IUCrData

ISSN 2414-3146

# Tetraethylammonium (acetonitrile)trichloridopalladate(II)

Alan J. Oberley,[a,b] Lava R. Kadel,[a] Nilmini K. Senaratne[a] and David M. Eichhorn[a]*

[a]Department of Chemistry, Wichita State University, 1845 Fairmount, Wichita, KS 67260-0051, USA, and [b]Division of Science and Mathematics, Newman University, 3100 McCormick, Wichita, KS 67213, USA. *Correspondence e-mail: david.eichhorn@wichita.edu

Received 17 May 2018
Accepted 17 May 2018

Edited by M. Bolte, Goethe-Universität Frankfurt, Germany

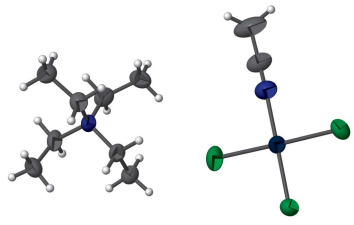
**Keywords:** crystal structure; palladium.

**CCDC reference**: 1843858

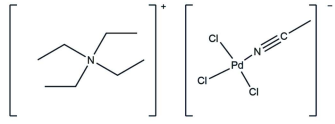
**Structural data**: full structural data are available from iucrdata.iucr.org

A new square-planar palladium complex salt, $(C_8H_{20}N)[PdCl_3(C_2H_3N)]$, has been formed with one of the Cl atoms in tetrachloridopalladate(II) replaced by an acetonitrile coordinated through the N atom. This compound could be a useful precursor for synthesis of palladium complexes. The complex salt crystallizes in the monoclinic $P2_1/c$ space group.

**3D view**



**Chemical scheme**




## Structure description

In the title compound (Fig. 1), the palladium is square planar, with three chlorine atoms, and one acetonitrile coordinated through the nitrogen. Charge balance for the mono-anionic complex is provided by a tetraethylammonium ion. A search of the Cambridge Structural Database reveals one other complex with a (nitrile)$PdCl_3$ structure (Chitsaz *et al.*, 2000) and ten complexes with the $PdCl_3$ moiety coordinated by a N donor (Urankar *et al.*, 2010; Maronna *et al.*, 2011; Gómez-Villarraga *et al.*, 2017; Savel'eva *et al.*, 2009; Lee *et al.*, 2005; von Arnim *et al.*, 1991; Kelly *et al.*, 1991; Makotchenko & Buidina, 2009; Kelly *et al.*, 1995; Aragay *et al.*, 2008). Structures have also been reported of $[(CH_3CN)_2PdCl_2]$ (Edwards *et al.*, 1998; Ramirez de Arellano *et al.*, 2006; Malecki, 2013; Malecki, 2017) and of $[(CH_3CN)_3PdCl]^+$ (Demchuk *et al.*, 2011). The title compound shows very similar Pd—N and Pd—Cl bond distances (Table 1) to all of the previously reported complexes.

## Synthesis and crystallization

The title compound was synthesized by dissolving 0.498 g of 3-ethyl-4-cyanopyrazole in 30 ml of acetonitrile, with some impurities left to settle. The solution was decanted, and added to a solution of 0.15 g of tetraethylammonium tetrachloridopalladate(II) in 50 ml of acetonitrile. The solvent was removed, and the precipitate was redissolved in aceto-

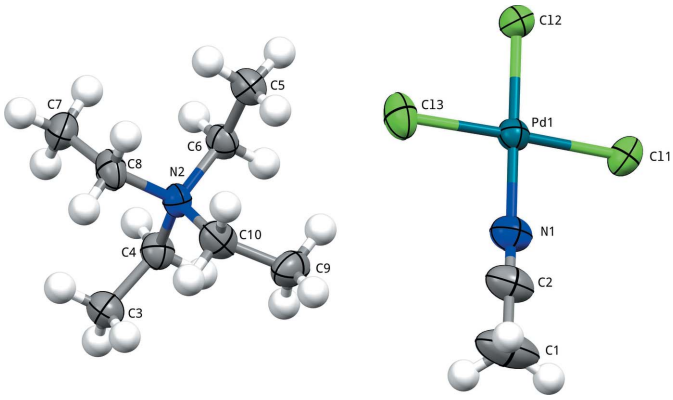



**Figure 1**
The title compound with displacement ellipsoids drawn at the 50% probability level. H atoms drawn as spheres of arbitrary radii.

nitrile. Diethyl ether was allowed to diffuse into the acetonitrile solution, and crystals appeared overnight.

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.


## Acknowledgements

AO acknowledges Newman University for providing sabbatical support.

