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ISSN 2414-3146

trans-Bis[2-(pyrimidin-2-yl)ethynyl]bis(triphenylphosphine)palladium

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Received 14 July 2025

Accepted 16 July 2025

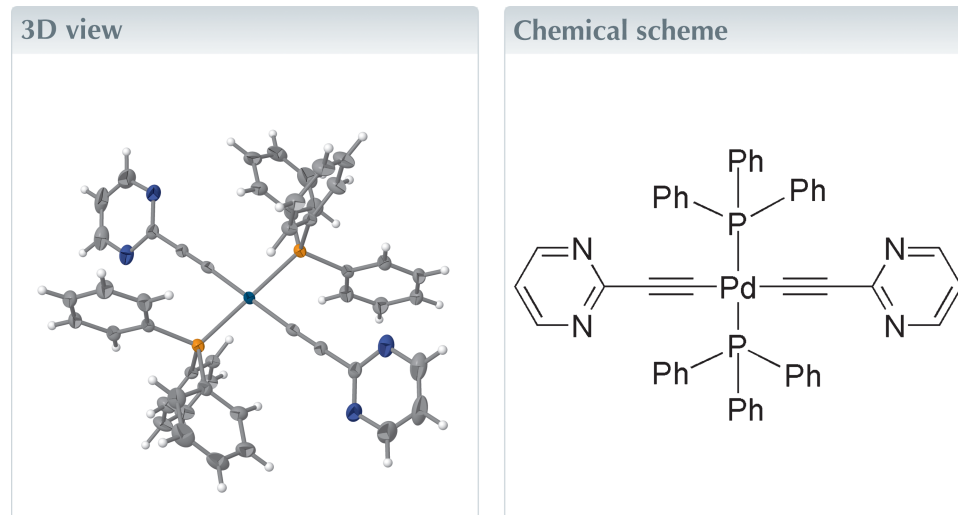
Edited by L. Van Meervelt, Katholieke Universiteit Leuven, Belgium

Keywords: crystal structure; Sonogashira coupling reaction; bis alkynylpalladium complex.

CCDC reference: 2473412

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

The title palladium complex, $[\text{Pd}(\text{C}_6\text{H}_3\text{N}_2)_2(\text{C}_{18}\text{H}_{15}\text{P})_2]$, was isolated as an impurity that co-eluted with the organic product of a palladium-catalyzed Sonogashira coupling. It crystallizes in the monoclinic space group $C2/c$ with one half of the complex in the asymmetric unit. The palladium atom (site symmetry $\bar{1}$) has a square-planar geometry with *trans* phosphine ligands. The P–Pd–C angle is $95.19(9)^\circ$.



Structure description

The Sonogashira reaction is a palladium-catalyzed cross-coupling reaction of aryl- and vinylhalides with terminal alkynes to form alkynylbenzenes (Sonogashira *et al.*, 1975). The mechanism involves a transient intermediate in which the aryl and alkynyl moieties are both bound to the palladium atom. Subsequently, reductive elimination yields the aryl alkyne. The intentional formation of mono- and bis-arylethynyl palladium complexes has separately been exploited in a variety of fields, including self-assembled metallocycles (Sepehrpour *et al.*, 2019) and nonlinear optical materials (Yang *et al.*, 1995). Herein we describe the structure of the title bis-alkynyl palladium complex, $[\text{Pd}(\text{C}_6\text{H}_3\text{N}_2)_2(\text{C}_{18}\text{H}_{15}\text{P})_2]$, fortuitously isolated during the workup of a Sonogashira coupling reaction performed with a slight excess of 2-ethynylpyrimidine.

