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Crystal structure of (*E*)-*N*-(4-bromophenyl)-2-cyano-3-[3-(2-methylpropyl)-1-phenyl-1*H*-pyrazol-4-yl]prop-2-enamide

Mamdouh A. Abu-Zaied,[a] Reham A. Mohamed-Ezzat,[b] Galal H. Elgemeie[c] and Peter G. Jones[d]*

[a]Green Chemistry Department, Chemical Industries Research Institute, National Research Centre, Dokki, Giza, Egypt, [b]Chemistry of Natural & Microbial Products Department, Pharmaceutical and Drug Industries Research Institute, National Research Centre, Cairo, Egypt, [c]Chemistry Department, Faculty of Science, Helwan University, Cairo, Egypt, and [d]Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30, D-38106 Braunschweig, Germany. *Correspondence e-mail: p.jones@tu-braunschweig.de

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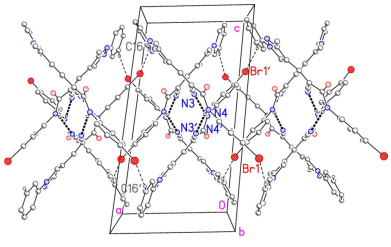
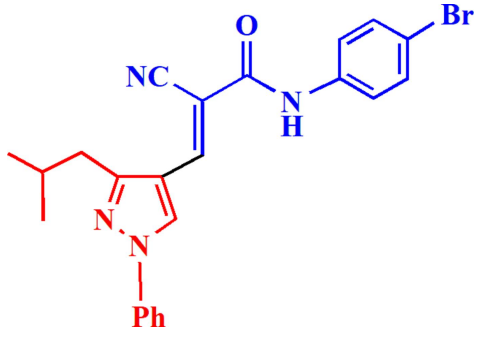
The structure of the title compound, $C_{23}H_{21}BrN_4O$, contains two independent molecules connected by hydrogen bonds of the type $N_{amide}—H\cdots N{\equiv}C$ to form a dimer. The configuration at the exocyclic C=C double bond is *E*. The molecules are roughly planar except for the isopropyl groups. There are minor differences in the orientations of these groups and the phenyl rings at N1. The dimers are further linked by 'weak' hydrogen bonds, two each of the types $H_{phenyl}\cdots O{=}C$ (H···O = 2.50, 2.51 Å) and $H_{phenyl}\cdots Br$ (H···Br = 2.89, 2.91 Å), to form ribbons parallel to the *b* and *c* axes, respectively. The studied crystal was a non-merohedral twin.

1. Chemical context

Pyrazoles contribute significantly to medicinal applications (Bennani *et al.*, 2020; Ansari *et al.*, 2017); their pharmacological activity is reflected in their presence in various therapeutic agents (Küçükgüzel & Şenkardeş, 2015), *e.g.* as agents against human colon cancer, leukaemia and melanoma (Elgemeie & Mohamed-Ezzat, 2022), as anti-inflammatory agents, and in the field of antiviral therapeutics against various targets such as CoX-1, CoX-2, NNRTI, HSV-1 and H1N1 (Khan *et al.*, 2016; Li *et al.*, 2015). Heterocyclic compounds containing pyrazole rings are also efficacious components in many multi-component syntheses (Tu *et al.*, 2014); we have reported and reviewed their use as novel synthetic intermediates (Elgemeie *et al.*, 2015; Abu-Zaied *et al.*, 2018, 2019; Metwally *et al.*, 2024). We have also synthesized various pyrazole-fused heterocyclic compounds as bioactive agents acting as antimetabolites (Elgemeie & Abu-Zaied, 2015; Elgemeie *et al.* 2017*a*,*b*, 2019; Mohamed-Ezzat & Elgemeie, 2023).





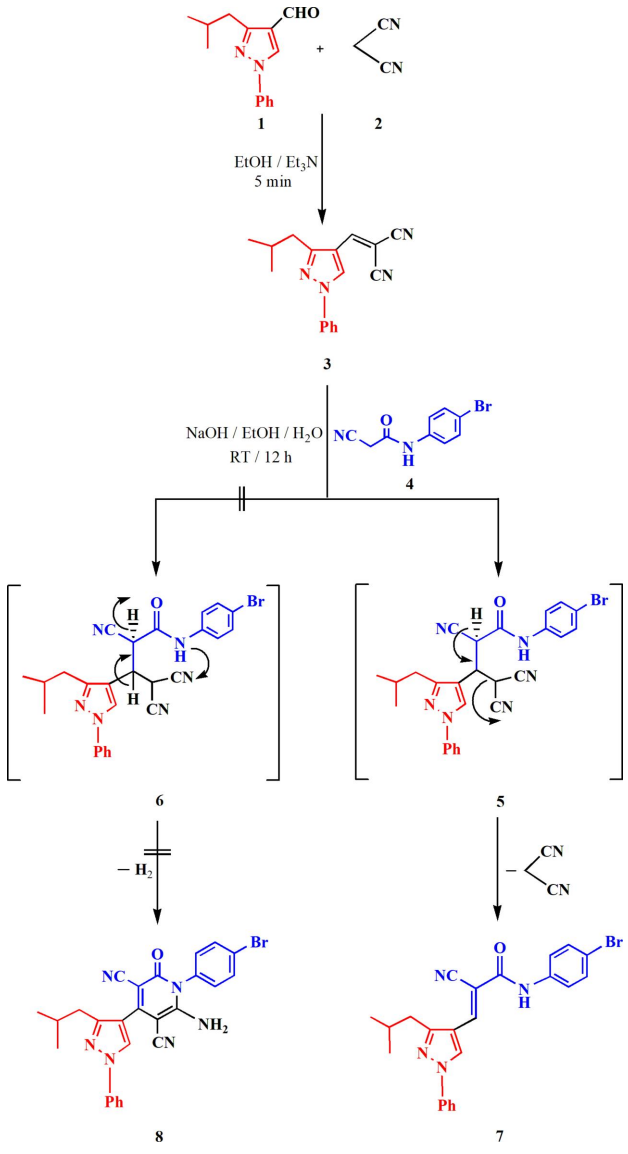


Figure 1
The reaction scheme leading to the title compound **7**.

In this article, we report the synthesis of the title compound **7**, which bears a substituted acrylamide side chain at the 4-position of the pyrazole ring, by the reaction between 2-[(3-isobutyl-1-phenyl-1*H*-pyrazol-4-yl)methylene]malononitrile **3** and *N*-(4-bromophenyl)-2-cyanoacetamide **4** in an ethanol–water mixture in the presence of sodium hydroxide (see Fig. 1, where the suggested mechanism is also shown). The reaction starts by the nucleophilic attack of the active methylene group of **4** at the double bond of **3** to give an intermediate Michael addition product **5**, which eliminates malononitrile to give the final product **7**. The structure of **7** was confirmed *via* spectroscopic techniques; thus, the IR spectrum indicated the presence of a characteristic NH absorption band at 3455 cm^{-1}, and the ^{1}H NMR spectrum revealed the presence of an NH signal at 10.36 ppm, a singlet vinylic signal at 8.10 ppm, and aromatic protons at 7.52–7.63 ppm. It is possible that compound **7** is the thermodynamically controlled product because of lower steric hindrance, and is thus formed instead of the *N*-aryl-2-pyridone **8** *via* intermediate **6**. The structure of compound **7** has now been been unambiguously confirmed by single-crystal X-ray diffraction and is presented here.

Table 1
Selected geometric parameters (Å, °).