## Funding information

Funding for this research was provided by: Newman University; Wichita State University.


**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Pd1—Cl1 | 2.3040 (11) | Pd1—N1 | 2.024 (3) |
| Pd1—Cl2 | 2.2621 (10) | N1—C2 | 1.108 (5) |
| Pd1—Cl3 | 2.2953 (11) | | |
| | | | |
| Cl2—Pd1—Cl1 | 90.44 (3) | Cl3—Pd1—Cl1 | 177.84 (3) |
| Cl2—Pd1—Cl3 | 90.26 (3) | N1—Pd1—Cl2 | 177.08 (8) |
| N1—Pd1—Cl1 | 90.55 (9) | C2—N1—Pd1 | 171.1 (3) |
| N1—Pd1—Cl3 | 88.84 (9) | | |

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $(C_8H_{20}N)[PdCl_3(C_2H_3N)]$ |
| $M_r$ | 384.05 |
| Crystal system, space group | Monoclinic, $P2_1/c$ |
| Temperature (K) | 150 |
| $a, b, c$ (Å) | 7.286 (2), 17.379 (5), 12.950 (3) |
| $\beta$ (°) | 102.769 (13) |
| $V$ (Å$^3$) | 1599.3 (8) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 1.64 |
| Crystal size (mm) | 0.63 × 0.57 × 0.31 |
| | |
| Data collection | |
| Diffractometer | Bruker APEXII CCD |
| Absorption correction | Numerical (*SADABS*; Bruker, 2012) |
| $T_{min}$, $T_{max}$ | 0.589, 0.746 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 54175, 3516, 2804 |
| $R_{int}$ | 0.054 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.642 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.033, 0.092, 1.06 |
| No. of reflections | 3516 |
| No. of parameters | 150 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.91, −0.61 |

Computer programs: *APEX2* and *SAINT* (Bruker, 2016), *SIR2004* (Burla *et al.*, 2007), *SHELXL* (Sheldrick, 2008) and *OLEX2* (Dolomanov *et al.*, 2009).

## References


Aragay, G., Pons, J., García-Antón, J., Solans, X., Font-Bardia, M. & Ros, J. (2008). *J. Organomet. Chem.* **693**, 3396–3404.
Arnim, H. von, Massa, W., Zinn, A. & Dehnicke, K. (1991). *Z. Naturforsch. Teil B*, **46**, 992–998.
Bruker (2012). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2016). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G., Siliqi, D. & Spagna, R. (2007). *J. Appl. Cryst.* **40**, 609–613.
Chitsaz, S., Neumüller, B. & Dehnicke, K. (2000). *Z. Anorg. Allg. Chem.* **626**, 634–638.
Demchuk, O. M., Kielar, K. & Pietrusiewicz, K. M. (2011). *Pure Appl. Chem.* **83**, 633–644.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Edwards, P. G., Paisey, S. J. & Albers, T. (1998). Private communication (refcode: FEQCOT). CCDC, Cambridge, England.
Gómez-Villarraga, F., De Tovar, J., Guerrero, M., Nolis, P., Parella, T., Lecante, P., Romero, N., Escriche, L., Bofill, R., Ros, J., Sala, X., Philippot, K. & García-Antón, J. (2017). *Dalton Trans.* **46**, 11768–11778.
Kelly, P. F. & Slawin, A. M. Z. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1758–1759.
Kelly, P. F., Slawin, A. M. Z., Williams, D. J. & Woollins, J. D. (1991). *Polyhedron*, **10**, 2337–2340.
Lee, H. M., Chiu, P. L., Hu, C.-H., Lai, C. L. & Chou, Y.-C. J. (2005). *J. Organomet. Chem.* **690**, 403–414.
Makotchenko, E. V. & Buidina, I. A. (2009). *Russ. J. Coord. Chem.* **35**, 212–216.
Malecki, J. G. (2013). Private communication (refcode: FEQCOT02). CCDC, Cambridge, England.
Malecki, J. G. (2017). Private communication (refcode: FEQCOT03). CCDC, Cambridge, England.
Maronna, A., Bindewald, E., Kaifer, E., Wadepohl, H. & Himmel, H. J. (2011). *Eur. J. Inorg. Chem.* pp. 1302–1314.
Ramirez de Arellano, R., Asensio, G., Medio-Simon, M., Rodriguez, N. & Mancha, G. (2006). Private communication (refcode: FEQCOT01). CCDC, Cambridge, England.
Savel'eva, Z. A., Glinskaya, L. A., Popov, S. A., Klevtsova, R. F., Tkachev, A. V. & Larionov, S. V. (2009). *Russ. J. Coord. Chem.* **35**, 668–673.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Urankar, D., Pevec, A., Turel, I. & Košmrlj, J. (2010). *Cryst. Growth Des.* **10**, 4920–4927.

