



Crystal structure of *N,N,N',N'*-tetramethylethanediamine

Tobias Schrimpf, Felix Otte and Carsten Strohmann*

Technische Universität Dortmund, Fakultät Chemie und Chemische Biologie, Otto-Hahn-Strasse 6, 44227 Dortmund, Germany. *Correspondence e-mail: carsten.strohmann@tu-dortmund.de

Received 17 November 2021

Accepted 23 November 2021

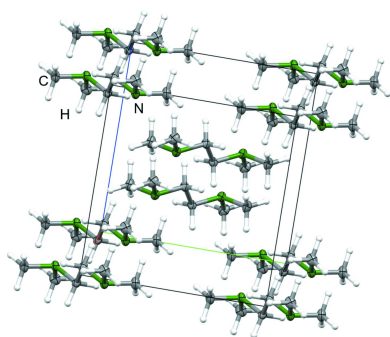
Edited by W. T. A. Harrison, University of Aberdeen, Scotland

Keywords: crystal structure; Hirshfeld surface analysis; bidentate ligand.**CCDC reference:** 2123810**Supporting information:** this article has supporting information at journals.iucr.org/e

The title compound *N,N,N',N'*-tetramethylethanediamine, C₆H₁₆N₂, is a bidentate amine ligand commonly used in organolithium chemistry for deaggregation. Crystals were grown at 243 K from *n*-pentane solution. The complete molecule is generated by a crystallographic center of symmetry and the conformation of the diamine is antiperiplanar. To investigate the intermolecular interactions, a Hirshfeld surface analysis was performed. It showed that H···H (van der Waals) interactions dominate with a contact percentage of 92.3%.

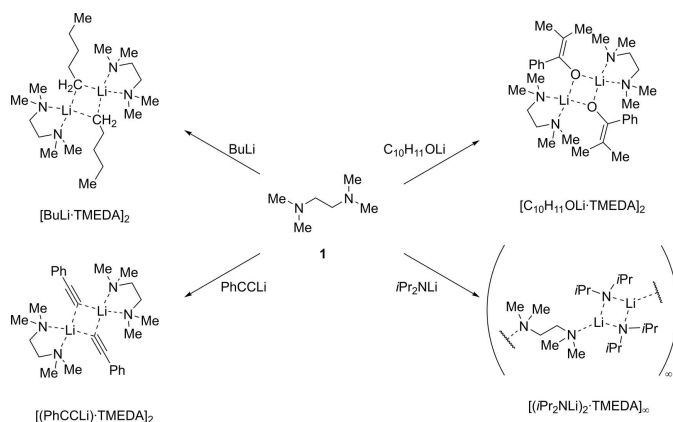
1. Chemical context

N,N,N',N'-tetramethylethanediamine (TMEDA, C₆H₁₆N₂, **1**) consists of two tertiary amine groups linked by an ethylene bridge. It can be used in cross-coupling or in olefin polymerization reactions where, *e.g.*, a complex between dimethylnickel and TMEDA is used as a catalyst (Göttker-Schnetmann & Mecking, 2020). However, TMEDA is most commonly used in the chemistry of organolithium compounds. The lithium–carbon bond is characterized by its high polarity, as it contains a cationic lithium and carbanionic residues. These organolithium compounds form unreactive aggregates in non-polar solvents, which can be deaggregated by adding Lewis-basic ligands (Gessner *et al.*, 2009). Compound **1** can be used as such a ligand, which can either chelate the metal center to form commonly dimeric structures or bridge two or more metal centers to form coordination polymers. The dimeric structural motif can be obtained in the butyl lithium TMEDA complex (Nichols & Williard, 1993), the enolate structure (Nichols *et al.*, 2007) and in the phenyl(ethynyl) lithium (Schubert & Weiss, 1983), whereas the lithium diisopropylamide forms a polymeric structure with **1** bridging the lithium amide groups (Bernstein *et al.*, 1992) (see scheme). The main benefit of deaggregation is the increased reactivity of organolithium compounds. Accompanying with smaller aggregates, the carbanionic center is more accessible for substrates due to an available coordination site at the metal center (Gessner *et al.*, 2009). In the case of sterically more demanding ligands, however, the reactivity can even be reduced, since the coordination site at the lithium center can be sterically shielded (Knauer *et al.*, 2019). Quantum chemical considerations of aggregation and deaggregation require knowledge of the energetically most favorable conformer. With knowledge about this conformer, quantum chemical equilibria can be used to calculate reasonable energies, for



OPEN ACCESS

example to predict the reactivity or the formation of certain aggregates.