The asymmetric unit contains one half of the complex as shown in Fig. 1. The palladium atom adopts square-planar geometry with symmetry-constrained linear P–Pd–P and C–Pd–C bonds and a P1–Pd1–C1 angle of $95.19(9)^\circ$. The pyrimidine rings are twisted by $28.42(9)^\circ$ relative to the plane defined by the four atoms directly bonded to palladium. The Pd1–C1 distance is 2.008(3) Å. A search of the Cambridge Structural Database (CSD, version 2025.1.1; Groom *et al.*, 2016) for related bis-ethynyl bis-phosphino palladium complexes yielded 14 unique structures. In these structures, the Pd–C distance ranges from 1.986 to 2.069 Å with an average of 2.012 Å.



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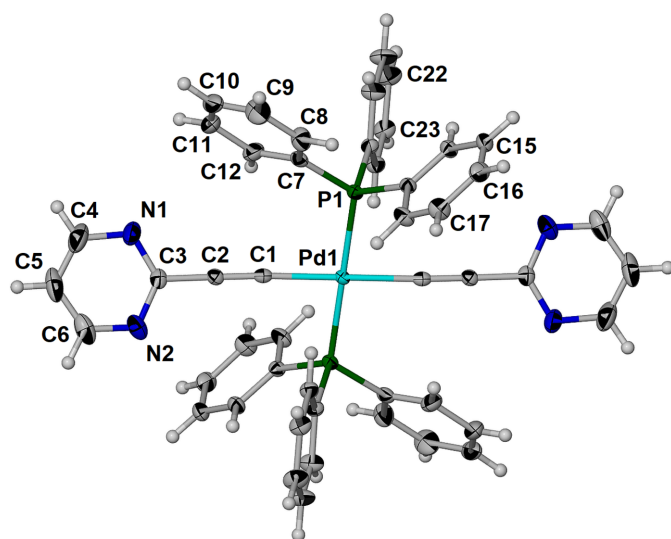


Figure 1
Partially labeled asymmetric unit of the title palladium complex, $[\text{Pd}(\text{C}_6\text{H}_3\text{N}_2)_2(\text{C}_{18}\text{H}_{15}\text{P})_2]$, including the symmetry-generated half of the complex (symmetry operation: $\frac{3}{2} - x, \frac{3}{2} - y, 1 - z$).

The crystal packing (Fig. 2) along with a view of the Hirshfeld surface (Fig. 3; Spackman *et al.*, 2021) show that, as expected, the major inter-complex interactions involve interdigitation of the aromatic moieties. Accordingly, element-to-element analysis of these interactions shows that major interactions are $\text{H} \cdots \text{H}$, $\text{C} \cdots \text{H}/\text{H} \cdots \text{C}$ and $\text{N} \cdots \text{H}/\text{H} \cdots \text{N}$ interactions corresponding to 52.3, 34.1 and 10.4% of the surface area, respectively.

We recently described the structures of arylpalladium iodide complexes also incidentally isolated from Sonogashira reaction products where the reactions were performed with a slight excess of the aryl iodide (Bosch, 2025). These results provide some insight into the fate of the palladium catalyst in the Sonogashira coupling reaction provided that one of the organic reagents is initially in slight excess.

Synthesis and crystallization

The complex was isolated after a Sonogashira coupling reaction between 1,3,5-trifluoro-2-iodobenzene and 2-ethynylpyrimidine. The reaction was performed with a slight excess,

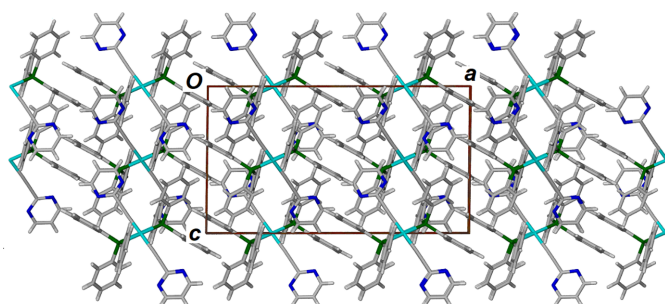


Figure 2
View along the *b* axis of the crystal packing of the title palladium complex $[\text{Pd}(\text{C}_6\text{H}_3\text{N}_2)_2(\text{C}_{18}\text{H}_{15}\text{P})_2]$.

