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## High-pressure crystal structure of *n*-hexylamine

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A primary amine, *n*-hexylamine (**HA**,  $C_6H_{15}N$ ), has been studied at high pressure by single-crystal X-ray diffraction. The structure of this compound has been determined, at ambient temperature, from the freezing pressure up to 1.40 GPa. **HA** at high pressure crystallizes in the space group  $Pca2_1$ , which was already found at ambient pressure and low temperature. The compressibility of the  $N-H\cdots N$  hydrogen bonds has been compared with that of the shortest  $C-H\cdots N$  and  $H\cdots H$  intermolecular distances, revealing that the  $H\cdots H$  distances exhibit the highest degree of compressibility among them.

### 1. Introduction

 $N-H\cdots N$  hydrogen bonds often compete with weaker  $C-H\cdots N$  hydrogen bonds in crystals (Huang *et al.*, 2013; Leigh *et al.*, 2013; Podsiadło *et al.*, 2017; Sacharczuk *et al.*, 2023; Vega *et al.*, 2005). The role of these interactions, as the main cohesion forces in crystals, has been well documented for biomolecules, self-organizing materials, pharmaceuticals and molecular switches (Desiraju & Steiner, 2001; Jeffrey & Saenger, 1994). The simplest aliphatic amines serve as model compounds for studying the nature of such interactions due to their molecular composition and the minimized effect of the molecular shape on dense packing.



Structural studies of the simplest *n*-aliphatic amines have been performed at low temperature and ambient pressure for methylamine (Atoji & Lipscomb, 1953), as well as for the series from ethylamine to *n*-decylamine (Maloney *et al.*, 2014). These studies described the role of various types of intermolecular interactions in molecular association.  $N-H\cdots N$ hydrogen bonds have been identified as the main cohesion force for the early primary amines; however, the role of dispersive interactions between alkyl chains was also emphasized (for the later compounds, the dispersion interactions dominate over hydrogen bonding). It was also found that dispersive interactions were particularly dominant in the regions between molecular layers linked by  $N-H\cdots N$  hydrogen bonds (Maloney *et al.*, 2014).

This study of *n*-hexylamine (**HA**; Scheme 1 and Fig. 1) extends our previous research on the simplest primary amines under high pressure. Recently, we have investigated the series from methylamine to *n*-pentylamine (Podsiadło *et al.*, 2017; Sacharczuk *et al.*, 2023). Only ethylamine crystallizes in the same phase under high pressure (phase II) as found at low temperature. In contrast, seven new polymorphs, different from the low-temperature ones, have been identified at high

### Table 1

#### Experimental details.

	<b>HA</b> at 0.50 GPa	HA at 0.65 GPa	<b>HA</b> at 1.40 GPa
Crystal data			
a, b, c (Å)	6.9050 (9), 17.549 (7), 5.5212 (13)	6.8591 (9), 17.494 (5), 5.4892 (4)	6.7241 (19), 17.052 (13), 5.3367 (7)
$V(\text{\AA}^3)$	669.1 (3)	658.7 (2)	611.9 (5)
$\mu (\text{mm}^{-1})$	0.06	0.06	0.06
Crystal size (mm)	$0.28 \times 0.28 \times 0.27$	$0.27 \times 0.27 \times 0.26$	$0.26 \times 0.26 \times 0.23$
Data collection			
Diffractometer	Rigaku Xcalibur Eos	Rigaku Xcalibur Atlas	Rigaku Xcalibur Atlas
$T_{\min}, T_{\max}$	0.573, 1.000	0.600, 1.000	0.447, 1.000
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	4308, 832, 373	5447, 1085, 527	4114, 852, 401
R <sub>int</sub>	0.071	0.063	0.068
$(\sin \theta / \lambda)_{\max} (\text{\AA}^{-1})$	0.663	0.732	0.713
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.054, 0.118, 1.04	0.047, 0.131, 0.98	0.061, 0.194, 1.04
No. of reflections	832	1085	852
$\Delta \rho_{\rm max},  \Delta \rho_{\rm min} \ ({\rm e} \ {\rm \AA}^{-3})$	0.09, -0.09	0.10, -0.10	0.17, -0.20
Absolute structure	Flack x determined using 128 quotients $[(I^+) - (I^-)]/[(I^+) +$	Flack x determined using 181 quotients $[(I^+) - (I^-)]/[(I^+) +$	Flack x determined using 130 quotients $[(I^+) - (I^-)]/[(I^+) +$
	(I)] (Parsons <i>et al.</i> , 2013)	(I)] (Parsons <i>et al.</i> , 2013)	(I) [Parsons <i>et al.</i> , 2013]
Absolute structure parameter	-10.0(10)	0.7 (10)	3.1 (10)