N1—C5	1.357 (4)	N1′—C5′	1.343 (4)
N1—N2	1.375 (3)	N1′—N2′	1.380 (3)
N2—C3	1.317 (4)	N2′—C3′	1.324 (4)
C3—C4	1.424 (4)	C3′—C4′	1.432 (4)
C4—C5	1.392 (4)	C4′—C5′	1.390 (4)
C12—O1	1.221 (3)	C12′—O1′	1.228 (3)
C13—N3	1.145 (4)	C13′—N3′	1.155 (4)
C23—Br1	1.911 (3)	C23′—Br1′	1.906 (3)
C5—N1—N2	112.2 (2)	C5′—N1′—N2′	112.5 (2)
C5—N1—C14	128.3 (2)	C5′—N1′—C14′	128.5 (2)
C3—N2—N1	104.9 (2)	C3′—N2′—N1′	104.6 (2)
N2—C3—C4	111.9 (2)	N2′—C3′—C4′	111.5 (3)
C4—C3—C6	128.0 (3)	C4′—C3′—C6′	128.2 (3)
C5—C4—C3	104.5 (2)	C5′—C4′—C10′	131.0 (3)
C5—C4—C10	130.7 (3)	C5′—C4′—C3′	104.3 (2)
N1—C5—C4	106.5 (2)	N1′—C5′—C4′	107.0 (2)
C11—C10—C4	130.1 (3)	C11′—C10′—C4′	130.4 (3)
N2—C3—C6—C7	−107.2 (3)	N2′—C3′—C6′—C7′	−102.1 (3)
C4—C3—C6—C7	73.5 (4)	C4′—C3′—C6′—C7′	78.5 (4)
C10—C11—C12—N4	156.4 (3)	C10′—C11′—C12′—N4′	155.5 (3)
C5—N1—C14—C15	10.7 (5)	C5′—N1′—C14′—C15′	23.4 (5)
N2—N1—C14—C15	−173.4 (3)	N2′—N1′—C14′—C15′	−159.4 (3)

2. Structural commentary

The structure of compound **7** is shown in Fig. 2, with selected molecular dimensions in Table 1 (and hydrogen bonds in Table 2); there are two independent molecules in the asymmetric unit. The configuration at the double bond C10═C11 is *E*, with the amide and pyrazolyl groups mutually *trans*, which leads to short intramolecular contacts H10···O1 of 2.43, 2.44 Å. The two independent molecules are linked to form a

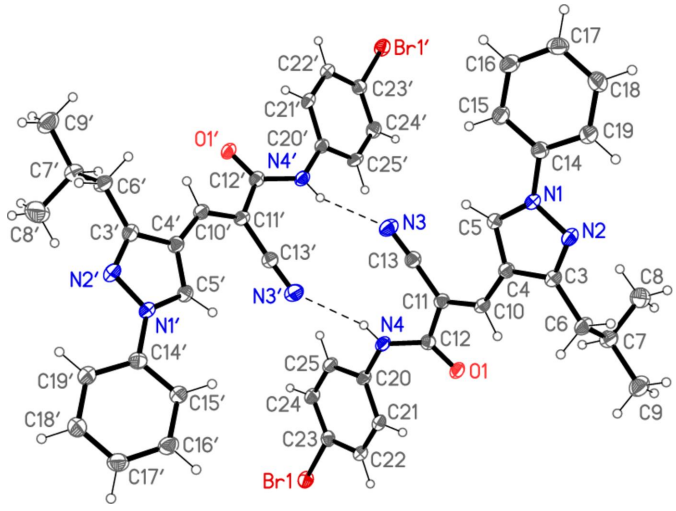


Figure 2
The structure of compound **7** in the crystal; two independent molecules are linked by hydrogen bonds (shown as dashed lines). Ellipsoids represent 50% probability levels.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4···N3′	0.82 (3)	2.31 (3)	3.107 (3)	162 (3)
N4′—H4′···N3	0.82 (3)	2.32 (4)	3.097 (3)	158 (4)
C15—H15···O1′^{i}	0.95	2.50	3.417 (4)	162
C15′—H15′···O1^{ii}	0.95	2.51	3.455 (4)	174
C16′—H16′···Br1^{iii}	0.95	2.91	3.813 (3)	159
C16—H16···Br1′^{iii}	0.95	2.89	3.726 (3)	148

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

dimer by hydrogen bonds of the type N_{amide}—H···N≡C; the graph set is $R_2^2(12)$. The atom numbering of both molecules is the same, but with the addition of primes (′) for the second molecule. The centre of gravity of the asymmetric unit lies close to the point (0.5, 0.75, 0.5).

Bond lengths and angles may be considered normal, although the narrow angles in the pyrazole rings are necessarily reflected in some wide exocyclic angles, and the angle C4—C10—C11 is also wide. A least-squares fit of both molecules (for all atoms except hydrogens; Fig. 3) gave an r.m.s. deviation of 0.12 Å, with minor differences in the orientations of the isopropyl groups and the ring C14–19 (the latter involving torsion angle differences of *ca* 13°). This corresponds to the presence of a local twofold axis passing through the centre of gravity of the asymmetric unit. A side view of molecule 1 shows that it is very roughly planar except for the isopropyl group (Fig. 4). The interplanar angles between the pyrazole ring and rings C14–C19 and C20–C25, respectively, are 10.4 (2), 22.5 (2)° in molecule 1 and 10.3 (2), 8.9 (2)° in molecule 2. Another factor associated with the lack of planarity is the central torsion angle of the atom sequence C4—C10—C11—C12—N4—C20, which differs by *ca* 24° from the 180° required for an ideally extended sequence. The geometry at the amide nitrogen atoms is almost exactly planar (r.m.s. deviations from the best plane through the nitrogen and its immediate substituents are 0.012 and 0.004 Å for the two molecules).

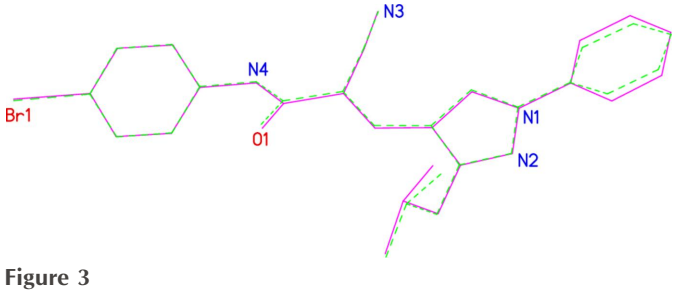


Figure 3
A least-squares fit of both independent molecules. The second independent molecule is indicated by dashed green bonds.

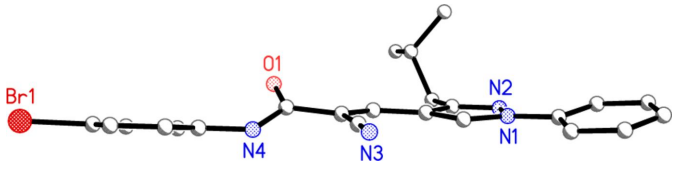


Figure 4
Side view of molecule 1 (hydrogen atoms omitted).

