University of Mysore, Manasagangotri, Mysuru-570 006, India, bDepartment of Studies in Chemistry, Mangalore University, Mangalagangotri, Mangalore-574199, India, cDepartment of Bioinformatics, School of Earth, Biological and Environmental Sciences, Central University of South Bihar, Gaya-824236, India, and dSchool of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, UK. *Correspondence e-mail: yathirajan@hotmail.com, ravindranath.rathore@gmail.com

Two new 1-(thiazol-2-yl)-4,5-dihydropyrazoles have been synthesized from simple precursors, and characterized both spectroscopically and structurally. In addition, two intermediates in the reaction pathway have been isolated and characterized, one of them structurally. The molecules of the intermediate (E)-1-(4-methoxyphenyl)-3-[4-(prop-2-ynyloxy)phenyl]prop-2-en-1-one, C$_{19}$H$_{16}$O$_{3}$ (I), are linked by a combination of C—H/π(arene) hydrogen bonds to form ribbons. The products (RS)-5-(4-methoxyphenyl)-1-(4-phenylthiazol-2-yl)-3-[4-(prop-2-ynyloxy)phenyl]-4,5-dihydro-1H-pyrazole, C$_{20}$H$_{21}$N$_{2}$O$_{3}$ (II), and (RS)-5-(4-methoxyphenyl)-1-[4-(4-methylphenyl)thiazol-2-yl]-3-[4-(prop-2-ynyloxy)phenyl]-4,5-dihydro-1H-pyrazole, C$_{22}$H$_{25}$N$_{3}$O$_{2}$S (III), are closely related – differing only by presence or absence of a methyl group at the arylthiazolyl substituent – and crystallize in an isomorphous setting. Both molecules contain an effectively planar dihydro-pyrazole ring, and possess an overall T-shaped structure, which is a characteristic of triaryl-substituted 4,5-dihydro-1-(thiazol-2-yl)pyrazole compounds. The crystal packing is characterized by intermolecular C—H⋯S and C—H⋯π(aryl/alkyne) interactions. A combination of two C—H⋯π(arene) hydrogen bonds links the product molecules into sheets.

1. Chemical context

Pyrazole derivatives are an important class of N-heterocyclic compounds with a wide spectrum of biological activities including antibacterial (Song et al., 2013; Yan et al., 2015), antifungal (Gondru et al., 2015), anti-inflammatory (El-Sayed et al., 2012; Kadambar et al., 2021), antimicrobial (Manju, Kalluraya & Kumar, 2019) and antitumor (Insuasty et al., 2010; Alam et al., 2016) activities. Thiazole derivatives similarly also exhibit a broad spectrum of biological activity, including anticancer (Bansal et al., 2020), anti-inflammatory (Sharma et al., 1998) and antimicrobial (Kalluraya et al., 2001) activity.

Accordingly, we have sought to combine pyrazole and thiazole pharmacophores in a single molecular skeleton and synthesized triaryl-substituted (thiazol-2-yl)pyrazole compounds (C3,C5-aryl substitutions on the pyrazole ring and C4-aryl substitution on the thiazole ring). We report here the synthesis of 1-(thiazolol-2-yl)-4,5-dihydropyrazoles from simple precursors. The reaction sequence is summarized in Fig. 1: a base-catalysed condensation reaction between
4-methoxybenzaldehyde (A) and a substituted acetophenone (B) yields the chalcone intermediate (I) (Shaibah et al., 2020). Compound (I) undergoes a cyclocondensation reaction with a thiosemicarbazide to provide thioamide intermediate (C), which in turn undergoes a further cyclocondensation reaction with a phenacyl bromide to give the thiazolyl-dihydropyrazoles (II) and (III) (Manju, Kalluraya, Asma et al., 2019).

Few triaryl-substituted (thiazol-2-yl)pyrazoles have previously been synthesized and characterized. The synthesis and crystal structure of a new thiazolyl-pyrazoline derivative bearing the 1,2,4-triazole moiety has been reported (CSD refcode BAKLOQ; Zeng et al., 2012). A new series of 1,3-thiazole integrated pyrazoline scaffolds have been synthesized and characterized (DADQIL, DADQEH; Salian et al., 2017). The synthesis, fluorescence, TGA and crystal structure of a thiazolyl-pyrazoline derived from chalcones has been described (JUNRAN; Suwunwong et al., 2015). In addition, the following crystal structures of related compounds have been reported: 2-[3-(4-bromophenyl)-5-(4-fluorophenyl)-4,5-dihydro-1H-pyrazol-1-yl]-4-phenyl-1,3-thiazole (IDOMOF; Abdel-Wahab et al., 2013c), 2-[5-(4-fluorophenyl)-3-(4-methylphenyl)-4,5-dihydro-1H-pyrazol-1-yl]-4-phenyl-1,3-thiazol (MEWQUC; Abdel-Wahab et al., 2013a), 2-[3-(4-chlorophenyl)-5-(4-fluorophenyl)-4,5-dihydro-1H-pyrazol-1-yl]-4-phenyl-1,3-thiazole (WIGQIO; Abdel-Wahab et al., 2013b), 2-[3-(4-chlorophenyl)-5-(4-fluorophenyl)-4,5-dihydro-1H-pyrazol-1-yl]-8H-indeno[1,2-d]thiazole (WOCFEC; El-Hiti et al., 2019) and 2-[3-(4-bromophenyl)-5-(4-fluorophenyl)-4,5-dihydro-1H-pyrazol-1-yl]-8H-indeno[1,2-d]thiazole (PUVVAG; Alotaibi et al., 2020).

The proposed synthetic route, as also applied to synthesize many of the aforementioned related compounds, was selected because in some cases, we have introduced mesoionic moieties like sydnone as a part of the triaryl. These sydnones are somewhat sensitive towards vigorous reaction conditions. Under the present conditions selected, the products are stable and the reactions gave reasonably good yields. The chosen synthetic routes of the reported compounds in this study are straightforward with limited steps and readily accessible, cheap starting materials, and yields are reasonably high (Nayak et al., 2013; Bansal et al., 2020). The biological activities of few of the related triaryl-substituted (thiazol-2-yl)pyrazole compounds have been reported in the literature, such as Salian et al. (2017) have demonstrated radical scavenging capacity owing to the destabilization of the radical formed during oxidation. In the present study, compounds (I)–(III) and the intermediate (C) have been characterized spectroscopically. Chalcone intermediate (I) (Fig. 2) and the di-
hydro(thiazolyl)pyrazole products (II) and (III) (Figs. 3 and 4) have also been characterized, and their structures will be described here.

2. Structural commentary

For the thiazolylpyrazole products (II) and (III), and for the intermediates (I) and (C) (Fig. 1), the \( ^{1}H \) NMR spectra contained all of the expected signals (Section 5). In particular, the spectra of each of (I), (II) and (III) contained signals from an ABX spin system arising from the H atoms bonded to atoms C4 and C5 (Figs. 2 and 3), consistent with the formation of a new 4,5-dihydropyrazole ring.

In the structure of the chalcone intermediate (I) (Fig. 2), the two aryl rings are both twisted away from the plane of the central spacer unit, atoms C11, C1, O1, C2, C3, C31 [maximum planar deviation of 0.033 (2) Å for C3 atom]. The dihedral angles between this spacer unit and the rings (C11–C16) and (C31–C36) are 21.48 (7) and 8.98 (7)°, respectively, while the dihedral angle between the (C11–C16) ring and the prop-2ynyloxy unit (O14, C17, C18, C19) is 73.48 (13)°. The molecule of (I) exhibits no internal symmetry and so is conformationally chiral, but the centrosymmetric space group confirms that equal numbers of the two conformational enantiomers are present.

Compounds (II) and (III), differing only in the presence or absence of a methyl group at the arylthiazolyl substituent, and are isomorphous and isostructural (Fig. 1 and Table 2). In the molecules of (II) and (III), there is a stereogenic centre at atom C5 and, for each, the reference molecule was selected as one having the R-configuration at atom C5. However, the space group confirms that both compounds have crystallized as racemic mixtures: this is as expected, as the synthesis of (II) and (III) involves no reagents that could plausibly induce enantioselectivity. In each of these compounds, the dihydro-pyrazole ring is effectively planar (Alex & Kumar, 2014). The maximum deviations from the mean planes through the ring atoms are 0.44 (3) Å for atom C4 in (II) and only 0.012 (2) Å for atom C3 in (III). The dihydro-pyrazole ring has been found to be effectively planar among triaryl-substituted (thiazol-2-yl)pyrazole compounds available in the literature (see Chemical context and Database survey for references).

In each of (I)–(III), the methoxy C atom is coplanar with the adjacent aryl ring [the maximum deviation of atom C37 in (I) and C57 in (II) and (III) from the respective planes are 0.003 (2), 0.529 (5) and 0.405 (7) Å, respectively).

Associated with this coplanarity, the values of the two exocyclic C—C—O angles, at atom C34 in (I) and at atom C54 in each of (II) and (III), differ by ca 10°, as typically found in planar alkoxyarenes (Seip & Seip, 1973; Ferguson et al., 1996; Kiran Kumar, Yathirajan, Foro et al., 2019; Kiran Kumar et al., 2020). Overall, both the molecules (II) and (III) adopt a T-shaped structure with the pyrazole C5-substituent anisyl units forming the blade. The remaining part of molecule, the thiazolyl-pyrazole ring and its substituents form a more or less planar structure, which constitutes the stock of the T-shape. The angle between the plane of the anisyl unit and the remaining part of molecule is 71.8 (1) and 75.3 (1)° in (II) and (III), respectively. Both molecules adopt a more or less similar conformation and a superimposed image of (II) and (III) is shown in Fig. 5.