2. Structural commentary

Compound **1** crystallizes from *n*-pentane solution at 243 K in the monoclinic crystal system in space group $P2_1/c$. The asymmetric unit consists of half of the molecule, with the other half generated by crystallographic inversion symmetry. The molecular structure of **1** is presented in Fig. 1 and selected bond angles are given in Table 1. The bond lengths for **1** are typical for C–C and C–N bonds and show no irregularities. The ethylene fragment is arranged in a staggered conformation where the nitrogen atoms are arranged in an anti-periplanar arrangement with $N1-C3-C3^i-N1^i$ [symmetry code: (i) $-x, 1-y, 1-z$] = 180.0° by symmetry. The conformations of the $C1-N1-C3-C3^i$ and $C2-N1-C3-C3^i$ groupings are *anti* [torsion angle = $167.33(6)^\circ$] and *gauche* [$-71.17(8)^\circ$], respectively.

A quantum chemical geometry optimization was performed at the M062X/6-31+G(d,p) (Walker *et al.*, 2013) theory level using *Gaussian 16* (Frisch *et al.*, 2016). The calculated geometry is shown in Fig. 2 and the bond angles are shown in

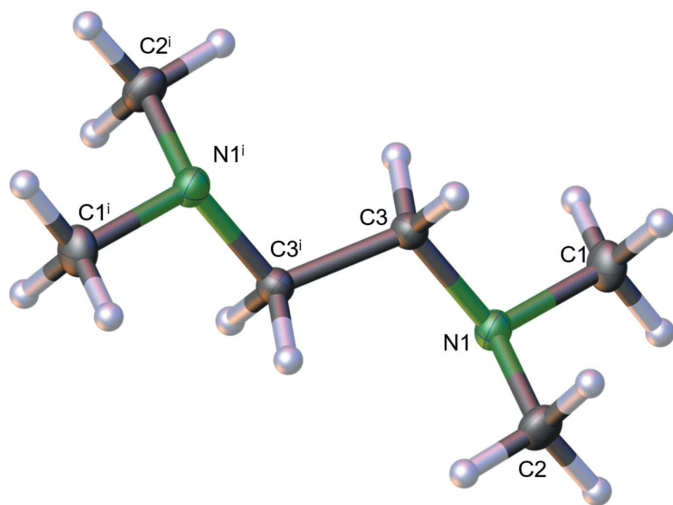


Figure 1
Crystal structure of **1** showing 50% displacement ellipsoids. Symmetry code: (i) $-x, 1-y, 1-z$.

Table 1

Comparison of the bond angles ($^\circ$) between the crystal structure and the quantum computed structure..

Atoms	Crystal structure	Calculated
C2–N1–C1	109.26 (5)	110.29
C2–N1–C3	111.96 (5)	110.26
N1–C3–C3'	112.37 (6)	112.32

Table 1. The angles of C2–N1–C1 and C2–N1–C3 differ by about 1° between the crystal structure and the quantum chemical calculated structure. Since these are gas phase calculations, this difference can be neglected. However, the N1–C3–C3 bond angles are in the same range. Therefore, we may assume that the presented conformation is at a local energy minimum.

3. Supramolecular features

The crystal packing of compound **1** is shown in Fig. 3. For the investigation of close contacts and intermolecular interactions,

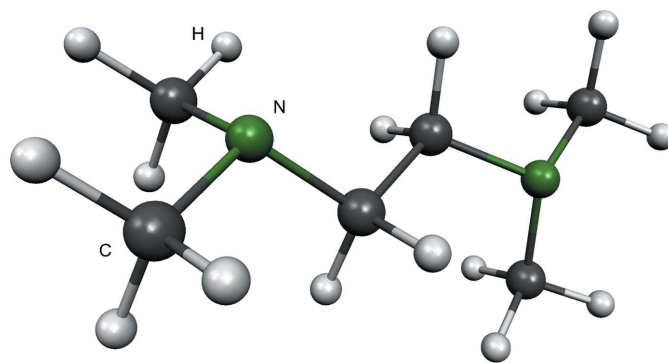


Figure 2
Structure of **1** obtained by geometry optimization at the M062X/6-31+g(d,p) theory level.