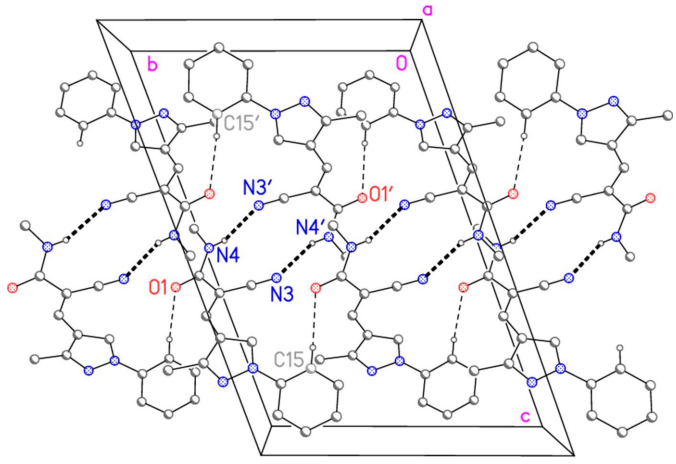


Figure 5
Packing diagram of compound **7** viewed parallel to the *a* axis. The dashed bonds indicate classical (thick) or 'weak' (thin) hydrogen bonds. For clarity, the bromophenyl rings have been reduced to their *ipso* carbon atoms and the isopropyl groups are omitted, as are the hydrogen atoms not involved in hydrogen bonding.

3. Supramolecular features

The association of the two independent molecules to form a hydrogen-bonded dimer was discussed in the previous section. The common hydrogen-bonding pattern for amides, with dimer formation *via* two N—H···O=C bonds, is not observed; this would require rotation around the amide C4—N12 bond to make the sequence O1=C12—N4—H4 synperiplanar rather than antiperiplanar, which would presumably involve a close approach of the bromophenyl and nitrile groups. There are also two pairs of 'weak' hydrogen bonds, namely H15···O1′/H15′···O1 and H16···Br1′/H16′···Br1 (for details see Table 2). The former link the dimers to form a ribbon structure parallel to the *b* axis (Fig. 5),

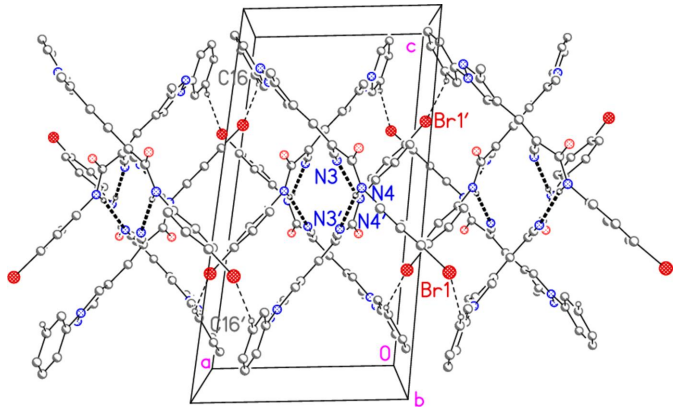


Figure 6
Packing diagram of compound **7** viewed parallel to the *b* axis. The dashed bonds indicate classical (thick) or 'weak' (thin) hydrogen bonds. For clarity, the isopropyl groups are omitted, as are the hydrogen atoms not involved in hydrogen bonding.

whereas the latter are associated with a ribbon structure parallel to the *c* axis (Fig. 6). The combination of the two ribbons leads to the final three-dimensional packing.

4. Database survey

The search employed the routine ConQuest (Bruno *et al.*, 2002), part of Version 2023.3.0 of the Cambridge Database (Groom *et al.*, 2016), and sought structures with pyrazole rings substituted at C4 by the group —C═C(CN)—C(═O)—N. Only one exact hit was registered: 2-cyano-3-(1-phenyl-3-(thiophen-2-yl)-1*H*-pyrazol-4-yl)prop-2-enamide (YEJVES; Kariuki *et al.*, 2022), which has a thiophenyl group instead of the isobutyl group in **7**, and an unsubstituted amide group. It too shows the *E* configuration; the hydrogen bonding involves hydrogen-bonded dimers *via* N—H···O═C contacts between the two independent molecules, crosslinked by further hydrogen bonds N—H···N≡C. There were, however, four other hits in which the substituent was involved in another ring fused with the pyrazole, *e.g.* methyl 5-cyano-6-oxo-3-[4-(trifluoromethyl)phenyl]-6,7-dihydro-2*H*-pyrazolo[3,4-*b*]pyridine-4-carboxylate (HUVXED; Ali *et al.*, 2013).

5. Synthesis and crystallization

Synthesis of compound **3**

To a solution of the pyrazole-4-carbaldehyde derivative **1** (10 mmol) in absolute ethanol (10 mL) containing 3 drops of triethylamine, malononitrile **2** (10 mmol) was added, and the mixture was stirred for 5 min. The precipitate thus formed was filtered off and recrystallized from ethanol to afford compound **3** as a colourless solid in 90% yield. M.p. 442 K; IR (KBr, cm^{-1}) ν 3132 (C—H aromatic), 2950 (CH), 2216, 2210, (2 CN), 1612 (C═N), 1594 (C═C); ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.90 (*d*, *J* = 6.4 Hz, 6H, 2 × CH_3), 1.94–1.96 (*m*, 1H, CH), 2.65 (*d*, *J* = 7.2 Hz, CH_2), 7.45–7.84 (*m*, 5H, C_6H_5), 8.08 (*s*, 1H, vinylic H), 9.01 (*s*, 1H, pyrazole H-5). Analysis calculated for $C_{17}H_{16}N_4$ (276.34): C 73.89, H 5.84, N 20.27. Found: C 73.80, H 5.75, N 20.18%.

Synthesis of compound **7**

A solution of 2-[(3-isobutyl-1-phenyl-1*H*-pyrazol-4-yl) methylene]malononitrile **3** (10 mmol) in an ethanol–water mixture (1:1) containing sodium hydroxide (10 mmol) was treated with *N*-(4-bromophenyl)-2-cyanoacetamide **4** (10 mmol) and heated under reflux for 12 h. The reaction mixture was then cooled to ambient temperature, and the precipitate thus formed was collected by filtration, dried and recrystallized from DMSO to furnish compound **7** as colourless crystals in 95% yield. M.p. 497–499 K; IR (KBr, cm^{-1}) ν 3455 (NH), 3045 (C—H aromatic), 2960 (CH), 2210 (CN), 1663 (C═O), 1602 (C═N), 1591 (C=C); ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.93 (*d*, 6H, *J* = 6.7 Hz, 2 × CH_3), 1.99–2.02 (*m*, 1H, CH), 2.71 (*d*, 2H, *J* = 7.15 Hz, CH_2), 7.52–7.63 (*m*, 9H, C_6H_5, C_6H_4), 8.10 (*s*, 1H, vinylic-H), 9.00 (*s*, 1H, pyrazole H-5), 10.36 (*br*, *s*, D_2O exch., 1H, NH); ^{13}C NMR (125 MHz, DMSO-d_6): δ 22.84 (2C, 2 × CH_3), 28.91 (CH), 34.3 (CH_2), 103 (pyrazole C4), 115.9 (C═CH), 117.45 (CN), 119.82 (2C, Ar-C), 123.41 (2C, Ar-C), 128.15 (Ar-C), 128.74 (pyrazole-C5), 130.36 (2C, Ar-C), 132.05 (2C, Ar-C), 138.22 (2C, Ar-C), 142.15 (Ar-C), 156.28 (pyrazole-C-3), 159.112 (–CH═C), 161.01 (C═O). Analysis calculated for $C_{23}H_{21}BrN_4O$ (449.34): C 61.48, H 4.71, Br 17.78, N 12.47. Found: C 61.38, H 4.60, Br 17.68, N 12.38%.