3. Supramolecular features

The supramolecular assembly of the chalcone (I) depends upon two hydrogen-bond-like interactions, one each of the

![Figure 3](image-url)  
**Figure 3**  
The molecular structure of compound (II) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

![Figure 4](image-url)  
**Figure 4**  
The molecular structure of compound (III) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

![Figure 5](image-url)  
**Figure 5**  
Superimposed image of (II) (shown in green) and (III).
C—H⋅⋅⋅O and the C—H⋅⋅⋅π(arene) type (Table 1). The molecules of (I) are linked into a ribbon of centrosymmetric rings running parallel to the [010] direction (Fig. 6), in which (propynyloxy-CH₂) C₁⁷—H₁⁷B⋅⋅⋅O₁ (carbonyl) bonded to R²(18) (Etter, 1990; Etter et al., 1990; Bernstein et al., 1995) rings centred at (0, n, 0.5) alternate with rings built from (propynyloxy-alkyne) C₁⁹—H₁⁹⋅⋅⋅π (arene of anisyl) hydrogen bonds, which are centred at (0, n + 0.5, 0.5), where n represents an integer in each case. The C—H(alkyne)⋅⋅⋅π interaction has been examined by Holme et al. (2013). Another (propynyloxy-phenyl) C₁₂—H₁₂⋅⋅⋅π (arene of anisyl) interaction is also observed.

The structure of compound (II) and (III) contains two C—H⋅⋅⋅π(arene) hydrogen bonds, namely, (propynyloxy-alkyne) C₃⁹—H₃⁹⋅⋅⋅Cg₂ (arene of anisyl) and (anisyl-C arH) C₅⁶—H₅⁶⋅⋅⋅Cg₁(propynyloxy-phenyl). Together, the two interactions generate a sheet (Fig. 7) lying parallel to (010) in the domain 0 < y < 0.5. The interaction is augmented by a (propynyloxy-phenyl) C₃₅—H₃₅⋅⋅⋅S₁₁ interaction (Ghosh et al., 2020) in (III). In (II) too, there is a short H₃₅⋅⋅⋅S₁₁ contact of 2.96 Å; however, it is only 0.04 Å shorter than the sum of van der Waals radii of the corresponding atoms. A second

### Table 1
Hydrogen-bond parameters (Å, °).

| Compound | D—H⋅⋅⋅A | D—H | H⋅⋅⋅A | D⋅⋅⋅A | D—H⋅⋅⋅A |
|----------|--------|------|-------|------|--------|
| (I)      | C₁⁷—H₁⁷B⋅⋅⋅O₁ | 0.97 | 2.59  | 3.456(2) | 148   |
|          | C₁⁹—H₁⁹—Cg₁ | 0.93 | 2.73  | 3.660(2) | 177   |
|          | C₁₂—H₁₂—Cg₁ii | 0.93 | 2.89  | 3.5117(18) | 126   |
| (II)     | C₃⁹—H₃⁹—Cg₂iv | 0.93 | 2.59  | 3.365(5) | 141   |
|          | C₅⁶—H₅⁶—Cg₁v | 0.93 | 2.91  | 3.688(3) | 142   |
| (III)    | C₃⁹—H₃⁹—Cg₂iv | 0.93 | 2.93  | 3.802(5) | 156   |
|          | C₅⁶—H₅⁶—Cg₁v | 0.93 | 2.92  | 3.689(3) | 141   |
|          | C₃₅—H₃₅—S₁₁vi | 0.93 | 2.86  | 3.560(4) | 133   |

Symmetry codes: (i) −x, −y, 1 − z; (ii) −x, 1 − y, 1 − z; (iii) −1 + x, y, z; (iv) 1 + x, y, z; (v) −1 + x, 1 − y, −1 + z; (vi) 1 − x, 1 − y, 1 − z.
sheet of this type, related to the first by the action of the glide planes lies in the domain 0.5 < y < 1.0, but there are no direction-specific interactions between adjacent sheets. With the exception of this, there are no significant differences in the packing of (II) and (III).

In (III), a C5—H5 ⋅ ⋅ ⋅ π(alkyne) interaction, also referred as a T-shaped C—H ⋅ ⋅ ⋅ π interaction (McAdam et al., 2012) is observed, with the shortest H5 ⋅ ⋅ ⋅ C38’ [symmetry code: (i) −1/4 + x, −1/2 − y, 1/2 + z] distance being 2.74 Å and a C5—H5 ⋅ ⋅ ⋅ C38 angle of 159°. In (II), two such short contacts of the C—H ⋅ ⋅ ⋅ π(alkyne) type are observed, with H4 ⋅ ⋅ ⋅ C39’ and H5 ⋅ ⋅ ⋅ C38’ distances of 2.80 and 2.81 Å, respectively, which are only 0.10 and 0.09 Å shorter than the sum of corresponding van der Waals radii.

Additional short intramolecular C—H ⋅ ⋅ ⋅ O and C—H ⋅ ⋅ ⋅ N contacts are observed in (I)–(III). The packing is devoid of C(alkyne)—H contacts.

4. Database survey

We briefly compare the structures reported here with those of compounds (I) and (II) or 4-methylphenacyl bromide (0.5 g, 2.0 mmol) for (III) in ethanol (10 ml). This mixture was then heated under reflux for 8 h, after which time the reaction was judged from TLC to be complete. The mixture was poured onto crushed ice and the resulting solid intermediate (C) was collected by filtration and crystallized from a mixture of ethanol and N,N-dimethylformamide (3/2, v/v) (Shaibah et al., 2020). Yield 79%, m.p. 422–423 K. Analysis: found C 65.8, H 5.2, N 11.5%. IR (cm⁻¹) 3339 (NH₂), 2120 (alkyne). 1H NMR (DMSO-d₆) δ 3.09 (1H, dd, J = 17.5 Hz and 3.2 Hz) and 3.71 (1H, dd, J = 17.5 Hz and 11.5 Hz) (pyrazole CH₂), 3.69 (1H, t, J = 2.3 Hz, alkynic CH), 3.78 (3H, s, OMe), 4.52 (2H, d, J = 2.3 Hz, O-CH₂), 5.76 (1H, dd, J = 11.5 Hz and 3.2 Hz, pyrazole CH), 6.75 (2H, d, J = 8.8 Hz) and 7.02 (2H, d, J = 8.8 Hz) (–C₆H₄–), 7.13 (2H, d, J = 8.1 Hz) and 7.64 (2H, d, J = 8.1 Hz) (–C₆H₄–).

Mixtures of this intermediate (1.00 g, 2.0 mmol) and either phenacyl bromide (0.5 g, 2.0 mmol) for (II) or 4-methylphenacyl bromide (0.58 g, 2.0 mmol) for (III) in ethanol (20 ml) were heated under reflux for 1 h. The mixtures were then allowed to cool to ambient temperature and the resulting solid products were collected by filtration and then crystallized from mixtures of ethanol and N,N-dimethylformamide (3/2, v/v) (Manju, Kalluraya, Asma et al., 2019). Compound (II), yield 88%, m.p. 435–438 K. IR (cm⁻¹) 2198 (alkyne), 1618 (C==N), 1600 (C=C). 1H NMR (CDCl₃) δ 2.41 (1H, t, J = 1.8 Hz), H-39), 3.46 (1H, dd, J = 16.9 Hz and 5.2 Hz) and 4.10 (1H, dd, J = 16.9 Hz and 12.4 Hz) (pyrazole CH₂), 3.90 (3H, s, OMe), 4.56 (2H, d, J = 1.8 Hz, O-CH₂), 5.43 (1H, dd, J = 12.4 Hz and 5.2 Hz, pyrazole CH), 6.95 (2H, d, J = 8.8 Hz) and 7.20 (2H, d, J = 8.8 Hz, –C₆H₄–) 7.26–7.63 (9H, m, arol), 7.90 (1H, s, H-15). Compound (III), yield 82%, m.p. 453–455 K. IR (cm⁻¹) 2210 (alkyne), 1620 (C==N), 1605 (C=C). 1H NMR (CDCl₃) δ 2.32 (3H, s, C—CH₃), 2.54 (1H, t, J = 2.0 Hz), H-39), 3.28 (1H, dd, J = 17.0 Hz and 6.4 Hz) and 3.84 (1H, dd, J = 17.0 Hz and 11.8 Hz) (pyrazole CH₂), 3.77 (3H, s, OMe), 4.75 (2H, d, J = 2.0 Hz, O—CH₂), 5.69 (1H, dd, J = 11.8 Hz and 5.4 Hz, pyrazole CH), 6.86 (2H, d, J = 8.8 Hz), 7.01 (2H, d, J = 8.8 Hz), 7.11 (2H, d, J = 8.8 Hz), 7.34 (2H, d, J = 8.8 Hz), 7.57 (2H, d, J = 8.8 Hz) and 7.72 (2H, d, J = 8.8 Hz) (3 × –C₆H₄–), 8.00 (1H, s, H-15). Crystals of compounds (I)–(III) that were suitable for single-crystal X-ray diffraction were selected directly from the prepared samples.