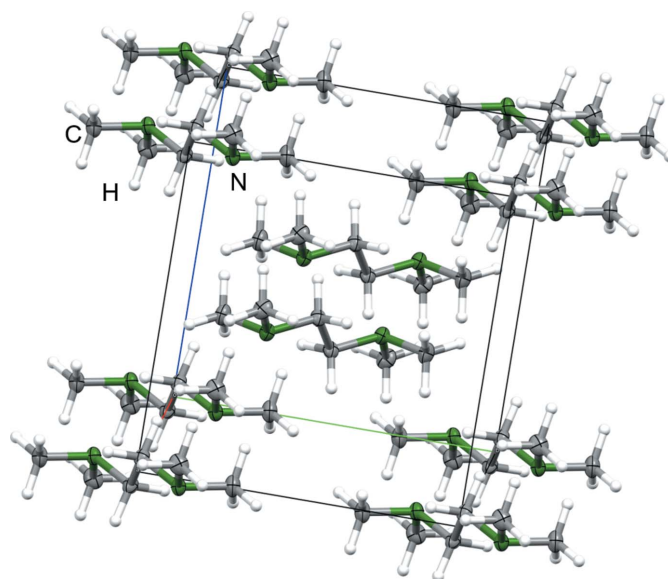


Figure 3
A view along the *b*-axis direction of the crystal packing of **1**.

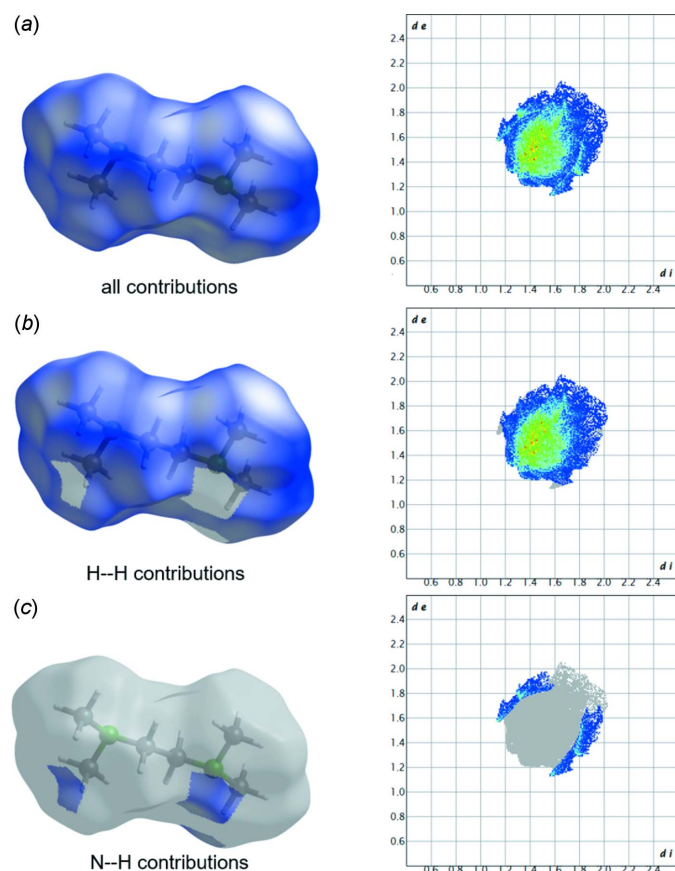


Figure 4
Two-dimensional fingerprint plots of **1**, (a) showing all contributions, (b) showing the H/H contributions and (c) showing the contributions of nitrogen and hydrogen (blue areas). The corresponding surfaces obtained by Hirshfeld surface analysis are also displayed.

a Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) was carried out: Fig. 4 illustrates the Hirshfeld surface mapped over d_{norm} in the range from -0.072 to 1.201 arbitrary units and the related fingerprint plots generated by *CrystalExplorer* (Spackman *et al.*, 2021; McKinnon *et al.*, 2007). Weak van der Waals H \cdots H contacts are the largest region (92.3%). The remaining 6.7% are generated by N \cdots H contacts, whereby C \cdots H contacts do not contribute to crystal packing. In addition, no red spots are visible, which leads to the conclusion that the packing of the crystal is caused only by van der Waals interactions. The absence of packing effects such as hydrogen bonds also suggests that the most energetically favorable conformer is present.