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_{23}H_{21}BrN_4O$
M_r	449.35
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	100
a, *b*, *c* (Å)	9.2260 (6), 12.7703 (9), 18.6607 (13)
α, β, γ (°)	109.790 (6), 96.720 (6), 90.657 (6)
V (Å^3)	2051.4 (3)
Z	4
Radiation type	Cu *K*α
μ (mm^{-1})	2.90
Crystal size (mm)	0.15 × 0.08 × 0.02
Data collection	
Diffractometer	XtaLAB Synergy
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2023)
T_{min}, T_{max}	0.778, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8658, 8658, 8436
θ values (°)	θ_{max} = 80.7, θ_{min} = 2.5
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.640
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.040, 0.102, 1.05
No. of reflections	8658
No. of parameters	536
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.45, −0.75

Computer programs: *CrysAlis PRO* (Rigaku OD, 2023), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2019/3* (Sheldrick, 2015*b*) and *XP* (Bruker, 1998).

6. Data collection and reduction

Most crystals were fine needles that diffracted very weakly. However, a few broader laths were found, one of which was used for the data collection despite its somewhat diffuse reflection form. The reflections found in the initial cell determination were 93% indexed using a *C*-centred monoclinic cell with approximate cell constants *a* = 35.16, *b* = 12.77, *c* = 9.22 Å, β = 97.3°. During the course of the data collection, this was automatically changed to the final triclinic cell, presumably on the basis of a prohibitively high R_{int} value for the monoclinic cell. A closer inspection of the complete data then revealed the twinning, and the data reduction was repeated accordingly.

7. Refinement

The structure was refined using the 'HKLF 5' command as a two-component non-merohedral twin (by 180° rotation

around c^*), whereby the relative volume of the smaller component refined to 0.2500 (8). The two largest peaks in the residual electron density (*ca* 1.4 e Å^{-3}) are arithmetically related to the coordinates of the two bromine atoms and are probably attributable to residual twinning effects. As is often the case for non-merohedral twins, some intensities were badly in error; six such reflections were omitted from the refinement. Because of the special methods involved in the data reduction of non-merohedral twins, equivalent reflections were merged and R(int) is thus meaningless; because reflections from both twinning components are included, the number of reflections should be interpreted with caution. The weighting parameters did not converge, but oscillated over a small range (*e.g.* the *SHELXL* 'a' parameter between 0.0504 and 0.0507); arbitrarily, we chose the former value. Crystal data, data collection and structure refinement details are summarized in Table 3.

The hydrogen atoms of the NH groups were refined freely, but with the N—H distances restrained to be approximately equal (command 'SADI'). The methyl groups were included as idealized rigid groups allowed to rotate but not tip (command 'AFIX 137'), with C—H = 0.99 Å and H—C—H = 109.5°. Other hydrogen atoms were included using a riding model starting from calculated positions (C—H$_{methylene}$ = 0.99, C—H$_{methine}$ = 1.00, C—H$_{arom}$ = 0.95 Å). The U(H) values were fixed at 1.5 × U_{eq} of the parent carbon atoms for the methyl group and 1.2 × U_{eq} for other hydrogens.

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supporting information

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Crystal structure of (*E*)-*N*-(4-bromophenyl)-2-cyano-3-[3-(2-methylpropyl)-1-phenyl-1*H*-pyrazol-4-yl]prop-2-enamide

Mamdouh A. Abu-Zaied, Reham A. Mohamed-Ezzat, Galal H. Elgemeie and Peter G. Jones

Computing details

(*E*)-*N*-(4-Bromophenyl)-2-cyano-3-[3-(2-methylpropyl)-1-phenyl-1*H*-pyrazol-4-yl]prop-2-enamide

Crystal data

$C_{23}H_{21}BrN_4O$
$M_r = 449.35$
Triclinic, $P\overline{1}$
$a = 9.2260$ (6) Å
$b = 12.7703$ (9) Å
$c = 18.6607$ (13) Å
$\alpha = 109.790$ (6)°
$\beta = 96.720$ (6)°
$\gamma = 90.657$ (6)°
$V = 2051.4$ (3) Å^3
$Z = 4$
$F(000) = 920$
$D_x = 1.455$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Cell parameters from 28092 reflections
$\theta = 4.8$–$80.0°$
$\mu = 2.90$ mm^{-1}
$T = 100$ K
Lath, colourless
0.15 × 0.08 × 0.02 mm

Data collection

XtaLAB Synergy diffractometer
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source
Mirror monochromator
Detector resolution: 10.0000 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2023)
$T_{min} = 0.778$, $T_{max} = 1.000$
8658 measured reflections
8658 independent reflections
8436 reflections with $I > 2\sigma(I)$
$\theta_{max} = 80.7°$, $\theta_{min} = 2.5°$
$h = -11 \rightarrow 11$
$k = -16 \rightarrow 16$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.102$
$S = 1.05$
8658 reflections
536 parameters
1 restraint
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 3.4902P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 1.45$ e Å^{-3}
$\Delta\rho_{min} = -0.75$ e Å^{-3}

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.8296 (3)	0.93208 (19)	0.80174 (13)	0.0195 (5)
N2	0.8728 (3)	1.0434 (2)	0.83283 (14)	0.0223 (5)
C3	0.7898 (3)	1.0913 (2)	0.79189 (16)	0.0204 (5)
C4	0.6899 (3)	1.0129 (2)	0.73414 (15)	0.0192 (5)
C5	0.7208 (3)	0.9108 (2)	0.74228 (15)	0.0194 (5)
H5	0.674853	0.840171	0.712139	0.023*
C6	0.8085 (3)	1.2144 (2)	0.80848 (17)	0.0234 (6)
H6A	0.814865	1.227362	0.759512	0.028*
H6B	0.902540	1.242139	0.841653	0.028*
C7	0.6856 (4)	1.2837 (3)	0.84792 (18)	0.0269 (6)
H7	0.592945	1.261373	0.811598	0.032*
C8	0.6612 (5)	1.2636 (3)	0.9211 (2)	0.0364 (8)
H8A	0.633489	1.184622	0.909325	0.055*
H8B	0.582845	1.309233	0.944196	0.055*
H8C	0.751428	1.283761	0.957285	0.055*
C9	0.7220 (4)	1.4066 (3)	0.8637 (2)	0.0331 (7)
H9A	0.814866	1.429449	0.897552	0.050*
H9B	0.644192	1.450826	0.888617	0.050*
H9C	0.730456	1.418601	0.815190	0.050*
C10	0.5809 (3)	1.0408 (2)	0.68333 (15)	0.0188 (5)
H10	0.581156	1.117548	0.688873	0.023*
C11	0.4770 (3)	0.9745 (2)	0.62836 (16)	0.0191 (5)
C12	0.3728 (3)	1.0298 (2)	0.58637 (15)	0.0188 (5)
C13	0.4618 (3)	0.8564 (2)	0.60891 (16)	0.0215 (6)
N3	0.4422 (3)	0.7617 (2)	0.59075 (15)	0.0274 (5)
N4	0.3098 (3)	0.9632 (2)	0.51592 (14)	0.0204 (5)
H4	0.334 (4)	0.899 (3)	0.497 (2)	0.026 (9)*
O1	0.3486 (2)	1.12794 (16)	0.61581 (11)	0.0224 (4)
C14	0.8933 (3)	0.8565 (2)	0.83581 (16)	0.0217 (6)
C15	0.8624 (3)	0.7422 (2)	0.80079 (17)	0.0242 (6)
H15	0.801738	0.713321	0.752930	0.029*
C16	0.9223 (4)	0.6715 (3)	0.83729 (18)	0.0279 (6)
H16	0.901761	0.593388	0.814056	0.033*
C17	1.0113 (4)	0.7126 (3)	0.90700 (18)	0.0282 (6)
H17	1.050090	0.663052	0.931612	0.034*
C18	1.0436 (4)	0.8263 (3)	0.94063 (18)	0.0301 (7)
H18	1.105799	0.854788	0.988046	0.036*
C19	0.9854 (4)	0.8986 (3)	0.90518 (18)	0.0278 (6)
H19	1.008014	0.976494	0.928011	0.033*
C20	0.2082 (3)	0.9978 (2)	0.46651 (15)	0.0181 (5)
C21	0.2181 (3)	1.1050 (2)	0.46342 (16)	0.0197 (5)
H21	0.294543	1.156414	0.494685	0.024*
C22	0.1169 (3)	1.1369 (2)	0.41490 (16)	0.0211 (5)
H22	0.122820	1.209905	0.412529	0.025*
C23	0.0071 (3)	1.0600 (2)	0.36994 (16)	0.0205 (5)