6. Refinement

Crystal data, data collection and refinement details are summarized in Table 2. A number of low-angle reflections,
Table 2
Experimental details.

|                | (I)                  | (II)                  | (III)                 |
|----------------|----------------------|-----------------------|-----------------------|
| Crystal data   |                      |                       |                       |
| Chemical formula | C₁₉H₁₆O₃            | C₂₉H₂₃N₃O₂S          | C₂₉H₂₃N₃O₂S          |
| M₁             | 292.32               | 465.55                | 479.58                |
| Crystal system, space group | Triclinic, PT | Monoclinic, Cc | Monoclinic, Cc |
| Temperature (K) | 297                  | 297                   | 297                   |
| a, b, c (Å)    | 8.6450 (15), 9.9526 (16), 10.0677 (18) | 15.7724 (12), 17.6042 (15), 9.3589 (9) | 16.5634 (17), 17.7250 (19), 9.4032 (11) |
| α, β, γ (°)    | 79.039 (6), 70.124 (6), 68.366 (5) | 90, 114.259 (3), 90 | 90, 116.401 (3), 90 |
| V (Å³)         | 755.0 (2)            | 2369.1 (4)           | 2472.7 (5)           |
| Z              | 2                    | 4                     | 4                     |
| Radiation type | Mo Kα                | Mo Kα                 | Mo Kα                |
| μ (mm⁻¹)       | 0.09                 | 0.17                  | 0.16                  |
| Crystal size (mm) | 0.16 × 0.15 × 0.12   | 0.20 × 0.18 × 0.15    | 0.18 × 0.16 × 0.15   |

Data collection

|                |                      |                       |                       |
|----------------|----------------------|-----------------------|-----------------------|
| Diffractometer | Bruker D8 Venture    | Bruker D8 Venture     | Bruker D8 Venture     |
| Absorption correction | Multi-scan (SADABS; Bruker, 2016) | Multi-scan (SADABS; Bruker, 2016) | Multi-scan (SADABS; Bruker, 2016) |
| Tmin, Tmax     | 0.066, 0.096         | 0.949, 0.975          | 0.949, 0.976          |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 45325, 5029, 3072 | 46650, 6087, 4331 | 40416, 5578, 3802 |
| Rint           | 0.066                | 0.062                 | 0.058                 |
| (sin θ/λ)max (Å⁻¹) | 0.735               | 0.692                 | 0.652                 |

Refinement

|                |                      |                       |                       |
|----------------|----------------------|-----------------------|-----------------------|
| R[F² > 2σ(F²)], wR(F²), S | 0.053, 0.162, 1.01 | 0.040, 0.103, 1.05 | 0.042, 0.121, 1.08 |
| No. of reflections | 5029                | 6087                  | 5578                  |
| No. of parameters | 200                 | 308                   | 318                   |
| No. of restraints | 0                   | 2                     | 2                     |
| H-atom treatment | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained |
| Δρmax, Δρmin (e Å⁻³) | 0.36, −0.20         | 0.12, −0.16           | 0.15, −0.17           |
| Absolute structure | —                   | Flack x determined using 1715 quotients [(I')−(I')][(I')+(I')] (Parsons et al., 2013) |
| Absolute structure parameter | 0.00 (3)            | —                     | −0.01 (3)             |

Absolute structure parameter –

Computer programs: APEX3 (Bruker, 2016), APEX3, SAINT and XPREP (Bruker, 2016), SHELXT2014/5 (Sheldrick, 2015a), SHELXL2014 (Sheldrick, 2015b) and PLATON (Spek, 2020).

which had been attenuated by the beam stop, were omitted from the data sets: for (I), (100), (011), (011) and (111); for (II), (111), (111) and (200); and for (III), (111) and (200). All H atoms were located in difference maps and they were then treated as riding atoms in geometrically idealized positions with C—H distances of 0.98 Å (saturated aliphatic C—H), 0.97 Å (CH₃), 0.96 Å (CH₂) or 0.93 Å for all other H atoms, and with Uiso(H) = kUeq(C), where k = 1.5 for the methyl groups, which were permitted to rotate but not to tilt, and k = 1.2 for all other H atoms. For compounds (II) and (III), the correct orientation of the structures with respect to the polar axis directions was established by means of the Flack x parameter (Flack, 1983), calculated using quotients of the type (I’)(−I’)(I’)+(I’) (Parsons et al., 2013). For (II), x = 0.00 (3), calculated using 1715 quotients, and for (III) x = −0.01 (3), calculated using 1613 quotients.

Acknowledgements

NM thanks the University of Mysore for research facilities. RSR thanks the DST and the SAIF, IIT Madras, for access to their X-ray crystallography facilities.

Funding information

HSY is grateful to the UGC, New Delhi, for the award of a BSR Faculty Fellowship for three years.

References

Abdel-Wahab, B. F., Mohamed, H. A., Ng, S. W. & Tiekink, E. R. T. (2013a). Acta Cryst. E69, o392–o393.
Abdel-Wahab, B. F., Mohamed, H. A., Ng, S. W. & Tiekink, E. R. T. (2013c). Acta Cryst. E69, o735.
Abdel-Wahab, B. F., Ng, S. W. & Tiekink, E. R. T. (2013b). Acta Cryst. E69, o576.
Alam, R., Wahi, D., Singh, R., Sinha, D., Tandon, V., Grover, A. & Rahisuddin (2016). Bioorg. Chem. 69, 77–90.
Alex, J. M. & Kumar, R. (2014). J. Enzyme Inhib. Med. Chem. 29, 427–442.
Alotaibi, A. A., Abdel-Wahab, B. F., Hegazy, A. S., Kariuki, B. M. & El-Hiti, G. A. (2020). Z. Krist. New Cryst. Struct. 235, 897–899.
Banasi, K. K., Bhardwaj, J. K., Saraf, P., Thakur, V. K. & Sharma, P. C. (2020). Materials Today Chemistry, 17, 100335.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). Angew. Chem. Int. Ed. Engl. 34, 1555–1573.
Bruker (2016). APEX3, SAINT and XPREP. Bruker AXS Inc., Madison, Wisconsin, USA.
El-Hiti, G. A., Abdel-Wahab, B. F., Alqahtani, A., Hegazy, A. S. & Kariuki, B. M. (2019). IUCrData, 4, x190218.

Jerry P. Jasinski tribute

890 Mahesha et al. • C₁₉H₁₆O₃, C₂₉H₂₃N₃O₂S and C₂₉H₂₃N₃O₂S

Acta Cryst. (2021). E77, 975–981
Formation of 1-(thiazol-2-yl)-4,5-dihydropyrazoles from simple precursors: synthesis, spectroscopic characterization and the structures of an intermediate and two products

Ninganayaka Mahesha, Hemmige S. Yathirajan, Holalagudu A. Nagma Banu, Balakrishna Kalluraya, Ravindranath S. Rathore and Christopher Glidewell

Computing details

For all structures, data collection: APEX3 (Bruker, 2016); cell refinement: APEX3 and SAINT (Bruker, 2016); data reduction: SAINT and XPREP (Bruker, 2016); program(s) used to solve structure: SHELXT2014/5 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2014 (Sheldrick, 2015b); molecular graphics: PLATON (Spek, 2020); software used to prepare material for publication: SHELXL2014 (Sheldrick, 2015b) and PLATON (Spek, 2020).

(E)-1-(4-Methoxyphenyl)-3-[4-(prop-2-ynyloxy)phenyl]prop-2-en-1-one (I)

Crystal data

\[\text{C}_{19}\text{H}_{16}\text{O}_{3}\]  
\[M_r = 292.32\]  
Triclinic, \(P\bar{1}\)  
\(a = 8.6430\) (15) Å  
\(b = 9.9526\) (16) Å  
\(c = 10.0677\) (18) Å  
\(\alpha = 79.039\) (6)\(^\circ\)  
\(\beta = 70.124\) (6)\(^\circ\)  
\(\gamma = 68.366\) (5)\(^\circ\)  
\(V = 755.0\) (2) Å\(^3\)  

\(Z = 2\)  
\(F(000) = 308\)  
\(D_x = 1.286\) Mg m\(^{-3}\)  
Mo \(K\alpha\) radiation, \(\lambda = 0.71073\) Å  
Cell parameters from 5248 reflections  
\(\theta = 2.7\text{–}32.5\text{\(^\circ\)}\)  
\(\mu = 0.09\) mm\(^{-1}\)  
\(T = 297\) K  
Block, colourless  
0.16 × 0.15 × 0.12 mm

Data collection

Bruker D8 Venture diffractometer  
Radiation source: INCOATEC high brilliance microfocus sealed tube  
Multilayer mirror monochromator  
\(\phi\) and \(\omega\) scans  
Absorption correction: multi-scan (SADABS; Bruker, 2016)  
\(T_{\text{min}} = 0.966, T_{\text{max}} = 0.969\)  
45325 measured reflections  
5029 independent reflections  
3072 reflections with \(I > 2\sigma(I)\)  
\(R_{\text{int}} = 0.066\)  
\(\theta_{\text{max}} = 31.5\text{\(^\circ\)}, \theta_{\text{min}} = 2.9\text{\(^\circ\)}\)  
\(h = -12\rightarrow 12\)  
\(k = -14\rightarrow 14\)  
\(l = -14\rightarrow 14\)
Refinement

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.162$
$S = 1.01$
5029 reflections
200 parameters
0 restraints

Primary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/\sigma^2(F_o^2) + (0.0578P)^2 + 0.2039P$

$\Delta/\sigma)_{\text{max}} < 0.001$
$\Delta\rho_{\text{max}} = 0.36 \text{ e Å}^{-3}$
$\Delta\rho_{\text{min}} = -0.20 \text{ e Å}^{-3}$