4. Database survey

There are a large number of compounds where **1** is used as a ligand. Selected examples found in the Cambridge Structural Database (CSD, version 5.41, update of May 2020; Groom *et al.*, 2016) include dilithium bis(trimethylsilyl)-*o*-xylene bis-(tetramethylethanediamine) (CSD refcode BECWEL; Lappert *et al.*, 1982), allyl lithium *N,N,N',N'*-tetramethylethanediamine (BITNEX; Köster & Weiss, 1982), tetrasodium

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₆ H ₁₆ N ₂
M_r	116.21
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	5.6987 (13), 8.311 (2), 8.453 (2)
β (°)	106.954 (9)
V (Å ³)	382.92 (18)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.06
Crystal size (mm)	0.56 × 0.35 × 0.30
Data collection	
Diffractometer	Bruker Venture D8
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
$T_{\text{min}}, T_{\text{max}}$	0.371, 0.567
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16732, 1720, 1434
R_{int}	0.037
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.813
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.038, 0.110, 1.05
No. of reflections	1720
No. of parameters	39
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.41, -0.15

Computer programs: *APEX2* and *SAINT* (Bruker, 2018), *SHELXT* (Sheldrick, 2015a), *SHELXL2014/7* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

tetrakis(tetramethylethylenediamine) octachloroditungsten (BORZUD; Cotton *et al.*, 1982), sodium (2,2,6,6-tetramethylpiperidin-1-ide)ferrocenyl-*t*-butyl-zinc *N,N,N',N'*-tetramethylethane-1,2-diamine solvate (BUQJII; Clegg *et al.*, 2015), hexakis(μ_2 -methyl)-tris(tetramethylethylenediamine-lithium)methylthorium(IV) tetramethylethylenediamine (COSZOZ; Lauke *et al.*, 1984), dilithium tribenzylidene-methane bis(tetramethylethylenediamine) (COZJUW; Wilhelm *et al.*, 1984), cyclopentadienyl sodium tetramethylethylenediamine (CPNATM10; Aoyagi *et al.*, 1979).

Since **1** plays a major role in organolithium chemistry, it also finds application in the group of Strohmann *et al.* Thus, some publications are included here: *t*-butyl lithium *N,N,N',N'*-tetramethylethanediamine (Gessner & Strohmann, 2008), isopropyl lithium *N,N,N',N'*-tetramethylethanediamine (Strohmann *et al.*, 2008), (diethylamino)diphenylsilyl *N,N,N',N'*-tetramethylethanediamine (Strohmann *et al.*, 2006), [(*R*)-((*S*)-2-(methoxymethyl)pyrrolidin-1-yl)methyl]dimethylsilyl(phenyl)methyl]lithium *N,N,N',N'*-tetramethylethanediamine (Strohmann *et al.*, 2003), methyl lithium *N,N,N',N'*-tetramethylethanediamine (Gessner *et al.*, 2011) and zinc bromide *N,N,N',N'*-tetramethylethanediamine (Eckert *et al.*, 2013).

5. Synthesis and crystallization

N,N,N',N'-Tetramethylethanediamine (C₆H₁₆N₂, **1**) was purchased by Sigma-Aldrich and was used without further purification. A solution of TMEDA (0.5 mmol) in *n*-pentane

(1 ml) was prepared at 243 K and **1** crystallized in the form of colorless blocks.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. For both compounds, the H atoms were positioned geometrically ($C-H = 0.95-1.00 \text{ \AA}$) and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$ for CH_2 and CH hydrogen atoms and $U_{iso}(H) = 1.5U_{eq}(C)$ for CH_3 hydrogen atoms.