Br1	−0.13165 (3)	1.10741 (2)	0.30445 (2)	0.02507 (8)
C24	−0.0026 (3)	0.9522 (2)	0.37003 (17)	0.0227 (6)
H24	−0.076916	0.900263	0.337075	0.027*
C25	0.0985 (3)	0.9211 (2)	0.41927 (16)	0.0220 (6)
H25	0.092915	0.847572	0.420802	0.026*
N1′	0.6634 (3)	0.5581 (2)	0.19407 (13)	0.0212 (5)
N2′	0.6975 (3)	0.4479 (2)	0.16639 (14)	0.0232 (5)
C3′	0.6367 (3)	0.4009 (2)	0.20969 (16)	0.0219 (6)
C4′	0.5604 (3)	0.4795 (2)	0.26490 (16)	0.0206 (5)
C5′	0.5837 (3)	0.5796 (2)	0.25271 (16)	0.0204 (5)
H5′	0.549638	0.649800	0.280581	0.024*
C6′	0.6537 (3)	0.2800 (2)	0.19788 (18)	0.0237 (6)
H6A′	0.675875	0.271529	0.248784	0.028*
H6B′	0.738793	0.255432	0.169796	0.028*
C7′	0.5204 (4)	0.2024 (3)	0.15374 (18)	0.0290 (7)
H7′	0.437221	0.223875	0.184710	0.035*
C8′	0.4739 (6)	0.2124 (4)	0.0759 (2)	0.0559 (13)
H8A′	0.448415	0.289057	0.082456	0.067*
H8B′	0.388753	0.161378	0.050055	0.067*
H8C′	0.554472	0.193070	0.044653	0.067*
C9′	0.5519 (4)	0.0823 (3)	0.1454 (2)	0.0364 (8)
H9A′	0.579375	0.076961	0.196370	0.044*
H9B′	0.632326	0.058781	0.114547	0.044*
H9C′	0.464345	0.033882	0.120015	0.044*
C10′	0.4783 (3)	0.4527 (2)	0.31708 (16)	0.0197 (5)
H10′	0.475359	0.376301	0.312449	0.024*
C11′	0.4033 (3)	0.5191 (2)	0.37249 (16)	0.0190 (5)
C12′	0.3216 (3)	0.4648 (2)	0.41656 (16)	0.0201 (5)
C13′	0.3989 (3)	0.6369 (2)	0.39099 (16)	0.0209 (5)
N3′	0.3903 (3)	0.7323 (2)	0.40865 (15)	0.0274 (5)
N4′	0.2974 (3)	0.5319 (2)	0.48735 (14)	0.0206 (5)
H4′	0.328 (5)	0.597 (3)	0.504 (3)	0.046 (13)*
O1′	0.2807 (2)	0.36590 (16)	0.38837 (11)	0.0221 (4)
C14′	0.7091 (3)	0.6320 (2)	0.15749 (17)	0.0227 (6)
C15′	0.7193 (3)	0.7463 (2)	0.19677 (17)	0.0234 (6)
H15′	0.696881	0.775749	0.247998	0.028*
C16′	0.7630 (4)	0.8168 (3)	0.15950 (18)	0.0276 (6)
H16′	0.770824	0.895077	0.185682	0.033*
C17′	0.7951 (4)	0.7743 (3)	0.08488 (19)	0.0288 (6)
H17′	0.824273	0.823276	0.059927	0.035*
C18′	0.7847 (4)	0.6603 (3)	0.04658 (19)	0.0322 (7)
H18′	0.807749	0.631370	−0.004554	0.039*
C19′	0.7409 (4)	0.5874 (3)	0.08222 (18)	0.0290 (7)
H19′	0.732788	0.509238	0.055784	0.035*
C20′	0.2234 (3)	0.4972 (2)	0.53829 (15)	0.0184 (5)
C21′	0.2400 (3)	0.3921 (2)	0.54385 (16)	0.0199 (5)
H21′	0.302404	0.342360	0.513082	0.024*
C22′	0.1665 (3)	0.3593 (2)	0.59383 (16)	0.0216 (6)

H22′	0.176915	0.287245	0.597366	0.026*
C23′	0.0771 (3)	0.4338 (2)	0.63876 (16)	0.0207 (5)
Br1′	−0.02465 (4)	0.38496 (3)	0.70597 (2)	0.02632 (8)
C24′	0.0621 (3)	0.5396 (2)	0.63612 (17)	0.0237 (6)
H24′	0.002619	0.589873	0.668537	0.028*
C25′	0.1352 (3)	0.5716 (2)	0.58544 (17)	0.0221 (6)
H25′	0.125442	0.644200	0.582714	0.026*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0240 (12)	0.0131 (11)	0.0200 (11)	0.0007 (9)	0.0023 (9)	0.0041 (8)
N2	0.0240 (12)	0.0152 (11)	0.0244 (12)	−0.0013 (9)	0.0012 (9)	0.0032 (9)
C3	0.0208 (14)	0.0169 (13)	0.0227 (13)	−0.0002 (10)	0.0034 (10)	0.0057 (10)
C4	0.0204 (13)	0.0170 (13)	0.0200 (12)	0.0001 (10)	0.0030 (10)	0.0060 (10)
C5	0.0225 (14)	0.0161 (12)	0.0181 (12)	0.0006 (10)	0.0005 (10)	0.0047 (10)
C6	0.0225 (14)	0.0172 (13)	0.0283 (14)	−0.0035 (11)	0.0002 (11)	0.0061 (11)
C7	0.0299 (16)	0.0214 (14)	0.0286 (15)	0.0015 (12)	0.0012 (12)	0.0082 (12)
C8	0.050 (2)	0.0303 (17)	0.0289 (16)	0.0076 (15)	0.0096 (15)	0.0092 (13)
C9	0.0348 (18)	0.0229 (15)	0.0378 (17)	0.0036 (13)	−0.0010 (14)	0.0073 (13)
C10	0.0205 (13)	0.0140 (12)	0.0218 (12)	0.0002 (10)	0.0045 (10)	0.0056 (10)
C11	0.0201 (13)	0.0172 (13)	0.0200 (12)	0.0027 (10)	0.0048 (10)	0.0058 (10)
C12	0.0190 (13)	0.0184 (13)	0.0190 (12)	−0.0003 (10)	0.0036 (10)	0.0059 (10)
C13	0.0204 (14)	0.0208 (14)	0.0222 (13)	0.0008 (11)	0.0008 (10)	0.0065 (11)
N3	0.0268 (13)	0.0190 (13)	0.0339 (13)	−0.0013 (10)	−0.0021 (11)	0.0080 (10)
N4	0.0239 (12)	0.0132 (11)	0.0218 (11)	0.0025 (9)	−0.0002 (9)	0.0037 (9)
O1	0.0269 (11)	0.0145 (9)	0.0224 (9)	0.0023 (8)	0.0007 (8)	0.0027 (7)
C14	0.0237 (14)	0.0203 (14)	0.0218 (13)	0.0027 (11)	0.0037 (11)	0.0077 (11)
C15	0.0266 (15)	0.0190 (14)	0.0247 (14)	0.0016 (11)	0.0029 (11)	0.0046 (11)
C16	0.0323 (17)	0.0207 (14)	0.0307 (15)	0.0062 (12)	0.0060 (13)	0.0080 (12)
C17	0.0335 (17)	0.0255 (15)	0.0304 (15)	0.0091 (13)	0.0076 (13)	0.0141 (12)
C18	0.0335 (17)	0.0307 (16)	0.0246 (14)	0.0057 (13)	−0.0021 (12)	0.0092 (12)
C19	0.0339 (17)	0.0206 (14)	0.0266 (14)	0.0029 (12)	−0.0017 (12)	0.0067 (11)
C20	0.0187 (13)	0.0143 (12)	0.0205 (12)	0.0035 (10)	0.0027 (10)	0.0050 (10)
C21	0.0199 (13)	0.0158 (12)	0.0204 (12)	−0.0012 (10)	0.0030 (10)	0.0022 (10)
C22	0.0258 (15)	0.0155 (12)	0.0210 (13)	0.0007 (11)	0.0026 (11)	0.0052 (10)
C23	0.0198 (13)	0.0213 (13)	0.0187 (12)	0.0043 (11)	0.0028 (10)	0.0044 (10)
Br1	0.02476 (15)	0.02211 (15)	0.02525 (15)	0.00458 (11)	−0.00201 (11)	0.00573 (12)
C24	0.0220 (14)	0.0188 (13)	0.0247 (14)	−0.0009 (11)	0.0003 (11)	0.0050 (11)
C25	0.0257 (14)	0.0148 (12)	0.0237 (13)	0.0000 (11)	0.0036 (11)	0.0041 (10)
N1′	0.0272 (13)	0.0144 (11)	0.0218 (11)	0.0036 (9)	0.0049 (9)	0.0054 (9)
N2′	0.0256 (13)	0.0155 (11)	0.0261 (12)	0.0017 (9)	0.0046 (10)	0.0034 (9)
C3′	0.0232 (14)	0.0191 (13)	0.0219 (13)	0.0019 (11)	0.0030 (11)	0.0050 (11)
C4′	0.0207 (14)	0.0189 (13)	0.0210 (13)	0.0035 (10)	0.0017 (10)	0.0054 (10)
C5′	0.0218 (14)	0.0184 (13)	0.0206 (12)	0.0054 (10)	0.0056 (10)	0.0051 (10)
C6′	0.0260 (15)	0.0175 (13)	0.0291 (14)	0.0047 (11)	0.0072 (11)	0.0089 (11)
C7′	0.0369 (18)	0.0221 (15)	0.0282 (15)	0.0012 (13)	0.0033 (13)	0.0091 (12)
C8′	0.089 (4)	0.038 (2)	0.035 (2)	−0.019 (2)	−0.018 (2)	0.0147 (17)