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{Å}^2$)

|     | x          | y          | z          | $U_{eq}$  |
|-----|------------|------------|------------|-----------|
| C1  | 0.35447 (18)| 0.15799 (16)| 0.42144 (16)| 0.0472 (3) |
| O1  | 0.36622 (16)| 0.11332 (14)| 0.31105 (12)| 0.0652 (3) |
| C2  | 0.47763 (19)| 0.22583 (17)| 0.42604 (16)| 0.0498 (3) |
| H2  | 0.4598      | 0.2643      | 0.5094      | 0.060*     |
| C3  | 0.61295 (19)| 0.23433 (16)| 0.31606 (16)| 0.0480 (3) |
| H3  | 0.6285      | 0.1928      | 0.2351      | 0.058*     |
| C11 | 0.21298 (18)| 0.14699 (14)| 0.55306 (15)| 0.0436 (3) |
| C12 | 0.06427 (19)| 0.13056 (16)| 0.54368 (16)| 0.0469 (3) |
| H12 | 0.0557      | 0.1266      | 0.4550      | 0.056*     |
| C13 | −0.07138 (19)| 0.11992 (16)| 0.66299 (16)| 0.0485 (3) |
| H13 | −0.1707     | 0.1106      | 0.6545      | 0.058*     |
| C14 | −0.05751 (18)| 0.12334 (15)| 0.79527 (15)| 0.0456 (3) |
| C15 | 0.0910 (2)  | 0.13783 (17)| 0.80677 (16)| 0.0514 (3) |
| H15 | 0.1007      | 0.1390      | 0.8957      | 0.062*     |
| C16 | 0.22343 (19)| 0.15049 (16)| 0.68757 (16)| 0.0496 (3) |
| H16 | 0.3216      | 0.1616      | 0.6965      | 0.060*     |
| O14 | −0.18261 (15)| 0.11348 (14)| 0.92107 (11)| 0.0599 (3) |
| C17 | −0.3326 (2) | 0.0850 (2)  | 0.91866 (19)| 0.0601 (4) |
| H17A| −0.3898     | 0.0520      | 1.0133      | 0.072*     |
| H17B| −0.2950     | 0.0076      | 0.8573      | 0.072*     |
| C18 | −0.4578 (2) | 0.2122 (2)  | 0.86912 (17)| 0.0562 (4) |
| C19 | −0.5601 (3) | 0.3130 (2)  | 0.8308 (2)  | 0.0709 (5) |
| H19 | −0.6414     | 0.3932      | 0.8004      | 0.085*     |
| C31 | 0.74006 (18)| 0.30161 (15)| 0.30821 (14)| 0.0439 (3) |
| C32 | 0.72813 (19)| 0.37748 (16)| 0.41724 (15)| 0.0485 (3) |
| H32 | 0.6349      | 0.3862      | 0.4995      | 0.058*     |
| C33 | 0.8511 (2)  | 0.43923 (17)| 0.40517 (16)| 0.0513 (3) |
| H33 | 0.8398      | 0.4896      | 0.4787      | 0.062*     |
| C34 | 0.9922 (2)  | 0.42693 (16)| 0.28368 (16)| 0.0485 (3) |
### Atomic displacement parameters (Å²)

|   | U¹¹ | U¹² | U¹³ | U²² | U²³ | U³³ |
|---|-----|-----|-----|-----|-----|-----|
| C1 | 0.0429 (7) | 0.0456 (7) | 0.0533 (8) | -0.0111 (6) | -0.0155 (6) | -0.0091 (6) |
| O1 | 0.0602 (7) | 0.0829 (8) | 0.0585 (7) | -0.0276 (6) | -0.0111 (5) | -0.0229 (6) |
| C2 | 0.0463 (8) | 0.0541 (8) | 0.0498 (8) | -0.0162 (6) | -0.0111 (6) | -0.0119 (6) |
| C3 | 0.0460 (7) | 0.0493 (8) | 0.0485 (8) | -0.0130 (6) | -0.0136 (6) | -0.0097 (6) |
| C11 | 0.0419 (7) | 0.0390 (6) | 0.0507 (8) | -0.0105 (5) | -0.0160 (6) | -0.0067 (5) |
| C12 | 0.0489 (8) | 0.0475 (7) | 0.0503 (8) | -0.0157 (6) | -0.0201 (6) | -0.0078 (6) |
| C13 | 0.0458 (7) | 0.0528 (8) | 0.0556 (8) | -0.0203 (6) | -0.0204 (6) | -0.0055 (6) |
| C14 | 0.0444 (7) | 0.0463 (7) | 0.0482 (7) | -0.0164 (6) | -0.0167 (6) | 0.0004 (6) |
| C15 | 0.0502 (8) | 0.0626 (9) | 0.0472 (8) | -0.0186 (7) | -0.0228 (6) | -0.0017 (6) |
| C16 | 0.0435 (7) | 0.0559 (8) | 0.0561 (8) | -0.0172 (6) | -0.0212 (6) | -0.0055 (6) |
| O14 | 0.0540 (6) | 0.0838 (8) | 0.0505 (8) | -0.0341 (6) | -0.0190 (5) | 0.0056 (5) |
| C17 | 0.0565 (9) | 0.0690 (10) | 0.0619 (10) | -0.0341 (8) | -0.0172 (7) | 0.0058 (8) |
| C18 | 0.0520 (9) | 0.0707 (10) | 0.0522 (8) | -0.0287 (8) | -0.0116 (7) | -0.0086 (7) |
| C19 | 0.0636 (11) | 0.0788 (12) | 0.0701 (12) | -0.0172 (9) | -0.0236 (9) | -0.0106 (9) |
| C31 | 0.0413 (7) | 0.0449 (7) | 0.0423 (7) | -0.0104 (5) | -0.0111 (5) | -0.0062 (5) |
| C32 | 0.0422 (7) | 0.0549 (8) | 0.0428 (7) | -0.0098 (6) | -0.0088 (6) | -0.0106 (6) |
| C33 | 0.0527 (8) | 0.0546 (8) | 0.0482 (8) | -0.0136 (7) | -0.0162 (6) | -0.0136 (6) |
| C34 | 0.0492 (8) | 0.0474 (7) | 0.0520 (8) | -0.0160 (6) | -0.0183 (6) | -0.0043 (6) |
| C35 | 0.0518 (8) | 0.0662 (10) | 0.0451 (8) | -0.0241 (7) | -0.0032 (6) | -0.0101 (7) |
| C36 | 0.0550 (9) | 0.0632 (9) | 0.0442 (8) | -0.0224 (7) | -0.0078 (6) | -0.0152 (6) |
| O34 | 0.0631 (7) | 0.0746 (8) | 0.0666 (7) | -0.0335 (6) | -0.0154 (6) | -0.0131 (6) |
| C37 | 0.0687 (12) | 0.0856 (13) | 0.0734 (12) | -0.0436 (10) | -0.0164 (9) | 0.0015 (10) |

### Geometric parameters (Å, °)

|   | C1—O1 | C1—C2 | C11—C12 | C1—H17A | C17—H17A |
|---|-------|-------|----------|---------|---------|
| C1—C2 | 1.2332 (18) | 1.472 (2) | 1.485 (2) | 1.326 (2) | 0.9300 |
| C11—C12 | 1.3896 (19) | 1.395 (2) | 1.384 (2) | 1.384 (2) | 1.390 (2) |
| C3—H3 | 0.9300 | 0.9300 | 0.9300 | 0.9300 | 0.9300 |

---

Acta Cryst. (2021). E77, 975-981
| Bond  | Distance (Å) | Bond  | Distance (Å) | Bond  | Distance (Å) |
|-------|--------------|-------|--------------|-------|--------------|
| C12—H12 | 0.9300 | C34—O34 | 1.3594 (18) |
| C13—C14 | 1.385 (2) | C34—C35 | 1.384 (2) |
| C13—H13 | 0.9300 | C35—C36 | 1.385 (2) |
| C14—O14 | 1.3721 (17) | C35—H35 | 0.9300 |
| C14—C15 | 1.387 (2) | C36—H36 | 0.9300 |
| C15—C16 | 1.372 (2) | O34—C37 | 1.419 (2) |
| C15—H15 | 0.9300 | C37—H37A | 0.9600 |
| C16—H16 | 0.9300 | C37—H37B | 0.9600 |
| O14—C17 | 1.4341 (19) | C37—H37C | 0.9600 |
| C17—C18 | 1.462 (2) |          |              |
Crystal data

C28H23N3O2S

Monoclinic, Cc

a = 15.7724 (12) Å
b = 17.6042 (15) Å
c = 9.3589 (9) Å
β = 114.259 (3)°
V = 2369.1 (4) Å³
Z = 4

Data collection

Bruker D8 Venture diffractometer
Radiation source: INCOATEC high brilliance microfocus sealed tube
Multilayer mirror monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
Tmin = 0.949, Tmax = 0.975