# full crystallographic data

*IUCrData* (2018). **3**, x180750 [https://doi.org/10.1107/S2414314618007502]

## Tetraethylammonium (acetonitrile)trichloridopalladate(II)

**Alan J. Oberley, Lava R. Kadel, Nilmini K. Senaratne and David M. Eichhorn**

### Tetraethylammonium (acetonitrile)trichloridopalladate(II)

*Crystal data*

$(C_8H_{20}N)[PdCl_3(C_2H_3N)]$
$M_r$ = 384.05
Monoclinic, $P2_1/c$
$a$ = 7.286 (2) Å
$b$ = 17.379 (5) Å
$c$ = 12.950 (3) Å
$\beta$ = 102.769 (13)°
$V$ = 1599.3 (8) Å$^3$
$Z$ = 4
$F(000)$ = 776
$D_x$ = 1.595 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 8735 reflections
$\theta$ = 3.2–26.2°
$\mu$ = 1.64 mm$^{-1}$
$T$ = 150 K
Irregular, reddish brown
0.63 × 0.57 × 0.31 mm

*Data collection*

Bruker APEXII CCD diffractometer
Radiation source: sealed X-ray tube
Graphite monochromator
Detector resolution: 5.6 pixels mm$^{-1}$
$\varphi$ and $\omega$ scans
Absorption correction: numerical (SADABS; Bruker, 2012)
$T_{min}$ = 0.589, $T_{max}$ = 0.746
54175 measured reflections
3516 independent reflections
2804 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.054
$\theta_{max}$ = 27.2°, $\theta_{min}$ = 3.7°
$h$ = −9→9
$k$ = −22→22
$l$ = −16→16