Table 1
Experimental details.

Crystal data	
Chemical formula	$[\text{Pd}(\text{C}_6\text{H}_3\text{N}_2)_2(\text{C}_{18}\text{H}_{15}\text{P})_2]$
M_r	837.15
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	100
a, b, c (Å)	22.1529 (13), 13.7110 (13), 12.3853 (9)
β (°)	90.690 (2)
V (Å ³)	3761.6 (5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.62
Crystal size (mm)	0.35 × 0.20 × 0.02
Data collection	
Diffractometer	Bruker APEXI CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
$T_{\text{min}}, T_{\text{max}}$	0.564, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	24110, 4171, 3041
R_{int}	0.079
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.642
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.039, 0.091, 1.02
No. of reflections	4171
No. of parameters	250
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.59, -0.66

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT2018/2* (Sheldrick, 2015a), *SHELXL2019/2* (Sheldrick, 2015b) and *X-SEED-4* (Barbour, 2020).

1.05 molar equiv., of the ethynylpyrimidine. The product was detected as an orange crystalline impurity in the bulk product 2-(2,4,6-trifluorophenylethynyl)pyrimidine isolated after flash chromatography with mixtures of hexane and ethyl acetate. Manual separation afforded small amounts of the complex in crystalline form suitable for single-crystal X-ray crystallography.

Refinement

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

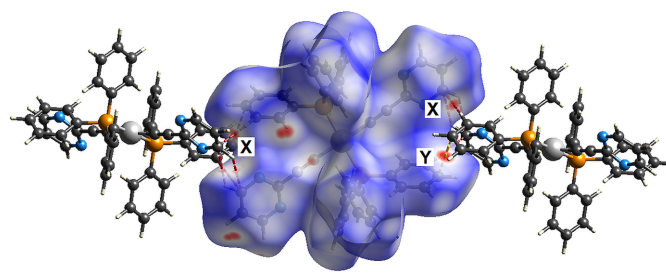


Figure 3
Hirshfeld surface of the title palladium complex $[\text{Pd}(\text{C}_6\text{H}_3\text{N}_2)_2(\text{C}_{18}\text{H}_{15}\text{P})_2]$, with two adjacent interacting complexes. $\text{C} \cdots \text{H}$ and $\text{C} \cdots \text{C}$ intermolecular interactions are shown as red and yellow dashed lines, respectively, and labelled X and Y.

Acknowledgements

We thank the Missouri State University Provost Incentive Fund that funded the purchase of the X-ray diffractometer.

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full crystallographic data

IUCrData (2025). **10**, x250636 [<https://doi.org/10.1107/S2414314625006364>]

***trans*-Bis[2-(pyrimidin-2-yl)ethynyl]bis(triphenylphosphine)palladium**

Eric Bosch

(I)

Crystal data[Pd(C₆H₅N₂)₂(C₁₈H₁₅P)₂] $M_r = 837.15$ Monoclinic, *C2/c* $a = 22.1529$ (13) Å $b = 13.7110$ (13) Å $c = 12.3853$ (9) Å $\beta = 90.690$ (2)° $V = 3761.6$ (5) Å³ $Z = 4$ $F(000) = 1712$ $D_x = 1.478$ Mg m⁻³Mo *K* α radiation, $\lambda = 0.71073$ Å

Cell parameters from 3308 reflections

 $\theta = 2.4$ – 23.5 ° $\mu = 0.62$ mm⁻¹ $T = 100$ K

Plate, orange

0.35 × 0.20 × 0.02 mm

*Data collection*Bruker APEXI CCD
diffractometerDetector resolution: 8.3660 pixels mm⁻¹ φ and ω scansAbsorption correction: multi-scan
(SADABS; Krause *et al.*, 2015) $T_{\min} = 0.564$, $T_{\max} = 0.746$