For all determinations:  $C_6H_{15}N$ ,  $M_r = 101.19$ , orthorhombic,  $Pca2_1$ , Z = 4. Experiments were carried out at 295 K with Mo K $\alpha$  radiation. Absorption was corrected for by multi-scan methods (*CrysAlis PRO*; Rigaku OD, 2022). Refinement was on 64 parameters with 1 restraint. H-atom parameters were constrained.

Computer programs: CrysAlis PRO (Rigaku OD, 2022), SHELXT2018 (Sheldrick, 2015a), SHELXL2018 (Sheldrick, 2015b), Mercury (Macrae et al., 2020) and OLEX2 (Dolomanov et al., 2009).

pressure for the remaining amines, *i.e.* one for methylamine (Podsiadło *et al.*, 2017) and two each for propylamine, butylamine and pentylamine (Sacharczuk *et al.*, 2023). In all these polymorphs, molecules interact through  $N-H\cdots N$  hydrogen bonds. However, at high pressure, the role of  $C-H\cdots N$  hydrogen bonds increases (Sacharczuk *et al.*, 2023).



### Figure 1

The molecular structures of **HA** at (*a*) 0.50 GPa, (*b*) 0.65 GPa and (*c*) 1.40 GPa (all at 295 K), showing the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

In the present study, we have investigated **HA** at high pressure using single-crystal X-ray diffraction. The crystal structure has been determined previously at ambient pressure and low temperature only (Maloney *et al.*, 2014). We have obtained and investigated single crystals of **HA** in a diamond-anvil cell (DAC) in the range between the freezing pressure at ambient temperature of 0.33 GPa up to 1.40 GPa.

### 2. Experimental

n-Hexylamine, HA (99%), from Sigma-Aldrich was crystallized in situ in a modified Merrill-Basset diamond-anvil cell (DAC; Bassett, 2009). The DAC was equipped with a 0.3 mm thick steel gasket with a hole of diameter 0.3 mm. At 295 K, HA froze at 0.33 GPa, in the form of a polycrystalline mass, filling the whole volume of the DAC chamber. A single crystal of HA was obtained under isothermal conditions. The polycrystalline mass was melted, except for one crystallite, by decreasing the pressure slowly. Then, again slowly, the pressure was increased allowing a single crystal of HA to grow and eventually fill the entire volume of the chamber (Fig. 2). Afterwards, the pressure was increased by ca 0.2 GPa to achieve a stable single crystal required for the X-ray diffraction measurement. Several attempts were made to grow a single crystal under isochoric conditions at pressures above 0.50 GPa; however, all were unsuccessful. The growing single crystals were very sensitive to temperature changes, and each time additional crystallites occurred, even with slow cooling. For this reason, single crystals at pressures of 0.65 and 1.40 GPa were obtained at room temperature by increasing the pressure in the chamber after performing the X-ray

measurements at 0.50 and 0.65 GPa. The pressure was calibrated by the ruby fluorescence method (Mao *et al.*, 1986; Piermarini *et al.*, 1975) using a Photon Control spectrometer with an accuracy of 0.02 GPa. The calibrations were performed before and after each X-ray diffraction experiment. The progress of the growth of the **HA** single crystal is shown in Fig. 2 and Fig. S1 in the supporting information.