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.092
$S$ = 1.06
3516 reflections
150 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 0.4406P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.91 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.61 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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Pd1 | 0.25580 (3) | 0.43656 (2) | 0.67953 (2) | 0.03879 (10) |
| Cl1 | 0.32497 (12) | 0.30742 (5) | 0.70147 (6) | 0.0518 (2) |
| Cl2 | 0.19617 (13) | 0.44208 (4) | 0.84354 (7) | 0.0518 (2) |
| Cl3 | 0.19872 (15) | 0.56612 (5) | 0.65811 (9) | 0.0645 (3) |
| N1 | 0.2950 (4) | 0.43234 (17) | 0.5297 (2) | 0.0567 (8) |
| C1 | 0.2887 (7) | 0.4325 (3) | 0.3309 (3) | 0.0967 (19) |
| H1A | 0.1600 | 0.4424 | 0.2911 | 0.145* |
| H1B | 0.3308 | 0.3824 | 0.3100 | 0.145* |
| H1C | 0.3725 | 0.4729 | 0.3154 | 0.145* |
| C2 | 0.2927 (5) | 0.4320 (2) | 0.4438 (3) | 0.0649 (10) |
| N2 | 0.2491 (3) | 0.80441 (13) | 0.48732 (17) | 0.0363 (5) |
| C3 | 0.5222 (5) | 0.8575 (2) | 0.4139 (3) | 0.0559 (8) |
| H3A | 0.4597 | 0.8401 | 0.3428 | 0.084* |
| H3B | 0.6589 | 0.8538 | 0.4223 | 0.084* |
| H3C | 0.4874 | 0.9110 | 0.4235 | 0.084* |
| C4 | 0.4611 (4) | 0.80727 (18) | 0.4959 (2) | 0.0450 (7) |
| H4A | 0.5222 | 0.8264 | 0.5672 | 0.054* |
| H4B | 0.5069 | 0.7543 | 0.4894 | 0.054* |
| C5 | 0.0118 (4) | 0.74911 (19) | 0.5853 (3) | 0.0529 (8) |
| H5A | −0.0551 | 0.7241 | 0.5200 | 0.079* |
| H5B | −0.0451 | 0.7994 | 0.5920 | 0.079* |
| H5C | 0.0030 | 0.7170 | 0.6462 | 0.079* |
| C6 | 0.2159 (4) | 0.75965 (17) | 0.5818 (2) | 0.0441 (7) |
| H6A | 0.2744 | 0.7082 | 0.5818 | 0.053* |
| H6B | 0.2806 | 0.7865 | 0.6472 | 0.053* |
| C7 | 0.2554 (5) | 0.93366 (18) | 0.5807 (3) | 0.0600 (9) |
| H7A | 0.1960 | 0.9846 | 0.5739 | 0.090* |
| H7B | 0.3905 | 0.9393 | 0.5844 | 0.090* |
| H7C | 0.2362 | 0.9087 | 0.6454 | 0.090* |
| C8 | 0.1677 (4) | 0.88483 (17) | 0.4855 (3) | 0.0499 (8) |
| H8A | 0.0308 | 0.8807 | 0.4815 | 0.060* |
| H8B | 0.1846 | 0.9114 | 0.4206 | 0.060* |
| C9 | 0.1992 (5) | 0.6812 (2) | 0.3746 (3) | 0.0612 (9) |
| H9A | 0.1275 | 0.6610 | 0.3070 | 0.092* |
| H9B | 0.1670 | 0.6521 | 0.4330 | 0.092* |
| H9C | 0.3341 | 0.6760 | 0.3774 | 0.092* |
| C10 | 0.1512 (5) | 0.7654 (2) | 0.3845 (2) | 0.0532 (8) |
| H10A | 0.0135 | 0.7698 | 0.3775 | 0.064* |
| H10B | 0.1834 | 0.7938 | 0.3247 | 0.064* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Pd1 | 0.03429 (15) | 0.03990 (17) | 0.04187 (15) | −0.00227 (9) | 0.00774 (10) | −0.00026 (9) |
| Cl1 | 0.0536 (4) | 0.0426 (4) | 0.0575 (4) | 0.0055 (4) | 0.0087 (3) | −0.0088 (3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| Cl2 | 0.0653 (5) | 0.0451 (5) | 0.0501 (4) | 0.0020 (4) | 0.0238 (4) | −0.0034 (3) |
| Cl3 | 0.0693 (6) | 0.0423 (5) | 0.0804 (6) | 0.0015 (4) | 0.0132 (5) | 0.0140 (4) |
| N1 | 0.0544 (18) | 0.070 (2) | 0.0474 (16) | −0.0053 (14) | 0.0142 (13) | −0.0013 (13) |
| C1 | 0.074 (3) | 0.167 (6) | 0.054 (2) | −0.021 (3) | 0.024 (2) | 0.003 (2) |
| C2 | 0.053 (2) | 0.095 (3) | 0.048 (2) | −0.0111 (18) | 0.0134 (16) | 0.0024 (17) |
| N2 | 0.0383 (12) | 0.0328 (13) | 0.0364 (11) | −0.0015 (10) | 0.0056 (9) | 0.0030 (9) |
| C3 | 0.055 (2) | 0.056 (2) | 0.0615 (19) | −0.0063 (16) | 0.0226 (16) | −0.0014 (16) |
| C4 | 0.0394 (16) | 0.0444 (18) | 0.0496 (16) | −0.0019 (13) | 0.0061 (13) | −0.0002 (13) |
| C5 | 0.058 (2) | 0.048 (2) | 0.0550 (17) | −0.0044 (15) | 0.0195 (15) | 0.0043 (14) |
| C6 | 0.0541 (18) | 0.0394 (17) | 0.0382 (14) | −0.0017 (14) | 0.0085 (13) | 0.0057 (12) |
| C7 | 0.069 (2) | 0.0399 (19) | 0.077 (2) | −0.0035 (16) | 0.030 (2) | −0.0095 (16) |
| C8 | 0.0473 (17) | 0.0362 (17) | 0.0653 (19) | 0.0015 (14) | 0.0107 (14) | 0.0114 (14) |
| C9 | 0.059 (2) | 0.064 (2) | 0.064 (2) | −0.0167 (18) | 0.0215 (17) | −0.0266 (17) |
| C10 | 0.0543 (19) | 0.063 (2) | 0.0388 (15) | −0.0153 (17) | 0.0036 (13) | −0.0013 (14) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Pd1—Cl1 | 2.3040 (11) | C5—H5A | 0.9800 |
| Pd1—Cl2 | 2.2621 (10) | C5—H5B | 0.9800 |
| Pd1—Cl3 | 2.2953 (11) | C5—H5C | 0.9800 |
| Pd1—N1 | 2.024 (3) | C5—C6 | 1.509 (4) |
| N1—C2 | 1.108 (5) | C6—H6A | 0.9900 |
| C1—H1A | 0.9800 | C6—H6B | 0.9900 |
| C1—H1B | 0.9800 | C7—H7A | 0.9800 |
| C1—H1C | 0.9800 | C7—H7B | 0.9800 |
| C1—C2 | 1.457 (5) | C7—H7C | 0.9800 |
| N2—C4 | 1.524 (4) | C7—C8 | 1.517 (5) |
| N2—C6 | 1.514 (3) | C8—H8A | 0.9900 |
| N2—C8 | 1.516 (4) | C8—H8B | 0.9900 |
| N2—C10 | 1.524 (4) | C9—H9A | 0.9800 |
| C3—H3A | 0.9800 | C9—H9B | 0.9800 |
| C3—H3B | 0.9800 | C9—H9C | 0.9800 |
| C3—H3C | 0.9800 | C9—C10 | 1.517 (5) |
| C3—C4 | 1.515 (4) | C10—H10A | 0.9900 |
| C4—H4A | 0.9900 | C10—H10B | 0.9900 |
| C4—H4B | 0.9900 | | |
| | | | |
| Cl2—Pd1—Cl1 | 90.44 (3) | H5B—C5—H5C | 109.5 |
| Cl2—Pd1—Cl3 | 90.26 (3) | C6—C5—H5A | 109.5 |
| N1—Pd1—Cl1 | 90.55 (9) | C6—C5—H5B | 109.5 |
| N1—Pd1—Cl3 | 88.84 (9) | C6—C5—H5C | 109.5 |
| Cl3—Pd1—Cl1 | 177.84 (3) | N2—C6—H6A | 108.5 |
| N1—Pd1—Cl2 | 177.08 (8) | N2—C6—H6B | 108.5 |
| C2—N1—Pd1 | 171.1 (3) | C5—C6—N2 | 114.9 (2) |
| H1A—C1—H1B | 109.5 | C5—C6—H6A | 108.5 |
| H1A—C1—H1C | 109.5 | C5—C6—H6B | 108.5 |
| H1B—C1—H1C | 109.5 | H6A—C6—H6B | 107.5 |
| C2—C1—H1A | 109.5 | H7A—C7—H7B | 109.5 |