24110 measured reflections

4171 independent reflections

3041 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.079$ $\theta_{\max} = 27.1$ °, $\theta_{\min} = 1.8$ ° $h = -28$ → 28 $k = -17$ → 17 $l = -15$ → 15 *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.039$ $wR(F^2) = 0.091$ $S = 1.02$

4171 reflections

250 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.034P)^2 + 7.3694P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.59$ e Å⁻³ $\Delta\rho_{\min} = -0.66$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Pd1	0.750000	0.750000	0.500000	0.01796 (10)
P1	0.66798 (4)	0.66217 (6)	0.56457 (6)	0.01975 (18)
N1	0.58722 (14)	0.9407 (2)	0.2463 (3)	0.0449 (9)
C1	0.70247 (14)	0.8220 (2)	0.3862 (2)	0.0209 (7)
N2	0.67884 (15)	0.9460 (2)	0.1481 (2)	0.0372 (8)
C2	0.67628 (14)	0.8677 (2)	0.3173 (2)	0.0211 (7)
C3	0.64549 (15)	0.9208 (2)	0.2336 (3)	0.0252 (7)
C4	0.5602 (2)	0.9855 (3)	0.1602 (4)	0.0638 (15)
H4	0.518332	1.000109	0.163862	0.077*
C5	0.5901 (2)	1.0098 (3)	0.0706 (4)	0.0581 (14)
H5	0.569826	1.038911	0.010696	0.070*
C6	0.6500 (2)	0.9914 (3)	0.0683 (3)	0.0473 (11)
H6	0.672319	1.011791	0.007286	0.057*
C7	0.59797 (15)	0.6599 (3)	0.4845 (2)	0.0253 (7)
C8	0.56959 (17)	0.5749 (3)	0.4499 (3)	0.0372 (9)
H8	0.587809	0.513304	0.463157	0.045*
C9	0.51444 (19)	0.5807 (4)	0.3958 (3)	0.0513 (12)
H9	0.495113	0.522482	0.372235	0.062*
C10	0.48739 (17)	0.6689 (4)	0.3759 (3)	0.0456 (11)
H10	0.449183	0.671727	0.340330	0.055*
C11	0.51582 (16)	0.7524 (4)	0.4074 (3)	0.0444 (10)
H11	0.497736	0.813819	0.392644	0.053*
C12	0.57103 (15)	0.7480 (3)	0.4611 (3)	0.0351 (8)
H12	0.590602	0.806847	0.482071	0.042*
C13	0.68175 (14)	0.5330 (2)	0.5896 (2)	0.0213 (7)
C14	0.67023 (15)	0.4879 (2)	0.6875 (3)	0.0252 (7)
H14	0.658594	0.525676	0.748053	0.030*
C15	0.67578 (15)	0.3873 (3)	0.6965 (3)	0.0304 (8)
H15	0.668344	0.356419	0.763764	0.036*
C16	0.69201 (16)	0.3318 (3)	0.6085 (3)	0.0338 (8)
H16	0.694506	0.262872	0.614631	0.041*
C17	0.70460 (17)	0.3766 (3)	0.5118 (3)	0.0344 (9)
H17	0.716307	0.338504	0.451546	0.041*
C18	0.70025 (16)	0.4772 (3)	0.5021 (3)	0.0306 (8)
H18	0.709901	0.508013	0.435808	0.037*
C19	0.64234 (14)	0.7144 (2)	0.6911 (3)	0.0216 (7)
C20	0.58997 (16)	0.6818 (3)	0.7404 (3)	0.0329 (8)
H20	0.567433	0.630066	0.708617	0.039*
C21	0.57048 (17)	0.7238 (3)	0.8348 (3)	0.0387 (10)
H21	0.535143	0.700015	0.868562	0.046*
C22	0.60193 (17)	0.8000 (3)	0.8802 (3)	0.0372 (9)
H22	0.588364	0.828918	0.945278	0.045*
C23	0.65326 (16)	0.8344 (3)	0.8313 (3)	0.0309 (8)
H23	0.674524	0.888152	0.861690	0.037*
C24	0.67402 (15)	0.7907 (2)	0.7374 (3)	0.0256 (7)