Refinement

Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.040
wR(F²) = 0.103
S = 1.05
6087 reflections
308 parameters
2 restraints
Primary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
\( w = 1/[\sigma^2(F_o^2) + (0.0465P)^2 + 0.3024P] \)
where \( P = (F_o^2 + 2F_c^2)/3 \)
\((\Delta/\sigma)_{\text{max}} < 0.001\)
\( \Delta \rho_{\text{max}} = 0.12 \text{ e} \AA^{-3} \)
\( \Delta \rho_{\text{min}} = -0.16 \text{ e} \AA^{-3} \)
\( \Delta \rho_{\text{max}} = 0.12 \text{ e} \AA^{-3} \)
Absolute structure: Flack \( x \) determined using 1715 quotients \( [(I^+) - (I^-)]/[(I^+) + (I^-)] \) (Parsons et al., 2013)
Absolute structure parameter: 0.00 (3)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\( \AA^2 \))

|   | x     | y     | z     | U_{iso}/U_{eq} |
|---|-------|-------|-------|----------------|
| N1| 0.37305 (18) | 0.29886 (13) | 0.5843 (3) | 0.0698 (7) |
| N2| 0.44590 (16) | 0.30871 (13) | 0.5400 (3) | 0.0615 (6) |
| C3| 0.50583 (18) | 0.25567 (14) | 0.6044 (3) | 0.0537 (6) |
| C4| 0.48110 (19) | 0.20499 (17) | 0.7111 (4) | 0.0657 (7) |
| H4A| 0.5241 | 0.2118 | 0.8197 | 0.079* |
| H4B| 0.4809 | 0.1520 | 0.6828 | 0.079* |
| C5| 0.38250 (19) | 0.23200 (15) | 0.6834 (3) | 0.0597 (6) |
| H5| 0.3811 | 0.2475 | 0.7830 | 0.072* |
| S11| 0.31763 (7) | 0.43908 (4) | 0.46457 (10) | 0.0756 (2) |
| C12| 0.3097 (2) | 0.35556 (14) | 0.5592 (3) | 0.0619 (7) |
| N13| 0.24061 (17) | 0.35145 (12) | 0.6003 (3) | 0.0640 (6) |
| C14| 0.1866 (2) | 0.41709 (15) | 0.5544 (3) | 0.0639 (8) |
| C15| 0.2173 (3) | 0.46935 (17) | 0.4794 (4) | 0.0760 (9) |
| H15| 0.1880 | 0.5155 | 0.4411 | 0.091* |
| C141| 0.1032 (2) | 0.42337 (16) | 0.5869 (4) | 0.0668 (8) |
| C142| 0.0831 (2) | 0.36891 (19) | 0.6757 (4) | 0.0764 (9) |
| H142| 0.1241 | 0.3287 | 0.7180 | 0.092* |
| C143| 0.0035 (3) | 0.3734 (2) | 0.7022 (5) | 0.0927 (11) |
| H143| −0.0088 | 0.3358 | 0.7610 | 0.111* |
| C144| −0.0578 (3) | 0.4323 (3) | 0.6432 (4) | 0.0912 (11) |
| H144| −0.1114 | 0.4348 | 0.6614 | 0.109* |
| C145| −0.0390 (3) | 0.4872 (2) | 0.5573 (5) | 0.0928 (13) |
| H145| −0.0799 | 0.5277 | 0.5179 | 0.111* |
| C146| 0.0401 (3) | 0.48317 (19) | 0.5284 (4) | 0.0812 (10) |
| H146| 0.0514 | 0.5209 | 0.4689 | 0.097* |
| C31| 0.59091 (18) | 0.24801 (14) | 0.5805 (3) | 0.0515 (6) |
| C32| 0.6202 (2) | 0.30393 (16) | 0.5045 (3) | 0.0601 (7) |
| H32| 0.5834 | 0.3467 | 0.4649 | 0.072* |
| C33| 0.7017 (2) | 0.29701 (17) | 0.4871 (3) | 0.0646 (7) |
| H33| 0.7203 | 0.3351 | 0.4375 | 0.078* |
| C34| 0.75702 (19) | 0.23232 (16) | 0.5444 (3) | 0.0576 (6) |
| C35| 0.7292 (2) | 0.17629 (15) | 0.6179 (3) | 0.0614 (7) |
### Supporting Information

| Atomic displacement parameters ($\AA^2$) |
|----------------------------------------|
| $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
| N1       | 0.0646 (14) | 0.0476 (12) | 0.0985 (18) | 0.0086 (11) | 0.0350 (13) | 0.0120 (12) |
| N2       | 0.0616 (14) | 0.0458 (12) | 0.0734 (15) | 0.0001 (10) | 0.0240 (11) | 0.0015 (10) |
| C3       | 0.0566 (15) | 0.0444 (12) | 0.0528 (14) | $-0.0031$ (11) | 0.0152 (11) | $-0.0044$ (11) |
| C4       | 0.0589 (16) | 0.0601 (16) | 0.0731 (18) | 0.0057 (13) | 0.0221 (14) | 0.0128 (14) |
| C5       | 0.0607 (16) | 0.0516 (14) | 0.0662 (17) | 0.0071 (12) | 0.0255 (13) | 0.0048 (12) |
| S11      | 0.0889 (9) | 0.0434 (3) | 0.0841 (5) | $-0.0019$ (4) | 0.0250 (4) | 0.0007 (4) |
| C12      | 0.0657 (17) | 0.0396 (12) | 0.0672 (18) | 0.0029 (12) | 0.0140 (14) | $-0.0030$ (12) |
| N13      | 0.0640 (15) | 0.0442 (12) | 0.0744 (16) | 0.0111 (10) | 0.0189 (12) | 0.0000 (10) |
| C14      | 0.0722 (18) | 0.0423 (13) | 0.0574 (16) | 0.0104 (12) | 0.0066 (13) | $-0.0089$ (11) |
| C15      | 0.089 (2) | 0.0418 (14) | 0.082 (2) | 0.0108 (14) | 0.0193 (17) | $-0.0013$ (14) |
| C141     | 0.0698 (18) | 0.0490 (15) | 0.0601 (16) | 0.0152 (13) | 0.0050 (13) | $-0.0135$ (12) |
| C142     | 0.085 (2) | 0.0637 (18) | 0.0719 (19) | 0.0242 (15) | 0.0232 (17) | $-0.0024$ (15) |
| C143     | 0.101 (3) | 0.091 (3) | 0.084 (2) | 0.020 (2) | 0.036 (2) | $-0.008$ (2) |
| C144     | 0.086 (2) | 0.096 (3) | 0.081 (2) | 0.022 (2) | 0.0222 (19) | $-0.024$ (2) |
| C145     | 0.081 (2) | 0.076 (2) | 0.091 (3) | 0.0353 (19) | 0.0053 (19) | $-0.021$ (2) |
| C146     | 0.083 (2) | 0.0587 (17) | 0.078 (2) | 0.0239 (16) | 0.0081 (17) | $-0.0047$ (15) |
| C31      | 0.0580 (15) | 0.0446 (12) | 0.0453 (13) | $-0.0020$ (10) | 0.0145 (10) | $-0.0046$ (10) |
| C32      | 0.0661 (17) | 0.0496 (14) | 0.0605 (16) | 0.0088 (12) | 0.0219 (13) | 0.0107 (12) |
| C33      | 0.0712 (19) | 0.0587 (16) | 0.0682 (18) | 0.0069 (13) | 0.0330 (15) | 0.0166 (13) |
| C34     | 0.0592 (16) | 0.0570 (15) | 0.0546 (15) | 0.0053 (12) | 0.0213 (12) | 0.0001 (12) |
| C35     | 0.0700 (18) | 0.0491 (14) | 0.0617 (16) | 0.0112 (12) | 0.0236 (13) | 0.0067 (12) |
| C36     | 0.0669 (17) | 0.0441 (13) | 0.0612 (16) | 0.0011 (12) | 0.0235 (13) | 0.0039 (11) |
| O34     | 0.0743 (14) | 0.0711 (13) | 0.0813 (14) | 0.0183 (11) | 0.0401 (11) | 0.0170 (10) |
| C37     | 0.086 (2)   | 0.076 (2)   | 0.114 (3)   | 0.0243 (18) | 0.049 (2)   | 0.025 (2)   |
| C38     | 0.079 (2)   | 0.075 (2)   | 0.087 (2)   | 0.0260 (17) | 0.0390 (19) | 0.0087 (16) |
| C39     | 0.086 (3)   | 0.098 (3)   | 0.105 (3)   | 0.037 (2)   | 0.047 (2)   | 0.008 (2)   |
| C51     | 0.0518 (13) | 0.0479 (12) | 0.0539 (13) | 0.0118 (13) | 0.0221 (12) | 0.0191 (12) |
| C52     | 0.0574 (15) | 0.0658 (16) | 0.0539 (14) | 0.0118 (13) | 0.0221 (12) | 0.0191 (12) |
| C53     | 0.0679 (17) | 0.0558 (16) | 0.0735 (19) | 0.0105 (13) | 0.0309 (15) | 0.0275 (14) |
| C54     | 0.0661 (17) | 0.0415 (13) | 0.079 (2)   | 0.0066 (12) | 0.0284 (15) | 0.0074 (12) |
| C55     | 0.0788 (19) | 0.0509 (14) | 0.0501 (14) | 0.0075 (13) | 0.0199 (13) | 0.0026 (12) |
| C56     | 0.0750 (18) | 0.0475 (14) | 0.0550 (15) | 0.0093 (12) | 0.0313 (13) | 0.0121 (11) |
| O54     | 0.0909 (17) | 0.0512 (12) | 0.120 (2)   | −0.0097 (11)| 0.0182 (15) | 0.0105 (12) |
| C57     | 0.094 (3)   | 0.077 (2)   | 0.115 (3)   | −0.020 (2)  | 0.013 (2)   | −0.011 (2)  |