Rigaku Xcalibur EOS and Xcalibur ATLAS diffractometers were used for the high-pressure studies. The DAC was centred by the gasket-shadow method (Budzianowski & Katrusiak, 2004).

The room-temperature compressibility measurement was performed up to *ca* 2 GPa in a piston-and-cylinder apparatus (Baranowski & Moroz, 1982; Dziubek & Katrusiak, 2014) with an initial volume of *ca* 8.5 cm<sup>3</sup>.

### 2.1. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The H atoms of the methylene and methyl groups were located based on the molecular geometry, with the C-H distances equal to 0.97 or 0.96 Å and their  $U_{\rm iso}$  factors constrained to 1.2 or 1.5 times the  $U_{\rm eq}$  value of their carrier. The H atoms of the amine (-NH<sub>2</sub>) group were located based on the molecular geometry, assuming N-H distances equal to 0.90 Å, and their  $U_{\rm iso}$  factors were constrained to 1.2 times the  $U_{\rm eq}$  value of their carrier. The crystal data and refinement details are summar-



### Figure 2

Stages of the **HA** single-crystal growth inside the DAC chamber (polarized-light mode): (*a*) one crystal seed at 295 K and 0.33 GPa, (*b*)/(*c*) the single-crystal growth with increasing pressure and a simultaneous decrease in the volume of the high-pressure chamber, and (*d*) the single crystal filling the DAC chamber at 295 K and 0.50 GPa. The ruby chip, for pressure calibration, is located by the left edge of the DAC.

### Table 2

Selected crystal data of HA at	).1 MPa/150 K	K and 0.50, 0.65 a	nd 1.40 GPa
(all at 295 K).			

	$C_6H_{15}N^a$	$C_6H_{15}N^b$	$C_6H_{15}N^b$	$C_6H_{15}N^b$
p (GPa)	0.0001	0.50 (2)	0.65 (2)	1.40 (2)
T (K)	150	295 (2)	295 (2)	295 (2)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$Pca2_1$	$Pca2_1$	$Pca2_1$	$Pca2_1$
a (Å)	6.9725 (3)	6.9050 (9)	6.8591 (9)	6.7241 (19)
b (Å)	17.7977 (6)	17.549 (7)	17.494 (5)	17.052 (13)
c (Å)	5.6105 (2)	5.5212 (13)	5.4892 (4)	5.3367 (7)
$V(\text{\AA}^3)$	696.23 (5)	669.1 (3)	658.7 (2)	611.9 (5)
Z, Z'	4, 1	4, 1	4, 1	4, 1
$D_x (\text{g cm}^{-3})$	0.965	1.005	1.020	1.098
$R_1 \left[ F^2 > 2\sigma(F^2) \right]$	0.0418	0.0544	0.0472	0.0612
$R_1$ (all data)	-	0.1726	0.1434	0.1624

References: (a) Maloney et al. (2014); (b) this work.

ized in Tables 1 and 2, and Table S1 in the supporting information.

### 3. Results and discussion

The single crystal of HA was obtained at the lowest possible pressure of 0.50 GPa (ca 0.2 GPa above the freezing pressure) to ensure the stability of the crystal during the X-ray diffraction data collection experiment. Two additional measurements were performed on this crystal compressed under isothermal conditions to 0.65 GPa and then to 1.40 GPa. The pressure of 1.40 GPa was the highest, at which the compressive stress on the crystal did not significantly affect the quality of the diffraction data. Above 1.40 GPa, the HA single crystal cracked due to mechanical stress. The crystals obtained under high pressure are denser than those crystallized at ambient pressure and low temperature (Table 2). All the unit-cell parameters of the investigated HA crystals decrease with increasing pressure, leading to the more dense structures. The molecular volume of HA as a function of pressure has been plotted in Fig. 3.