H24 0.710074 0.813407 0.705116 0.031*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.01900 (17)	0.01846 (16)	0.01646 (16)	-0.00124 (16)	0.00149 (12)	0.00134 (15)
P1	0.0215 (4)	0.0208 (4)	0.0170 (4)	-0.0020 (3)	0.0017 (3)	-0.0003 (3)
N1	0.0306 (18)	0.041 (2)	0.062 (2)	-0.0024 (15)	-0.0102 (16)	0.0225 (17)
C1	0.0194 (16)	0.0203 (16)	0.0232 (16)	-0.0026 (13)	0.0048 (13)	-0.0031 (13)
N2	0.058 (2)	0.0295 (17)	0.0238 (16)	0.0020 (15)	0.0020 (15)	0.0012 (13)
C2	0.0240 (17)	0.0203 (16)	0.0192 (16)	-0.0004 (13)	0.0023 (13)	-0.0015 (13)
C3	0.0289 (19)	0.0192 (17)	0.0275 (18)	-0.0030 (14)	-0.0054 (15)	0.0005 (14)
C4	0.036 (3)	0.059 (3)	0.096 (4)	-0.007 (2)	-0.025 (3)	0.032 (3)
C5	0.075 (4)	0.040 (3)	0.059 (3)	-0.015 (2)	-0.034 (3)	0.023 (2)
C6	0.080 (4)	0.032 (2)	0.029 (2)	-0.005 (2)	-0.010 (2)	0.0017 (17)
C7	0.0255 (18)	0.0334 (19)	0.0172 (16)	-0.0029 (15)	0.0028 (13)	0.0026 (14)
C8	0.040 (2)	0.040 (2)	0.031 (2)	-0.0081 (18)	-0.0111 (17)	0.0007 (17)
C9	0.043 (3)	0.067 (3)	0.043 (2)	-0.023 (2)	-0.016 (2)	0.002 (2)
C10	0.024 (2)	0.083 (3)	0.029 (2)	-0.006 (2)	-0.0055 (16)	0.014 (2)
C11	0.0243 (18)	0.064 (3)	0.045 (2)	0.006 (2)	0.0011 (16)	0.018 (2)
C12	0.0238 (17)	0.0376 (19)	0.044 (2)	0.0008 (19)	0.0023 (15)	0.003 (2)
C13	0.0206 (16)	0.0220 (16)	0.0213 (16)	-0.0035 (13)	-0.0001 (13)	0.0007 (13)
C14	0.0284 (19)	0.0279 (18)	0.0192 (16)	-0.0017 (15)	0.0011 (14)	0.0012 (14)
C15	0.0291 (19)	0.031 (2)	0.0306 (19)	-0.0011 (16)	0.0002 (15)	0.0108 (16)
C16	0.033 (2)	0.0231 (18)	0.046 (2)	-0.0005 (15)	0.0032 (17)	0.0059 (17)
C17	0.043 (2)	0.0261 (19)	0.034 (2)	0.0026 (17)	0.0046 (17)	-0.0057 (16)
C18	0.039 (2)	0.0305 (19)	0.0221 (17)	-0.0024 (16)	0.0057 (15)	0.0009 (15)
C19	0.0204 (16)	0.0213 (15)	0.0230 (16)	0.0003 (13)	0.0018 (13)	-0.0026 (13)
C20	0.031 (2)	0.040 (2)	0.0282 (19)	-0.0098 (17)	0.0043 (15)	-0.0097 (16)
C21	0.030 (2)	0.049 (3)	0.038 (2)	-0.0066 (17)	0.0128 (17)	-0.0106 (17)
C22	0.034 (2)	0.046 (2)	0.031 (2)	0.0018 (18)	0.0061 (17)	-0.0159 (18)
C23	0.030 (2)	0.034 (2)	0.0289 (19)	-0.0009 (16)	-0.0002 (15)	-0.0095 (16)
C24	0.0235 (18)	0.0278 (17)	0.0254 (17)	0.0002 (14)	0.0017 (14)	-0.0020 (14)