References

- Aoyagi, T., Shearer, H. M., Wade, K. & Whitehead, G. (1979). *J. Organomet. Chem.* **175**, 21–31.
- Bernstein, M. P., Romesberg, F. E., Fuller, D. J., Harrison, A. T., Collum, D. B., Liu, Q. Y. & Williard, P. G. (1992). *J. Am. Chem. Soc.* **114**, 5100–5110.
- Bruker (2018). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Clegg, W., Crosbie, E., Dale-Black, S. H., Hevia, E., Honeyman, G. W., Kennedy, A. R., Mulvey, R. E., Ramsay, D. L. & Robertson, S. D. (2015). *Organometallics*, **34**, 2580–2589.
- Cotton, F. A., Mott, G. N., Schrock, R. R. & Sturgeoﬀ, L. G. (1982). *J. Am. Chem. Soc.* **104**, 6781–6782.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Eckert, P. K., Vieira, I., Gessner, V. H., Börner, J., Strohmman, C. & Herres-Pawlis, S. (2013). *Polyhedron*, **49**, 151–157.
- Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Petersson, G. A., Nakatsuji, H., Li, X., Caricato, M., Marenich, A. V., Bloino, J., Janesko, B. G., Gomperts, R., Mennucci, B., Hratchian, H. P., Ortiz, J. V., Izmaylov, A. F., Sonnenberg, J. L., Williams-Young, D., Ding, F., Lipparini, F., Egidi, F., Goings, J., Peng, B., Petrone, A., Henderson, T., Ranasinghe, D., Zakrzewski, V. G., Gao, J., Rega, N., Zheng, G., Liang, W., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Throssell, K., Montgomery, J. A. Jr, Peralta, J. E., Ogliaro, F., Bearpark, M. J., Heyd, J. J., Brothers, E. N., Kudin, K. N., Staroverov, V. N., Keith, T. A., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A. P., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Millam, J. M., Klene, M., Adamo, C., Cammi, R., Ochterski, J. W., Martin, R. L., Morokuma, K., Farkas, O., Foresman, J. B. & Fox, D. J. (2016). *Gaussian 16*. Revision C01. Gaussian Inc., Wallingford, CT, USA. <http://www.gaussian.com>.
- Gessner, V. H., Däschlein, C. & Strohmman, C. (2009). *Chem. Eur. J.* **15**, 3320–3334.
- Gessner, V. H., Koller, S. G., Strohmman, C., Hogan, A.-M. & O'Shea, D. F. (2011). *Chemistry*, **17**, 2996–3004.
- Gessner, V. H. & Strohmman, C. (2008). *J. Am. Chem. Soc.* **130**, 14412–14413.
- Göttker-Schnetmann, I. & Mecking, S. (2020). *Organometallics*, **39**, 3433–3440.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Knauer, L., Wattenberg, J., Kroesen, U. & Strohmman, C. (2019). *Dalton Trans.* **48**, 11285–11291.
- Köster, H. & Weiss, E. (1982). *Chem. Ber.* **115**, 3422–3426.
- Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
- Lappert, M. F., Raston, C. L., Skelton, B. W. & White, A. H. (1982). *J. Chem. Soc. Chem. Commun.* pp. 14–15.
- Lauke, H., Swepston, P. J. & Marks, T. J. (1984). *J. Am. Chem. Soc.* **106**, 6841–6843.
- McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.
- Nichols, M. A., Leposa, C. M., Hunter, A. D. & Zeller, M. (2007). *J. Chem. Crystallogr.* **37**, 825–829.
- Nichols, M. A. & Williard, P. G. (1993). *J. Am. Chem. Soc.* **115**, 1568–1572.
- Schubert, B. & Weiss, E. (1983). *Chem. Ber.* **116**, 3212–3215.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.
- Spackman, P. R., Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Jayatilaka, D. & Spackman, M. A. (2021). *J. Appl. Cryst.* **54**, 1006–1011.
- Strohmman, C., Buchold, D. H. M., Seibel, T., Wild, K. & Schildbach, D. (2003). *Chem. Ber.* pp. 3453–3463.
- Strohmman, C., Däschlein, C. & Auer, D. (2006). *J. Am. Chem. Soc.* **128**, 704–705.
- Strohmman, C., Gessner, V. H. & Damme, A. (2008). *Chem. Commun.* pp. 3381–3383.
- Walker, M., Harvey, A. J. A., Sen, A. & Dessent, C. E. H. (2013). *J. Phys. Chem. A*, **117**, 12590–12600.
- Wilhelm, D., Dietrich, H., Clark, T., Mahdi, W., Kos, A. J., Schleyer, P. v. R. (1984). *J. Am. Chem. Soc.* **106**, 7279–7280.

supporting information

Acta Cryst. (2022). E78, 36-39 [https://doi.org/10.1107/S2056989021012457]

Crystal structure of *N,N,N',N'*-tetramethylethanediamine

Tobias Schrimpf, Felix Otte and Carsten Strohmann

Computing details

Data collection: *APEX2* (Bruker, 2018); cell refinement: *SAINT* (Bruker, 2018); data reduction: *SAINT* (Bruker, 2018); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