The compression of the molecular volume of **HA** measured at 295 K in a piston-and-cylinder press (Baranowski & Moroz, 1982; Dziubek & Katrusiak, 2014) changes abruptly by 2.6% on freezing the liquid at 0.33 GPa (Fig. 3). After freezing, the solid **HA** is initially strongly compressed until about 0.80 GPa; thereafter, the compression decreases monotonically, and at 1.96 GPa, the volume reaches about 65% of the liquid at 0.1 MPa and 80% of the solid at 0.33 GPa. The molecular volume determined using the piston-and-cylinder press is consistent with that obtained by single-crystal X-ray diffraction (Fig. 3).

**HA** at 0.1 MPa/150 K crystallizes in the noncentrosymmetric space group  $Pca2_1$ , adopting a layered arrangement with infinite N-H···N hydrogen-bonded chains running within the layers (Maloney *et al.*, 2014). These N-H···N hydrogen-bonded chains can be described by the symbol  $C_1^1(2)$  according to the graph-set notation of hydrogen bonds (Etter *et al.*, 1990). Within the chains, each N atom acts as a donor and an acceptor of an H atom. These chains are retained at high pressure when **HA** crystallizes in the same phase at

Table 3		
Hydrogen-bond geometry	(Å,	°).

$N1 - H1 \cdots N1^i$	0.50 GPa	0.65 GPa	1.40 GPa
N1-H1	0.900(7)	0.900 (4)	0.900(7)
$H1 \cdot \cdot \cdot N1^i$	2.229 (6)	2.230 (3)	2.168 (5)
$N1 \cdots N1^{i}$	3.116 (7)	3.115 (4)	3.050 (8)
$N1-H1\cdots N1^{i}$	168.2 (2)	167.44 (13)	166.4 (2)

Symmetry code: (i)  $-x + 1, -y, z - \frac{1}{2}$ .

0.33 GPa/295 K (Fig. 4). This structure remains stable up to at least a pressure of 1.40 GPa.

 $N-H\cdots N$  hydrogen bonds play a major role in the cohesion force in **HA** crystals at ambient pressure/low temperature and within the investigated pressure range at room temperature. These interactions at ambient pressure/low temperature are characterized by intermolecular  $H\cdots N$  distances shorter by *ca* 0.45 Å (Maloney *et al.*, 2014) than the sum of the van der Waals radii of H and N atoms of 2.75 Å (Bondi, 1964) (Figs. 4 and 5). At 0.50 GPa, these distances are 2.229 (6) Å, and they are even shorter at 1.40 GPa, *i.e.* 2.168 (5) Å (Figs. 4 and 5, and Table 3).

It is characteristic that the second shortest intermolecular  $H \cdots N$  distances from the  $N-H \cdots N$  hydrogen bonding are approximately 0.6 Å longer than the shortest. Within the investigated pressure range, these distances remain longer than the sum of the van der Waals radii (Fig. 5). Such a property was observed for the first time in the high-pressure structures of the simplest primary amines (Podsiadło *et al.*, 2017; Sacharczuk *et al.*, 2023). Furthermore, even in the **HA** structure at 1.40 GPa, no intermolecular  $H \cdots N$  distances from  $C-H \cdots N$  hydrogen bonds shorter than the sum of the van der Waals radii are observed. **HA** is therefore the first primary *n*-amine in the series from methyl- to hexylamine where, at high pressure, only single  $N-H \cdots N$  hydrogen-bonded chains



#### Figure 3

The molecular volume of **HA** at room temperature as a function of pressure measured in the piston-and-cylinder press (blue circles). The volumes measured at high pressure (red triangles) and low temperature (green square; Maloney *et al.*, 2014) by single-crystal X-ray diffraction have been indicated. The freezing pressure (f.p.) of 0.33 GPa is marked with a vertical dashed line.