C9′	0.043 (2)	0.0219 (16)	0.0423 (19)	−0.0015 (14)	0.0102 (15)	0.0075 (14)
C10′	0.0214 (13)	0.0161 (12)	0.0207 (12)	0.0008 (10)	0.0011 (10)	0.0057 (10)
C11′	0.0185 (13)	0.0154 (12)	0.0219 (13)	0.0010 (10)	−0.0002 (10)	0.0059 (10)
C12′	0.0196 (13)	0.0183 (13)	0.0212 (13)	0.0018 (10)	0.0017 (10)	0.0056 (10)
C13′	0.0212 (14)	0.0196 (14)	0.0223 (13)	0.0015 (11)	0.0037 (10)	0.0073 (11)
N3′	0.0300 (14)	0.0213 (13)	0.0323 (13)	0.0024 (10)	0.0089 (11)	0.0093 (10)
N4′	0.0250 (12)	0.0136 (11)	0.0221 (11)	−0.0015 (9)	0.0054 (9)	0.0040 (9)
O1′	0.0274 (11)	0.0142 (9)	0.0223 (9)	−0.0023 (8)	0.0034 (8)	0.0032 (7)
C14′	0.0242 (14)	0.0211 (14)	0.0240 (13)	−0.0011 (11)	0.0044 (11)	0.0090 (11)
C15′	0.0274 (15)	0.0198 (14)	0.0221 (13)	−0.0014 (11)	0.0018 (11)	0.0067 (11)
C16′	0.0309 (16)	0.0209 (14)	0.0295 (15)	−0.0058 (12)	−0.0014 (12)	0.0087 (12)
C17′	0.0325 (17)	0.0258 (15)	0.0300 (15)	−0.0031 (13)	0.0011 (13)	0.0132 (12)
C18′	0.046 (2)	0.0257 (16)	0.0248 (15)	−0.0039 (14)	0.0083 (13)	0.0072 (12)
C19′	0.0404 (18)	0.0198 (14)	0.0265 (14)	−0.0001 (13)	0.0082 (13)	0.0061 (12)
C20′	0.0194 (13)	0.0152 (12)	0.0195 (12)	−0.0008 (10)	0.0014 (10)	0.0048 (10)
C21′	0.0207 (13)	0.0148 (12)	0.0213 (13)	0.0023 (10)	0.0029 (10)	0.0021 (10)
C22′	0.0268 (15)	0.0161 (13)	0.0207 (13)	0.0011 (11)	0.0023 (11)	0.0050 (10)
C23′	0.0211 (14)	0.0203 (13)	0.0202 (13)	−0.0030 (11)	0.0018 (10)	0.0066 (10)
Br1′	0.02965 (17)	0.02193 (15)	0.02696 (15)	−0.00282 (11)	0.00926 (12)	0.00613 (12)
C24′	0.0242 (15)	0.0217 (14)	0.0235 (13)	0.0035 (11)	0.0059 (11)	0.0048 (11)
C25′	0.0255 (14)	0.0134 (12)	0.0268 (14)	0.0033 (11)	0.0029 (11)	0.0063 (10)

Geometric parameters (Å, º)

N1—C5	1.357 (4)	C16′—C17′	1.382 (5)
N1—N2	1.375 (3)	C17′—C18′	1.384 (5)
N1—C14	1.423 (4)	C18′—C19′	1.395 (4)
N2—C3	1.317 (4)	C20′—C21′	1.390 (4)
C3—C4	1.424 (4)	C20′—C25′	1.399 (4)
C3—C6	1.499 (4)	C21′—C22′	1.382 (4)
C4—C5	1.392 (4)	C22′—C23′	1.388 (4)
C4—C10	1.432 (4)	C23′—C24′	1.377 (4)
C6—C7	1.545 (4)	C23′—Br1′	1.906 (3)
C7—C8	1.514 (5)	C24′—C25′	1.386 (4)
C7—C9	1.521 (4)	C5—H5	0.9500
C10—C11	1.361 (4)	C6—H6A	0.9900
C11—C13	1.428 (4)	C6—H6B	0.9900
C11—C12	1.500 (4)	C7—H7	1.0000
C12—O1	1.221 (3)	C8—H8A	0.9800
C12—N4	1.357 (4)	C8—H8B	0.9800
C13—N3	1.145 (4)	C8—H8C	0.9800
N4—C20	1.417 (4)	C9—H9A	0.9800
C14—C15	1.392 (4)	C9—H9B	0.9800
C14—C19	1.395 (4)	C9—H9C	0.9800
C15—C16	1.387 (4)	C10—H10	0.9500
C16—C17	1.386 (5)	N4—H4	0.82 (3)
C17—C18	1.386 (5)	C15—H15	0.9500
C18—C19	1.385 (4)	C16—H16	0.9500