**Geometric parameters (Å, °)**

|                  |               |               |               |               |               |               |
|------------------|---------------|---------------|---------------|---------------|---------------|---------------|
| N1—C12           | 1.363 (4)     |               |               |               |               |               |
| N1—N2            | 1.383 (3)     |               |               |               |               | 0.9300        |
| N1—C5            | 1.468 (4)     |               |               |               |               | 1.401 (4)     |
| N2—C3            | 1.289 (4)     |               |               |               |               | 0.9300        |
| C3—C31           | 1.455 (4)     |               |               |               |               | 1.372 (3)     |
| C3—C4            | 1.505 (4)     |               |               |               |               | 1.373 (4)     |
| C4—C5            | 1.543 (4)     |               |               |               |               | 1.378 (4)     |
| C4—H4A           | 0.9700        |               |               |               |               | 0.9300        |
| C4—H4B           | 0.9700        |               |               |               |               | 0.9300        |
| C5—C51           | 1.513 (4)     |               |               |               |               | 1.430 (4)     |
| C5—H5            | 0.9800        |               |               |               |               | 1.443 (5)     |
| S11—C15          | 1.729 (4)     |               |               |               |               | 0.9700        |
| S11—C12          | 1.747 (3)     |               |               |               |               | 0.9700        |
| C12—N13          | 1.298 (4)     |               |               |               |               | 1.162 (5)     |
| N13—C14          | 1.395 (3)     |               |               |               |               | 0.9300        |
| C14—C15          | 1.361 (5)     |               |               |               |               | 1.375 (4)     |
| C14—C141         | 1.471 (5)     |               |               |               |               | 1.393 (4)     |
| C15—H15          | 0.9300        |               |               |               |               | 1.367 (4)     |
| C141—C142        | 1.388 (5)     |               |               |               |               | 0.9300        |
| C141—C146        | 1.397 (4)     |               |               |               |               | 1.385 (4)     |
| C142—C143        | 1.379 (5)     |               |               |               |               | 0.9300        |
| C142—H142        | 0.9300        |               |               |               |               | 1.371 (4)     |
| C143—C144        | 1.370 (5)     |               |               |               |               | 1.374 (4)     |
| C143—H143        | 0.9300        |               |               |               |               | 1.384 (4)     |
| C144—C145        | 1.365 (6)     |               |               |               |               | 0.9300        |
| C144—H144        | 0.9300        |               |               |               |               | 0.9300        |
| C145—C146        | 1.383 (6)     |               |               |               |               | 1.412 (5)     |
| C145—H145        | 0.9300        |               |               |               |               | 0.9600        |
| C146—H146        | 0.9300        |               |               |               |               | 0.9600        |
| C31—C36          | 1.396 (4)     |               |               |               |               | 0.9600        |
C31—C32 1.400 (4)

| Bond                  | Length (Å) | Estimated Standard Deviation (Å) |
|-----------------------|------------|----------------------------------|
| C12—N1—N2            | 119.8 (2)  |                                   |
| C12—N1—C5            | 125.0 (3)  |                                   |
| N2—N1—C5             | 114.1 (2)  |                                   |
| C3—N2—N1             | 108.0 (2)  |                                   |
| N2—C3—C31            | 122.7 (2)  |                                   |
| N2—C3—C4             | 113.6 (2)  |                                   |
| C31—C3—C4            | 123.7 (2)  |                                   |
| C3—C4—C5             | 102.9 (2)  |                                   |
| C3—C4—H4A            | 111.2      |                                   |
| C5—C4—H4A            | 111.2      |                                   |
| N1—C5—C51            | 116.2      |                                   |
| N1—C5—H5             | 109.9      |                                   |
| C15—S11—C12          | 87.71 (16) |                                   |
| N13—C12—S11          | 123.6 (3)  |                                   |
| C12—N13—C14          | 110.1 (3)  |                                   |
| C15—C14—N13          | 114.7 (3)  |                                   |
| C15—C14—C141         | 126.4 (3)  |                                   |
| N13—C14—C141         | 118.9 (3)  |                                   |
| C14—C15—S11          | 111.4 (2)  |                                   |
| C14—C15—H15          | 124.3      |                                   |
| S11—C15—H15          | 124.3      |                                   |
| C142—C141—C146       | 117.0 (4)  |                                   |
| C142—C141—C14        | 121.0 (3)  |                                   |
| C146—C141—C14        | 121.9 (3)  |                                   |
| C143—C142—C141       | 121.1 (3)  |                                   |
| C143—C142—H142       | 119.4      |                                   |
| C141—C142—H142       | 119.4      |                                   |
| C144—C143—C142       | 120.0 (4)  |                                   |
| C144—C143—H143       | 119.5      |                                   |
| C142—C143—H143       | 119.5      |                                   |
| C145—C144—C143       | 119.1 (4)  |                                   |
| C145—C144—H144       | 120.5      |                                   |
| C143—C144—H144       | 120.5      |                                   |
| C144—C145—C146       | 120.7 (3)  |                                   |
| C144—C145—H145       | 119.7      |                                   |
| C146—C145—H145       | 119.7      |                                   |
| C145—C146—C141       | 121.1 (4)  |                                   |

Acta Cryst. (2021). E77, 975-981
C145—C146—H146 119.5  H57A—C57—H57B 109.5
C141—C146—H146 119.5  O54—C57—H57C 109.5
C36—C31—C32 117.6 (3)  H57A—C57—H57C 109.5
C36—C31—C3 120.3 (2)  H57B—C57—H57C 109.5

C12—N1—N2—C3 166.6 (3)  C142—C141—C146—C145 −0.4 (5)
C5—N1—N2—C3 −2.0 (3)  C14—C141—C146—C145 178.5 (3)
N1—N2—C3—C31 178.9 (2)  N2—C3—C31—C36 −172.2 (2)
N1—N2—C3—C4 −3.5 (3)  C4—C3—C31—C36 10.5 (4)
N2—C3—C4—C5 7.2 (3)  N2—C3—C31—C32 9.5 (4)
C31—C3—C4—C5 −175.2 (2)  C4—C3—C31—C32 −167.9 (3)
C12—N1—C5—C51 78.2 (4)  C36—C31—C32—C33 −0.4 (4)
N2—N1—C5—C51 −113.9 (3)  C3—C31—C32—C33 178.0 (3)
C12—N1—C5—C4 −161.8 (3)  C31—C32—C33—C34 0.8 (4)
N2—N1—C5—C4 6.1 (3)  C3—C31—C32—C33 178.0 (3)
C3—C4—C5—N1 −7.3 (3)  C31—C32—C33—C34 −1.0 (4)
C3—C4—C5—C51 114.4 (2)  C32—C33—C34—C35 178.2 (3)
N2—N1—C12—N13 −178.5 (3)  C33—C34—C35—C36 −1.0 (4)
C5—N1—C12—N13 −11.2 (5)  C34—C35—C36—C31 1.5 (4)
N2—N1—C12—S11 2.5 (4)  C32—C31—C36—C35 −179.4 (3)
C5—N1—C12—S11 169.8 (2)  C3—C31—C36—C35 −0.7 (4)
C15—S11—C12—N13 −1.3 (2)  C31—C36—C35—C34 −179.1 (2)
C15—S11—C12—N1 177.9 (3)  C3—C31—C36—C35 −0.6 (4)
N1—C12—N13—C14 −178.1 (3)  C33—C34—C35—C36 178.6 (3)
S11—C12—N13—C14 1.0 (3)  C34—C35—C36—C31 −174.0 (3)
C12—N13—C14—C15 −174.7 (3)  N1—C5—C51—C56 16.6 (4)
C12—N13—C14—C141 1.1 (2)  C5—C51—C52—C53 −178.0 (3)
C15—C14—C141—C142 −0.2 (4)  C51—C52—C53—C54 −1.2 (4)
N13—C14—C141—C14 6.6 (4)  C52—C53—C54—O54 −176.3 (3)
C15—C14—C141—C146 6.3 (5)  C52—C53—C54—C55 2.7 (4)
N13—C14—C141—C146 −172.4 (3)  C52—C53—C54—C55 2.7 (4)
C146—C141—C142—C143 1.1 (5)  O54—C54—C55—C56 177.2 (3)
C14—C141—C142—C143 −177.9 (3)  C53—C54—C55—C56 −1.7 (4)
C141—C142—C143—C144 −0.8 (5)  C52—C51—C56—C55 2.5 (4)
C142—C143—C144—C145 −0.1 (6)  C5—C51—C56—C55 −178.9 (3)
C143—C144—C145—C146 0.8 (6)  C54—C55—C56—C51 1.0 (4)
C144—C145—C146—C141 −0.5 (5)  C55—C54—O54—C57 −21.0 (5)
C144—C145—C146—C141 157.9 (3)

| D—H···A | D—H | H···A | D···A | D—H···A |
|--------|-----|------|------|-------|
| C56—H56···N1 | 0.93 | 2.59 | 2.915 (4) | 101 |
| C142—H142···N13 | 0.93 | 2.53 | 2.864 (5) | 101 |
Crystal data

C$_{29}$H$_{25}$N$_3$O$_2$S

$F(000) = 1008$

$D_x = 1.288$ Mg m$^{-3}$

Monoclinic, $Cc$

$a = 16.5634$ (17) Å

$b = 17.7250$ (19) Å

$c = 9.4032$ (11) Å

$\theta = 2.5$–$27.6^\circ$

$\mu = 0.16$ mm$^{-1}$

$\beta = 116.401$ (3)$^\circ$

$T = 297$ K

$V = 2472.7$ (5) Å$^3$

$Z = 4$

$D_x = 1.288$ Mg m$^{-3}$

Cell parameters from 5580 reflections

Block, colourless

0.18 × 0.16 × 0.15 mm

Data collection

Bruker D8 Venture diffractometer

Radiation source: INCOATEC high brilliance microfocus sealed tube

Multilayer mirror monochromator

$\varphi$ and $\omega$ scans

Absorption correction: multi-scan (SADABS; Bruker, 2016)

$T_{\text{min}} = 0.949$, $T_{\text{max}} = 0.976$

Refinement

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.121$

$S = 1.08$

5578 reflections

318 parameters

2 restraints

Primary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbour sites

H-atom parameters constrained

$P = (F^2 + 2F'^2)/3$

$\Delta \sigma_{\text{max}} < 0.001$

$\Delta \rho_{\text{max}} = 0.15$ e Å$^{-3}$

$\Delta \rho_{\text{min}} = -0.17$ e Å$^{-3}$

Absolute structure: Flack $x$ determined using 1613 quotients [(I)+I]/[(I)+I] (Parsons et al., 2013)

Absolute structure parameter: $-0.01$ (3)

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.