#### Figure 4

Structures of **HA** at low-temperature (Maloney *et al.*, 2014) and highpressure conditions: (*a*) 0.1 MPa/150 K and (*b*) 1.40 GPa/295 K. Four hydrogen bonds (N-H $\cdot$ ··N) and one short intermolecular H $\cdot$ ··H distance at the end of the carbon chains are marked with dashed lines (distances are indicated). The intermolecular space accessible to a probe with a radius of 0.7 Å and a grid spacing of 0.1 Å (Macrae *et al.*, 2020) is indicated in yellow.

are observed. The C-H···N hydrogen bonds are not formed at all and no phase transition, that would allow molecular rearrangement and the formation of C-H···N interactions, occurred (Podsiadło *et al.*, 2017; Sacharczuk *et al.*, 2023). In the series from methyl- to pentylamine, high pressure does not affect the main cohesive force (N-H···N hydrogen bonds); however, intermolecular C-H···N interactions are observed in the high-pressure polymorphs (Podsiadło *et al.*, 2017; Sacharczuk *et al.*, 2023).

In the **HA** crystals, only at a pressure of 1.40 GPa do the shortest intermolecular  $H \cdots H$  distances, at the end of the carbon chains, become shorter than the sum of the van der Waals radii of two H atoms of 2.4 Å (Bondi, 1964) (Figs. 4 and 5, and Fig. S2 in the supporting information). It is characteristic that, with increasing pressure, these shortest intermolecular  $H \cdots H$  distances are more compressible than the main  $N-H \cdots N$  contacts (Figs. 4 and 5). This is related to the voids observed in the crystals between the ends of the carbon chains (Fig. 4).

In the series from methyl- to hexylamine, **HA** forms the least dense crystals in the structures determined just above their freezing pressure. The crystal density of methylamine determined at 3.65 GPa is 1.165 g cm<sup>-3</sup> (Podsiadło *et al.*, 2017), ethylamine at 1.40 GPa is 1.046 g cm<sup>-3</sup> (Sacharczuk *et al.*, 2023), propylamine at 2.25 GPa is 1.109 g cm<sup>-3</sup> (Sacharczuk *et al.*, 2023), butylamine at 1.45 GPa is 1.059 g cm<sup>-3</sup> (Sacharczuk *et al.*, 2023) and pentylamine at 1.05 GPa is 1.049 g cm<sup>-3</sup> (Sacharczuk *et al.*, 2023). The crystal density of **HA**, determined within this study, at 0.50 GPa is 1.005 g cm<sup>-3</sup>. This correlates with the void volumes in the structures



Figure 5

Intermolecular  $H \cdots N$  and  $H \cdots H$  distances (Å) observed in **HA** structures plotted as a function of pressure. The two shortest distances for each type are presented: blue circles represent the  $N-H \cdots N$  and blue squares depict the  $C-H \cdots N$  hydrogen-acceptor  $(H \cdots A)$  distances, while red triangles represent intermolecular  $H \cdots H$  distances. Blue and red horizontal lines show the sum of the van der Waals radii of H and N of 2.75 Å, and of two H atoms of 2.40 Å (Bondi, 1964). The estimated standard deviations are smaller than the plotted symbols.

mentioned above, which, in the series from methyl- to hexylamine, are 0, 7.15, 7.86, 12.94, 13.65 and 38.45 Å<sup>3</sup>, respectively (the intermolecular space accessible to a probe with a radius of 0.6 Å and a grid spacing of 0.1 Å; the parameters used in the calculations differ from those used in Fig. 4, ensuring distinguishable void volumes across the entire series; Macrae *et al.*, 2020).