| | | | |
|---|---|---|---|
| C2—C1—H1B | 109.5 | H7A—C7—H7C | 109.5 |
| C2—C1—H1C | 109.5 | H7B—C7—H7C | 109.5 |
| N1—C2—C1 | 179.3 (5) | C8—C7—H7A | 109.5 |
| C6—N2—C4 | 107.4 (2) | C8—C7—H7B | 109.5 |
| C6—N2—C8 | 110.8 (2) | C8—C7—H7C | 109.5 |
| C6—N2—C10 | 110.5 (2) | N2—C8—C7 | 114.2 (3) |
| C8—N2—C4 | 111.0 (2) | N2—C8—H8A | 108.7 |
| C8—N2—C10 | 106.9 (2) | N2—C8—H8B | 108.7 |
| C10—N2—C4 | 110.5 (2) | C7—C8—H8A | 108.7 |
| H3A—C3—H3B | 109.5 | C7—C8—H8B | 108.7 |
| H3A—C3—H3C | 109.5 | H8A—C8—H8B | 107.6 |
| H3B—C3—H3C | 109.5 | H9A—C9—H9B | 109.5 |
| C4—C3—H3A | 109.5 | H9A—C9—H9C | 109.5 |
| C4—C3—H3B | 109.5 | H9B—C9—H9C | 109.5 |
| C4—C3—H3C | 109.5 | C10—C9—H9A | 109.5 |
| N2—C4—H4A | 108.6 | C10—C9—H9B | 109.5 |
| N2—C4—H4B | 108.6 | C10—C9—H9C | 109.5 |
| C3—C4—N2 | 114.7 (2) | N2—C10—H10A | 108.4 |
| C3—C4—H4A | 108.6 | N2—C10—H10B | 108.4 |
| C3—C4—H4B | 108.6 | C9—C10—N2 | 115.6 (3) |
| H4A—C4—H4B | 107.6 | C9—C10—H10A | 108.4 |
| H5A—C5—H5B | 109.5 | C9—C10—H10B | 108.4 |
| H5A—C5—H5C | 109.5 | H10A—C10—H10B | 107.4 |

| | | | |
|---|---|---|---|
| C4—N2—C6—C5 | −178.5 (3) | C8—N2—C4—C3 | −52.5 (3) |
| C4—N2—C8—C7 | −57.2 (3) | C8—N2—C6—C5 | 60.2 (3) |
| C4—N2—C10—C9 | 64.6 (3) | C8—N2—C10—C9 | −174.6 (3) |
| C6—N2—C4—C3 | −173.7 (3) | C10—N2—C4—C3 | 65.8 (3) |
| C6—N2—C8—C7 | 61.9 (3) | C10—N2—C6—C5 | −58.0 (3) |
| C6—N2—C10—C9 | −54.0 (3) | C10—N2—C8—C7 | −177.7 (3) |