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

|     | x     | y     | z     | $U_{	ext{eq}}$ |
|-----|-------|-------|-------|---------------|
| N1  | 0.3744 (3) | 0.29841 (18) | 0.5726 (4) | 0.0839 (9) |

(RS)-5-(4-Methoxyphenyl)-1-[4-(4-methylphenyl)thiazol-2-yl]-3-[4-(prop-2-ynyloxy)phenyl]-4,5-dihydro-1H-pyrazole (III)

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

$C_{39}$—$H_{39}$···$Cg_{2i}$ 0.93 2.59 3.365 (5) 141

$C_{56}$—$H_{56}$···$Cg_{1ii}$ 0.93 2.91 3.688 (3) 142

sup-11
| Atom | X      | Y      | Z      | U1    |
|------|--------|--------|--------|-------|
| N2   | 0.4454 | 0.3091 | 0.5355 | 0.0737|
| C3   | 0.5038 | 0.2557 | 0.6007 | 0.0669|
| C4   | 0.4776 | 0.2029 | 0.6985 | 0.0865|
| H4A  | 0.5215 | 0.2044 | 0.8093 | 0.104*|
| H4B  | 0.4725 | 0.1515 | 0.6600 | 0.104*|
| C5   | 0.3853 | 0.2328 | 0.6773 | 0.0756|
| H5   | 0.3904 | 0.2505 | 0.7797 | 0.091*|
| S11  | 0.3218 | 0.4406 | 0.4624 | 0.0854|
| C12  | 0.3157 | 0.3557 | 0.5522 | 0.0724|
| N13  | 0.2519 | 0.3508 | 0.5945 | 0.0747|
| C14  | 0.1990 | 0.4159 | 0.5524 | 0.0709|
| C15  | 0.2266 | 0.4692 | 0.4798 | 0.0824|
| H15  | 0.1979 | 0.5153 | 0.4437 | 0.099*|
| C141 | 0.1221 | 0.4193 | 0.5878 | 0.0713|
| C142 | 0.1041 | 0.3605 | 0.6669 | 0.0872|
| H142 | 0.1428 | 0.3192 | 0.6997 | 0.105*|
| C143 | 0.0302 | 0.3619 | 0.6979 | 0.0973|
| H143 | 0.0210 | 0.3216 | 0.7523 | 0.117*|
| C144 | −0.0303| 0.4203 | 0.6517 | 0.0905|
| C145 | −0.0122| 0.4792 | 0.5748 | 0.0996|
| H145 | −0.0509| 0.5205 | 0.5439 | 0.120*|
| C146 | 0.0608 | 0.4798 | 0.5416 | 0.0942|
| H146 | 0.0697 | 0.5206 | 0.4881 | 0.113*|
| C147 | −0.1117| 0.4210 | 0.6812 | 0.126*|
| H14A | −0.0998| 0.4509 | 0.7735 | 0.190*|
| H14B | −0.1260| 0.3703 | 0.6981 | 0.190*|
| H14C | −0.1616| 0.4422 | 0.5909 | 0.190*|
| C31  | 0.5854 | 0.2478 | 0.5802 | 0.0656|
| C32  | 0.6106 | 0.3016 | 0.4991 | 0.0738|
| H32  | 0.5744 | 0.3438 | 0.4569 | 0.089*|
| C33  | 0.6869 | 0.2937 | 0.4803 | 0.0773|
| H33  | 0.7023 | 0.3303 | 0.4258 | 0.093*|
| C34  | 0.7425 | 0.2308 | 0.5428 | 0.0717|
| C35  | 0.7184 | 0.1771 | 0.6216 | 0.0769|
| H35  | 0.7544 | 0.1347 | 0.6621 | 0.092*|
| C36  | 0.6411 | 0.1854 | 0.6415 | 0.0751|
| H36  | 0.6261 | 0.1488 | 0.6966 | 0.090*|
| O34  | 0.8184 | 0.2281 | 0.5206 | 0.0846|
| C37  | 0.8746 | 0.1632 | 0.5821 | 0.1023|
| H37A | 0.8416 | 0.1183 | 0.5288 | 0.123*|
| H37B | 0.8916 | 0.1582 | 0.6946 | 0.123*|
| C38  | 0.9547 | 0.1703 | 0.5582 | 0.0952|
| C39  | 1.0224 | 0.1735 | 0.5477 | 0.1132|
| H39  | 1.0762 | 0.1761 | 0.5393 | 0.136*|
| C51  | 0.3113 | 0.1752 | 0.6090 | 0.0651|
| C52  | 0.2983 | 0.1276 | 0.7136 | 0.0749|
| H52  | 0.3335 | 0.1335 | 0.8222 | 0.090*|
| C53  | 0.2344 | 0.0719 | 0.6598 | 0.0817|
### Atomic displacement parameters (Å²)

|   | $U_{11}$  | $U_{22}$  | $U_{33}$  | $U_{12}$  | $U_{13}$  | $U_{23}$  |
|---|-----------|-----------|-----------|-----------|-----------|-----------|
| N1| 0.099 (2) | 0.0566 (18) | 0.098 (3) | 0.0104 (16) | 0.046 (2) | 0.0159 (16) |
| N2| 0.091 (2) | 0.0502 (15) | 0.073 (2) | 0.0009 (15) | 0.0296 (17) | 0.0010 (14) |
| C3| 0.082 (2) | 0.0499 (17) | 0.0531 (19) | -0.0041 (16) | 0.0163 (16) | -0.0014 (14) |
| C4| 0.089 (3) | 0.069 (2) | 0.094 (3) | 0.009 (2) | 0.033 (2) | 0.023 (2) |
| C5| 0.091 (3) | 0.060 (2) | 0.073 (2) | 0.0107 (19) | 0.034 (2) | 0.0101 (17) |
| S11| 0.1088 (8) | 0.0476 (4) | 0.0845 (6) | -0.0078 (5) | 0.0290 (5) | -0.0009 (5) |
| C12| 0.087 (3) | 0.0471 (18) | 0.069 (2) | 0.0006 (17) | 0.022 (2) | 0.0008 (16) |
| C13| 0.092 (2) | 0.0472 (15) | 0.071 (2) | 0.0099 (15) | 0.0238 (17) | 0.0051 (13) |
| C14| 0.089 (3) | 0.0447 (17) | 0.056 (2) | 0.0020 (16) | 0.0108 (18) | -0.0061 (15) |
| C15| 0.102 (3) | 0.0448 (17) | 0.083 (3) | 0.0007 (19) | 0.025 (2) | -0.0027 (18) |
| C141| 0.086 (3) | 0.0486 (17) | 0.057 (2) | 0.0062 (17) | 0.0117 (18) | -0.0087 (15) |
| C142| 0.108 (3) | 0.068 (2) | 0.079 (3) | 0.025 (2) | 0.036 (2) | 0.011 (2) |
| C143| 0.121 (4) | 0.081 (3) | 0.086 (3) | 0.013 (3) | 0.042 (3) | 0.003 (2) |
| C144| 0.093 (3) | 0.081 (3) | 0.078 (3) | 0.007 (2) | 0.021 (2) | -0.023 (2) |
| C145| 0.092 (3) | 0.079 (3) | 0.102 (4) | 0.025 (3) | 0.019 (3) | -0.013 (3) |
| C146| 0.108 (4) | 0.057 (2) | 0.091 (3) | 0.013 (2) | 0.020 (3) | 0.005 (2) |
| C147| 0.107 (4) | 0.138 (5) | 0.123 (5) | 0.005 (4) | 0.041 (3) | -0.042 (4) |
| C31| 0.075 (2) | 0.0540 (18) | 0.0511 (19) | -0.0016 (16) | 0.0130 (16) | -0.0023 (14) |
| C32| 0.081 (3) | 0.0548 (19) | 0.069 (2) | 0.0055 (17) | 0.0191 (19) | 0.0100 (16) |
| C33| 0.084 (3) | 0.064 (2) | 0.074 (3) | 0.0034 (19) | 0.025 (2) | 0.0148 (19) |
| C34| 0.083 (3) | 0.057 (2) | 0.061 (2) | 0.0065 (17) | 0.0198 (19) | 0.0017 (16) |
| C35| 0.088 (3) | 0.055 (2) | 0.069 (2) | 0.0114 (18) | 0.019 (2) | 0.0077 (16) |
| C36| 0.093 (3) | 0.0531 (19) | 0.068 (2) | 0.0006 (18) | 0.025 (2) | 0.0067 (16) |
| O34| 0.0885 (19) | 0.0718 (17) | 0.0859 (18) | 0.0176 (15) | 0.0320 (15) | 0.0155 (13) |
| C37| 0.107 (4) | 0.071 (3) | 0.121 (4) | 0.021 (2) | 0.044 (3) | 0.018 (3) |
| C38| 0.105 (4) | 0.079 (3) | 0.090 (3) | 0.033 (3) | 0.033 (3) | 0.010 (2) |
| C39| 0.104 (4) | 0.118 (4) | 0.110 (4) | 0.045 (3) | 0.041 (3) | 0.015 (3) |
| C51| 0.078 (2) | 0.0539 (17) | 0.063 (2) | 0.0140 (15) | 0.0306 (17) | 0.0074 (15) |
| C52| 0.076 (2) | 0.087 (3) | 0.058 (2) | 0.009 (2) | 0.0264 (18) | 0.0138 (18) |
| C53| 0.080 (3) | 0.088 (3) | 0.076 (3) | 0.011 (2) | 0.034 (2) | 0.028 (2) |
| C54| 0.073 (2) | 0.0547 (19) | 0.086 (3) | 0.0147 (18) | 0.028 (2) | 0.0107 (18) |
| C55| 0.106 (3) | 0.065 (2) | 0.063 (2) | 0.004 (2) | 0.023 (2) | 0.0024 (19) |
| C56| 0.114 (3) | 0.061 (2) | 0.061 (2) | 0.003 (2) | 0.039 (2) | 0.0118 (17) |
|    | 0.093 (2) | 0.078 (2) | 0.116 (3) | −0.0087 (16) | 0.0193 (19) | 0.0156 (17) |
|----|-----------|-----------|-----------|--------------|-------------|-------------|
| O54| 0.101 (4) | 0.090 (3) | 0.120 (4) | −0.012 (3)   | 0.020 (3)   | −0.010 (3)  |