C20—C21	1.391 (4)	C17—H17	0.9500
C20—C25	1.395 (4)	C18—H18	0.9500
C21—C22	1.385 (4)	C19—H19	0.9500
C22—C23	1.384 (4)	C21—H21	0.9500
C23—C24	1.379 (4)	C22—H22	0.9500
C23—Br1	1.911 (3)	C24—H24	0.9500
C24—C25	1.388 (4)	C25—H25	0.9500
N1′—C5′	1.343 (4)	C5′—H5′	0.9500
N1′—N2′	1.380 (3)	C6′—H6A′	0.9900
N1′—C14′	1.425 (4)	C6′—H6B′	0.9900
N2′—C3′	1.324 (4)	C7′—H7′	1.0000
C3′—C4′	1.432 (4)	C8′—H8A′	0.9800
C3′—C6′	1.497 (4)	C8′—H8B′	0.9800
C4′—C5′	1.390 (4)	C8′—H8C′	0.9800
C4′—C10′	1.425 (4)	C9′—H9A′	0.9800
C6′—C7′	1.534 (4)	C9′—H9B′	0.9800
C7′—C8′	1.514 (5)	C9′—H9C′	0.9800
C7′—C9′	1.523 (5)	C10′—H10′	0.9500
C10′—C11′	1.361 (4)	N4′—H4′	0.82 (3)
C11′—C13′	1.427 (4)	C15′—H15′	0.9500
C11′—C12′	1.498 (4)	C16′—H16′	0.9500
C12′—O1′	1.228 (3)	C17′—H17′	0.9500
C12′—N4′	1.355 (4)	C18′—H18′	0.9500
C13′—N3′	1.155 (4)	C19′—H19′	0.9500
N4′—C20′	1.413 (4)	C21′—H21′	0.9500
C14′—C15′	1.390 (4)	C22′—H22′	0.9500
C14′—C19′	1.393 (4)	C24′—H24′	0.9500
C15′—C16′	1.392 (4)	C25′—H25′	0.9500

C5—N1—N2	112.2 (2)	C3—C6—H6A	108.5
C5—N1—C14	128.3 (2)	C7—C6—H6A	108.5
N2—N1—C14	119.4 (2)	C3—C6—H6B	108.5
C3—N2—N1	104.9 (2)	C7—C6—H6B	108.5
N2—C3—C4	111.9 (2)	H6A—C6—H6B	107.5
N2—C3—C6	120.1 (3)	C8—C7—H7	108.1
C4—C3—C6	128.0 (3)	C9—C7—H7	108.1
C5—C4—C3	104.5 (2)	C6—C7—H7	108.1
C5—C4—C10	130.7 (3)	C7—C8—H8A	109.5
C3—C4—C10	124.8 (3)	C7—C8—H8B	109.5
N1—C5—C4	106.5 (2)	H8A—C8—H8B	109.5
C3—C6—C7	115.1 (3)	C7—C8—H8C	109.5
C8—C7—C9	110.8 (3)	H8A—C8—H8C	109.5
C8—C7—C6	112.3 (3)	H8B—C8—H8C	109.5
C9—C7—C6	109.2 (3)	C7—C9—H9A	109.5
C11—C10—C4	130.1 (3)	C7—C9—H9B	109.5
C10—C11—C13	123.8 (3)	H9A—C9—H9B	109.5
C10—C11—C12	117.5 (2)	C7—C9—H9C	109.5
C13—C11—C12	118.7 (2)	H9A—C9—H9C	109.5

O1—C12—N4	124.3 (3)	H9B—C9—H9C	109.5
O1—C12—C11	120.4 (2)	C11—C10—H10	115.0
N4—C12—C11	115.3 (2)	C4—C10—H10	115.0
N3—C13—C11	176.0 (3)	C12—N4—H4	121 (3)
C12—N4—C20	124.9 (2)	C20—N4—H4	114 (3)
C15—C14—C19	120.6 (3)	C16—C15—H15	120.7
C15—C14—N1	120.3 (3)	C14—C15—H15	120.7
C19—C14—N1	119.0 (3)	C17—C16—H16	119.4
C16—C15—C14	118.5 (3)	C15—C16—H16	119.4
C17—C16—C15	121.3 (3)	C16—C17—H17	120.2
C16—C17—C18	119.7 (3)	C18—C17—H17	120.2
C19—C18—C17	120.1 (3)	C19—C18—H18	120.0
C18—C19—C14	119.7 (3)	C17—C18—H18	120.0
C21—C20—C25	120.1 (3)	C18—C19—H19	120.1
C21—C20—N4	121.4 (2)	C14—C19—H19	120.1
C25—C20—N4	118.5 (2)	C22—C21—H21	119.9
C22—C21—C20	120.2 (3)	C20—C21—H21	119.9
C23—C22—C21	118.6 (3)	C23—C22—H22	120.7
C24—C23—C22	122.5 (3)	C21—C22—H22	120.7
C24—C23—Br1	120.1 (2)	C23—C24—H24	120.7
C22—C23—Br1	117.4 (2)	C25—C24—H24	120.7
C23—C24—C25	118.6 (3)	C24—C25—H25	120.0
C24—C25—C20	120.0 (3)	C20—C25—H25	120.0
C5′—N1′—N2′	112.5 (2)	N1′—C5′—H5′	126.5
C5′—N1′—C14′	128.5 (2)	C4′—C5′—H5′	126.5
N2′—N1′—C14′	118.9 (2)	C3′—C6′—H6A′	108.5
C3′—N2′—N1′	104.6 (2)	C7′—C6′—H6A′	108.5
N2′—C3′—C4′	111.5 (3)	C3′—C6′—H6B′	108.5
N2′—C3′—C6′	120.3 (3)	C7′—C6′—H6B′	108.5
C4′—C3′—C6′	128.2 (3)	H6A′—C6′—H6B′	107.5
C5′—C4′—C10′	131.0 (3)	C8′—C7′—H7′	107.9
C5′—C4′—C3′	104.3 (2)	C9′—C7′—H7′	107.9
C10′—C4′—C3′	124.6 (3)	C6′—C7′—H7′	107.9
N1′—C5′—C4′	107.0 (2)	C7′—C8′—H8A′	109.5
C3′—C6′—C7′	115.2 (3)	C7′—C8′—H8B′	109.5
C8′—C7′—C9′	110.5 (3)	H8A′—C8′—H8B′	109.5
C8′—C7′—C6′	112.6 (3)	C7′—C8′—H8C′	109.5
C9′—C7′—C6′	110.0 (3)	H8A′—C8′—H8C′	109.5
C11′—C10′—C4′	130.4 (3)	H8B′—C8′—H8C′	109.5
C10′—C11′—C13′	123.8 (3)	C7′—C9′—H9A′	109.5
C10′—C11′—C12′	117.7 (2)	C7′—C9′—H9B′	109.5
C13′—C11′—C12′	118.5 (2)	H9A′—C9′—H9B′	109.5
O1′—C12′—N4′	124.0 (3)	C7′—C9′—H9C′	109.5
O1′—C12′—C11′	120.5 (3)	H9A′—C9′—H9C′	109.5
N4′—C12′—C11′	115.5 (2)	H9B′—C9′—H9C′	109.5
N3′—C13′—C11′	176.4 (3)	C11′—C10′—H10′	114.8
C12′—N4′—C20′	124.6 (2)	C4′—C10′—H10′	114.8
C15′—C14′—C19′	121.5 (3)	C12′—N4′—H4′	120 (3)