N,N,N',N'-Tetramethylethane-1,2-diamine

Crystal data

$C_6H_{16}N_2$	$F(000) = 132$
$M_r = 116.21$	$D_x = 1.008 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 5.6987 (13) \text{ \AA}$	Cell parameters from 352 reflections
$b = 8.311 (2) \text{ \AA}$	$\theta = 3.5\text{--}22.8^\circ$
$c = 8.453 (2) \text{ \AA}$	$\mu = 0.06 \text{ mm}^{-1}$
$\beta = 106.954 (9)^\circ$	$T = 100 \text{ K}$
$V = 382.92 (18) \text{ \AA}^3$	Block, colourless
$Z = 2$	$0.56 \times 0.35 \times 0.30 \text{ mm}$

Data collection

Bruker Venture D8 diffractometer	$T_{\min} = 0.371$, $T_{\max} = 0.567$
Radiation source: microfocus sealed X-ray tube, Incoatec I μ s	16732 measured reflections
HELIOS mirror optics monochromator	1720 independent reflections
Detector resolution: 10.4167 pixels mm^{-1}	1434 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.037$
Absorption correction: multi-scan (SADABS; Krause <i>et al.</i> , 2015)	$\theta_{\max} = 35.3^\circ$, $\theta_{\min} = 3.5^\circ$
	$h = -9 \rightarrow 9$
	$k = -13 \rightarrow 13$
	$l = -12 \rightarrow 13$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.038$	$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 0.073P]$
$wR(F^2) = 0.110$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{\max} < 0.001$
1720 reflections	$\Delta\rho_{\max} = 0.41 \text{ e \AA}^{-3}$
39 parameters	$\Delta\rho_{\min} = -0.15 \text{ e \AA}^{-3}$
0 restraints	
Primary atom site location: dual	

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.25269 (10)	0.34528 (6)	0.53636 (6)	0.01749 (12)
C1	0.49338 (12)	0.33807 (9)	0.65977 (9)	0.02394 (15)
H1A	0.5794	0.4404	0.6608	0.036*
H1B	0.5896	0.2505	0.6320	0.036*
H1C	0.4725	0.3185	0.7692	0.036*
C2	0.12526 (13)	0.19303 (8)	0.53563 (9)	0.02363 (14)
H2A	0.0976	0.1764	0.6436	0.035*
H2B	0.2253	0.1048	0.5134	0.035*
H2C	-0.0328	0.1955	0.4494	0.035*
C3	0.11367 (10)	0.48144 (7)	0.57161 (7)	0.01782 (13)
H3A	0.2207	0.5776	0.5952	0.021*
H3B	0.0631	0.4573	0.6716	0.021*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0167 (2)	0.0154 (2)	0.0197 (2)	0.00035 (16)	0.00420 (16)	0.00150 (16)
C1	0.0170 (3)	0.0261 (3)	0.0265 (3)	0.0025 (2)	0.0028 (2)	0.0043 (2)
C2	0.0244 (3)	0.0157 (3)	0.0297 (3)	-0.0014 (2)	0.0063 (2)	0.0015 (2)
C3	0.0176 (2)	0.0163 (2)	0.0174 (2)	0.00014 (19)	0.00177 (17)	-0.00102 (18)

Geometric parameters (\AA , $^\circ$)

N1—C1	1.4624 (9)	C2—H2A	0.9800
N1—C2	1.4580 (9)	C2—H2B	0.9800
N1—C3	1.4610 (8)	C2—H2C	0.9800
C1—H1A	0.9800	C3—C3 ⁱ	1.5246 (12)
C1—H1B	0.9800	C3—H3A	0.9900
C1—H1C	0.9800	C3—H3B	0.9900
C2—N1—C1	109.26 (5)	N1—C2—H2C	109.5
C2—N1—C3	111.96 (5)	H2A—C2—H2B	109.5
C3—N1—C1	109.75 (5)	H2A—C2—H2C	109.5
N1—C1—H1A	109.5	H2B—C2—H2C	109.5
N1—C1—H1B	109.5	N1—C3—C3 ⁱ	112.37 (6)
N1—C1—H1C	109.5	N1—C3—H3A	109.1
H1A—C1—H1B	109.5	N1—C3—H3B	109.1
H1A—C1—H1C	109.5	C3 ⁱ —C3—H3A	109.1
H1B—C1—H1C	109.5	C3 ⁱ —C3—H3B	109.1

N1—C2—H2A	109.5	H3A—C3—H3B	107.9
N1—C2—H2B	109.5		
C1—N1—C3—C3 ⁱ	167.33 (6)	N1—C3—C3 ⁱ —N1 ⁱ	180.0
C2—N1—C3—C3 ⁱ	-71.17 (8)		

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