Geometric parameters (Å, °)

Pd1—C1	2.008 (3)	C8—C9	1.389 (5)
Pd1—C1 ⁱ	2.008 (3)	C9—C10	1.371 (6)
Pd1—P1 ⁱ	2.3293 (8)	C10—C11	1.362 (6)
Pd1—P1	2.3294 (8)	C11—C12	1.386 (5)
P1—C19	1.820 (3)	C13—C14	1.387 (4)
P1—C13	1.823 (3)	C13—C18	1.392 (4)
P1—C7	1.831 (3)	C14—C15	1.390 (5)
N1—C3	1.331 (5)	C15—C16	1.380 (5)
N1—C4	1.362 (5)	C16—C17	1.378 (5)
C1—C2	1.202 (4)	C17—C18	1.388 (5)
N2—C6	1.325 (5)	C19—C24	1.381 (4)
N2—C3	1.344 (4)	C19—C20	1.391 (5)

C2—C3	1.433 (4)	C20—C21	1.378 (5)
C4—C5	1.342 (6)	C21—C22	1.372 (5)
C5—C6	1.352 (6)	C22—C23	1.379 (5)
C7—C12	1.377 (5)	C23—C24	1.391 (5)
C7—C8	1.389 (5)		
C1—Pd1—C1 ⁱ	180.0	C12—C7—P1	117.5 (3)
C1—Pd1—P1 ⁱ	84.81 (9)	C8—C7—P1	124.0 (3)
C1 ⁱ —Pd1—P1 ⁱ	95.19 (9)	C9—C8—C7	119.6 (4)
C1—Pd1—P1	95.19 (9)	C10—C9—C8	121.1 (4)
C1 ⁱ —Pd1—P1	84.81 (9)	C11—C10—C9	119.3 (4)
P1 ⁱ —Pd1—P1	180.0	C10—C11—C12	120.3 (4)
C19—P1—C13	106.82 (14)	C7—C12—C11	121.1 (4)
C19—P1—C7	101.63 (15)	C14—C13—C18	119.6 (3)
C13—P1—C7	102.39 (15)	C14—C13—P1	123.3 (2)
C19—P1—Pd1	110.17 (11)	C18—C13—P1	116.9 (2)
C13—P1—Pd1	115.53 (11)	C13—C14—C15	119.8 (3)
C7—P1—Pd1	118.82 (11)	C16—C15—C14	120.4 (3)
C3—N1—C4	114.7 (4)	C17—C16—C15	119.9 (3)
C2—C1—Pd1	177.0 (3)	C16—C17—C18	120.3 (3)
C6—N2—C3	116.4 (4)	C17—C18—C13	120.0 (3)
C1—C2—C3	178.9 (4)	C24—C19—C20	118.9 (3)
N1—C3—N2	125.7 (3)	C24—C19—P1	119.6 (2)
N1—C3—C2	118.2 (3)	C20—C19—P1	121.4 (2)
N2—C3—C2	116.1 (3)	C21—C20—C19	120.6 (3)
C5—C4—N1	122.8 (4)	C22—C21—C20	120.2 (3)
C4—C5—C6	117.7 (4)	C21—C22—C23	119.8 (3)
N2—C6—C5	122.5 (4)	C22—C23—C24	120.2 (3)
C12—C7—C8	118.5 (3)	C19—C24—C23	120.1 (3)

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