C15′—C14′—N1′	119.8 (3)	C20′—N4′—H4′	115 (3)
C19′—C14′—N1′	118.7 (3)	C14′—C15′—H15′	120.7
C14′—C15′—C16′	118.6 (3)	C16′—C15′—H15′	120.7
C17′—C16′—C15′	120.8 (3)	C17′—C16′—H16′	119.6
C16′—C17′—C18′	119.9 (3)	C15′—C16′—H16′	119.6
C17′—C18′—C19′	120.7 (3)	C16′—C17′—H17′	120.1
C14′—C19′—C18′	118.5 (3)	C18′—C17′—H17′	120.1
C21′—C20′—C25′	119.7 (3)	C17′—C18′—H18′	119.6
C21′—C20′—N4′	121.2 (2)	C19′—C18′—H18′	119.6
C25′—C20′—N4′	119.1 (2)	C14′—C19′—H19′	120.8
C22′—C21′—C20′	120.5 (3)	C18′—C19′—H19′	120.8
C21′—C22′—C23′	118.7 (3)	C22′—C21′—H21′	119.8
C24′—C23′—C22′	122.0 (3)	C20′—C21′—H21′	119.8
C24′—C23′—Br1′	120.4 (2)	C21′—C22′—H22′	120.6
C22′—C23′—Br1′	117.5 (2)	C23′—C22′—H22′	120.6
C23′—C24′—C25′	119.0 (3)	C23′—C24′—H24′	120.5
C24′—C25′—C20′	120.1 (3)	C25′—C24′—H24′	120.5
N1—C5—H5	126.7	C24′—C25′—H25′	120.0
C4—C5—H5	126.7	C20′—C25′—H25′	120.0

C5—N1—N2—C3	−0.1 (3)	C5′—N1′—N2′—C3′	−0.1 (3)
C14—N1—N2—C3	−176.7 (2)	C14′—N1′—N2′—C3′	−177.8 (3)
N1—N2—C3—C4	0.7 (3)	N1′—N2′—C3′—C4′	1.1 (3)
N1—N2—C3—C6	−178.7 (2)	N1′—N2′—C3′—C6′	−178.4 (3)
N2—C3—C4—C5	−1.0 (3)	N2′—C3′—C4′—C5′	−1.6 (3)
C6—C3—C4—C5	178.3 (3)	C6′—C3′—C4′—C5′	177.8 (3)
N2—C3—C4—C10	176.7 (3)	N2′—C3′—C4′—C10′	176.9 (3)
C6—C3—C4—C10	−4.0 (5)	C6′—C3′—C4′—C10′	−3.7 (5)
N2—N1—C5—C4	−0.5 (3)	N2′—N1′—C5′—C4′	−0.9 (3)
C14—N1—C5—C4	175.6 (3)	C14′—N1′—C5′—C4′	176.5 (3)
C3—C4—C5—N1	0.9 (3)	C10′—C4′—C5′—N1′	−176.9 (3)
C10—C4—C5—N1	−176.6 (3)	C3′—C4′—C5′—N1′	1.4 (3)
N2—C3—C6—C7	−107.2 (3)	N2′—C3′—C6′—C7′	−102.1 (3)
C4—C3—C6—C7	73.5 (4)	C4′—C3′—C6′—C7′	78.5 (4)
C3—C6—C7—C8	54.6 (4)	C3′—C6′—C7′—C8′	56.1 (4)
C3—C6—C7—C9	177.9 (3)	C3′—C6′—C7′—C9′	179.8 (3)
C5—C4—C10—C11	−0.3 (5)	C5′—C4′—C10′—C11′	−3.0 (5)
C3—C4—C10—C11	−177.4 (3)	C3′—C4′—C10′—C11′	178.9 (3)
C4—C10—C11—C13	−2.5 (5)	C4′—C10′—C11′—C13′	−2.7 (5)
C4—C10—C11—C12	177.3 (3)	C4′—C10′—C11′—C12′	177.6 (3)
C10—C11—C12—O1	−24.1 (4)	C10′—C11′—C12′—O1′	−24.7 (4)
C13—C11—C12—O1	155.7 (3)	C13′—C11′—C12′—O1′	155.5 (3)
C10—C11—C12—N4	156.4 (3)	C10′—C11′—C12′—N4′	155.5 (3)
C13—C11—C12—N4	−23.8 (4)	C13′—C11′—C12′—N4′	−24.2 (4)
O1—C12—N4—C20	0.4 (5)	O1′—C12′—N4′—C20′	0.6 (5)
C11—C12—N4—C20	179.9 (3)	C11′—C12′—N4′—C20′	−179.6 (3)
C5—N1—C14—C15	10.7 (5)	C5′—N1′—C14′—C15′	23.4 (5)
N2—N1—C14—C15	−173.4 (3)	N2′—N1′—C14′—C15′	−159.4 (3)

C5—N1—C14—C19	−168.4 (3)	C5′—N1′—C14′—C19′	−155.8 (3)
N2—N1—C14—C19	7.5 (4)	N2′—N1′—C14′—C19′	21.5 (4)
C19—C14—C15—C16	1.6 (5)	C19′—C14′—C15′—C16′	−0.3 (5)
N1—C14—C15—C16	−177.6 (3)	N1′—C14′—C15′—C16′	−179.5 (3)
C14—C15—C16—C17	−0.2 (5)	C14′—C15′—C16′—C17′	0.3 (5)
C15—C16—C17—C18	−1.0 (5)	C15′—C16′—C17′—C18′	−0.4 (5)
C16—C17—C18—C19	0.9 (5)	C16′—C17′—C18′—C19′	0.6 (5)
C17—C18—C19—C14	0.4 (5)	C15′—C14′—C19′—C18′	0.5 (5)
C15—C14—C19—C18	−1.7 (5)	N1′—C14′—C19′—C18′	179.6 (3)
N1—C14—C19—C18	177.4 (3)	C17′—C18′—C19′—C14′	−0.6 (5)
C12—N4—C20—C21	34.5 (4)	C12′—N4′—C20′—C21′	37.1 (4)
C12—N4—C20—C25	−146.8 (3)	C12′—N4′—C20′—C25′	−144.8 (3)
C25—C20—C21—C22	1.7 (4)	C25′—C20′—C21′—C22′	2.1 (4)
N4—C20—C21—C22	−179.7 (3)	N4′—C20′—C21′—C22′	−179.8 (3)
C20—C21—C22—C23	−0.1 (4)	C20′—C21′—C22′—C23′	−0.6 (4)
C21—C22—C23—C24	−2.0 (4)	C21′—C22′—C23′—C24′	−1.4 (4)
C21—C22—C23—Br1	179.4 (2)	C21′—C22′—C23′—Br1′	179.1 (2)
C22—C23—C24—C25	2.5 (4)	C22′—C23′—C24′—C25′	1.9 (4)
Br1—C23—C24—C25	−178.9 (2)	Br1′—C23′—C24′—C25′	−178.6 (2)
C23—C24—C25—C20	−0.9 (4)	C23′—C24′—C25′—C20′	−0.4 (4)
C21—C20—C25—C24	−1.1 (4)	C21′—C20′—C25′—C24′	−1.5 (4)
N4—C20—C25—C24	−179.8 (3)	N4′—C20′—C25′—C24′	−179.7 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···N3′	0.82 (3)	2.31 (3)	3.107 (3)	162 (3)
N4′—H4′···N3	0.82 (3)	2.32 (4)	3.097 (3)	158 (4)
C15—H15···O1′^{i}	0.95	2.50	3.417 (4)	162
C15′—H15′···O1^{ii}	0.95	2.51	3.455 (4)	174
C16′—H16′···Br1^{iii}	0.95	2.91	3.813 (3)	159
C16—H16···Br1′^{iii}	0.95	2.89	3.726 (3)	148

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