**Geometric parameters (Å, °)**

| Bond                      | Distance (Å) | Angle (°)     |
|---------------------------|--------------|---------------|
| N1—C12                    | 1.359 (5)    |               |
| N1—N2                     | 1.381 (5)    |               |
| N1—C5                     | 1.482 (5)    |               |
| N2—C3                     | 1.297 (5)    |               |
| C3—C31                    | 1.454 (5)    |               |
| C3—C4                     | 1.505 (6)    |               |
| C4—C5                     | 1.544 (6)    |               |
| C4—H4A                    | 0.9700       |               |
| C4—H4B                    | 0.9700       |               |
| C5—C51                    | 1.501 (5)    |               |
| C5—H5                     | 0.9800       |               |
| S11—C15                   | 1.732 (5)    |               |
| N13—C14                   | 1.367 (6)    |               |
| C14—C15                   | 1.357 (6)    |               |
| C14—C141                  | 1.454 (6)    |               |
| C15—H15                   | 0.9300       |               |
| C141—C142                 | 1.388 (6)    |               |
| C141—C146                 | 1.406 (6)    |               |
| C142—C143                 | 1.379 (6)    |               |
| C142—H142                 | 0.9300       |               |
| C143—C144                 | 1.371 (7)    |               |
| C143—H143                 | 0.9300       |               |
| C144—C145                 | 1.377 (8)    |               |
| C144—C147                 | 1.492 (8)    |               |
| C145—C146                 | 1.376 (7)    |               |
| C145—H145                 | 0.9300       |               |
| C146—H146                 | 0.9300       |               |
| C147—H14A                 | 0.9600       |               |
| C147—H14B                 | 0.9600       |               |
| C147—H14C                 | 0.9600       |               |
| C12—N1—N2                 | 119.8 (3)    |               |
| C12—N1—C5                 | 123.3 (3)    |               |
| N2—N1—C5                  | 114.2 (3)    |               |
| C3—N2—N1                  | 108.6 (3)    |               |
| N2—C3—C31                 | 123.3 (3)    |               |
| N2—C3—C4                  | 112.7 (4)    |               |
| C31—C3—C4                 | 124.0 (3)    |               |
| C3—C4—C5                  | 104.2 (3)    |               |
| C3—C4—H4A                 | 110.9        |               |
| C5—C4—H4A                 | 110.9        |               |

*Acta Cryst. (2021). E77, 975-981*
| Bond          | Distance (Å) | Torsion (°) |
|---------------|--------------|-------------|
| C3—C4—H4B    | 110.9        |             |
| C5—C4—H4B    | 110.9        |             |
| H4A—C4—H4B   | 108.9        |             |
| N1—C5—C51    | 114.4 (3)    |             |
| N1—C5—C4     | 100.2 (3)    |             |
| C51—C5—C4    | 113.3 (3)    |             |
| N1—C5—H5     | 109.5        |             |
| C51—C5—H5    | 109.5        |             |
| C4—C5—H5     | 109.5        |             |
| C15—S11—C12  | 87.5 (2)     |             |
| N13—C12—N1   | 122.6 (3)    |             |
| N13—C12—S11  | 116.0 (3)    |             |
| N1—C12—S11   | 121.3 (3)    |             |
| C12—N13—C14  | 110.8 (3)    |             |
| C15—C14—N13  | 114.0 (4)    |             |
| C15—C14—C141 | 127.8 (4)    |             |
| N13—C14—C141 | 118.2 (3)    |             |
| C14—C15—S11  | 111.6 (3)    |             |
| C14—C15—H15  | 124.2        |             |
| C142—C141—C146 | 116.1 (4) |             |
| C142—C141—C14 | 120.7 (3)    |             |
| C146—C141—C14 | 123.1 (4)    |             |
| C143—C142—C141 | 121.5 (4) |             |
| C143—C142—H142 | 119.3        |             |
| C141—C142—H142 | 119.3        |             |
| C144—C143—C142 | 122.6 (5)    |             |
| C144—C143—H143 | 118.7        |             |
| C142—C143—H143 | 118.7        |             |
| C143—C144—C145 | 116.1 (5)    |             |
| C143—C144—C147 | 122.7 (6)    |             |
| C145—C144—C147 | 121.2 (5)    |             |
| C146—C145—C144 | 122.9 (4)    |             |
| C146—C145—H145 | 118.5        |             |
| C144—C145—H145 | 118.5        |             |
| C145—C146—C141 | 120.7 (5)    |             |
| C145—C146—H146 | 119.6        |             |
| C141—C146—H146 | 119.6        |             |
| C144—C147—H146 | 119.6        |             |
| C144—C147—C146 | 109.5        |             |
| C144—C147—H146 | 109.5        |             |
| H14A—C147—H146 | 109.5        |             |
| H14A—C147—H144 | 109.5        |             |
| C12—N1—N2—C3 | 163.9 (3)    |             |
| C5—N1—N2—C3  | 1.9 (4)      |             |
| N1—N2—C3—C31 | 177.2 (3)    |             |
| N1—N2—C3—C4  | −2.4 (5)     |             |

**Notes:**
- Bond distances and torsion angles are given in angstroms (Å) and degrees (°), respectively.
- Values in parentheses indicate uncertainty in the last digit.
N2—C3—C4—C5 2.0 (5) C4—C3—C31—C36 5.5 (5)
C31—C3—C4—C5 −177.7 (3) N2—C3—C31—C32 5.7 (5)
C12—N1—C5—C51 76.7 (5) C4—C3—C31—C32 −174.7 (4)
N2—N1—C5—C51 −122.1 (4) C36—C31—C32—C33 0.1 (5)
C12—N1—C5—C4 −161.9 (4) C3—C31—C32—C33 −179.9 (3)
N2—N1—C5—C4 −0.6 (4) C31—C32—C33—C34 0.6 (6)
C3—C4—C5—N1 −0.7 (4) C3—C31—C32—C33 −174.7 (4)
C3—C4—C5—C51 121.6 (3) C3—C31—C32—C33 179.9 (3)
N2—N1—C12—N13 −175.2 (4) O34—C34—C35—C36 178.5 (4)
C5—N1—C12—N13 −15.0 (6) C33—C34—C35—C36 −1.0 (6)
N2—N1—C12—N13 6.0 (5) C34—C35—C36—C31 −0.4 (5)
C5—N1—C12—N13 166.3 (3) C32—C31—C36—C35 179.5 (3)
C15—S11—C12—N13 −2.1 (3) C3—C31—C36—C35 179.5 (3)
C15—S11—C12—N1 176.8 (3) C36—C31—C36—C35 1.5 (6)
N1—C12—N13—C14 −176.8 (4) C33—C34—O34—C37 179.0 (4)
S11—C12—N13—C14 2.0 (4) C34—C35—C36—C31 −176.6 (4)
C12—N13—C14—C15 −0.8 (4) N1—C5—C51—C56 25.0 (5)
C12—N13—C14—C141 178.5 (3) C4—C5—C51—C56 −89.0 (4)
N13—C14—C141—C142 0.7 (4) N1—C5—C51—C52 −158.0 (3)
C141—C14—C141—C142 −178.4 (4) C4—C5—C51—C52 88.0 (4)
C15—C14—C141—C142 2.4 (5) C56—C51—C52—C53 −0.3 (6)
N13—C14—C141—C142 −178.3 (4) C5—C51—C52—C53 −177.5 (4)
C15—C14—C141—C146 3.5 (6) C51—C52—C53—C54 −0.7 (6)
N13—C14—C141—C146 −175.7 (4) C52—C53—C54—C55 1.0 (6)
C146—C141—C142—C143 −0.1 (6) C52—C53—C54—O54 −178.4 (4)
C14—C141—C142—C143 −178.3 (4) C53—C54—C55—C56 −0.3 (6)
C141—C142—C143—C144 0.8 (7) C52—C51—C56—C55 1.0 (6)
C142—C143—C144—C145 −1.5 (7) C5—C51—C56—C55 178.0 (4)
C142—C143—C144—C147 178.3 (5) C54—C55—C56—C51 −0.7 (7)
C143—C144—C145—C146 1.5 (7) C55—C54—O54—C57 −17.9 (7)
C147—C144—C145—C146 −178.2 (4) C53—C54—O54—C57 161.5 (4)

### Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|-----|------|-------|--------|
| C142—H142···N13 | 0.93 | 2.48 | 2.823 (6) | 102 |
| C35—H35···S11 | 0.93 | 2.86 | 3.560 (4) | 133 |
| C39—H39···Cg2 | 0.93 | 2.93 | 3.802 (5) | 156 |
| C56—H56···Cg1 | 0.93 | 2.92 | 3.689 (3) | 141 |

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