### 4. Conclusions

The high-pressure crystal structure of **HA** is isostructural with the phase determined at low temperature at 0.1 MPa (Maloney *et al.*, 2014). This represents the first example among the series of the simplest aliphatic amines where the crystal symmetry remains unchanged between low-temperature and high-pressure conditions. The space group symmetry of  $Pca2_1$  remains stable within the investigated pressure range. Similar to other aliphatic *n*-amines, the main cohesion force in the **HA** crystals involves the N-H···N hydrogen-bonded chains. However, no additional intermolecular distances shorter than the sum of the van der Waals radii are observed. This is unique within the high-pressure studies of the methyl- to pentylamine series, where high pressure enhances the role of intermolecular C-H···N interactions. Only at 1.40 GPa does the

first intermolecular  $H \cdots H$  distance become shorter than the sum of the van der Waals radii of two H atoms. The compressibility of this distance exceeds that of the intermolecular  $N-H \cdots N$  hydrogen bonds. This effect results from the voids surrounding the methyl groups at the ends of the carbon chains. The **HA** crystal obtained just above the freezing pressure is the least dense structure among the high-pressure structures determined in the methyl- to hexylamine series.

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### High-pressure crystal structure of *n*-hexylamine

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**Computing details** 

n-Hexylamine (hexylamine\_0\_50GPa)

Crystal data

C<sub>6</sub>H<sub>15</sub>N  $M_r = 101.19$ Orthorhombic,  $Pca2_1$  a = 6.9050 (9) Å b = 17.549 (7) Å c = 5.5212 (13) Å V = 669.1 (3) Å<sup>3</sup> Z = 4F(000) = 232

### Data collection

### Refinement

Refinement on  $F^2$ Least-squares matrix: full  $R[F^2 > 2\sigma(F^2)] = 0.054$  $wR(F^2) = 0.118$ S = 1.04832 reflections 64 parameters 1 restraint Primary atom site location: dual Hydrogen site location: mixed  $D_x = 1.005 \text{ Mg m}^{-3}$ Mo K $\alpha$  radiation,  $\lambda = 0.71073 \text{ Å}$ Cell parameters from 598 reflections  $\theta = 3.8-17.7^{\circ}$  $\mu = 0.06 \text{ mm}^{-1}$ T = 295 KDisc, colourless  $0.28 \times 0.28 \times 0.27 \text{ mm}$ 

832 independent reflections 373 reflections with  $I > 2\sigma(I)$   $R_{int} = 0.071$   $\theta_{max} = 28.1^{\circ}, \ \theta_{min} = 3.2^{\circ}$   $h = -9 \rightarrow 9$   $k = -16 \rightarrow 16$  $l = -6 \rightarrow 6$ 

H-atom parameters constrained  $w = 1/[\sigma^2(F_o^2) + (0.0376P)^2]$ where  $P = (F_o^2 + 2F_c^2)/3$   $(\Delta/\sigma)_{max} < 0.001$   $\Delta\rho_{max} = 0.09 \text{ e } \text{Å}^{-3}$   $\Delta\rho_{min} = -0.09 \text{ e } \text{Å}^{-3}$ Absolute structure: Flack *x* determined using 128 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013) Absolute structure parameter: -10.0 (10)

### 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.

**Refinement**. Rigaku Xcalibur EOS and Xcalibur ATLAS diffractometers were used for the high-pressure studies. The X-ray wavelength used in all experiments was 0.71073 Å. The DAC was centred by the gasket-shadow method (Budzianowski & Katrusiak, 2004). The *CrysAlis PRO* program suite was used for data collection, determination of the *UB* matrices and data reductions. All data were accounted for the Lorentz, polarization and absorption effects. *OLEX2* (Dolomanov *et al.*, 2009), *SHELXT* (Sheldrick, 2015a) and *SHELXL* (Sheldrick, 2015b) were used to solve the structures by direct methods, and then to the full-matrix least-squares refinement.

	x	У	Ζ	$U_{ m iso}$ */ $U_{ m eq}$
N1	0.5556 (7)	0.0349 (4)	0.9147 (10)	0.0687 (19)
H2	0.682796	0.038908	0.947803	0.082*
H1	0.539765	0.010808	0.772063	0.082*
C1	0.4704 (8)	0.1102 (6)	0.9009 (13)	0.063 (3)
H12	0.488877	0.134938	1.056331	0.076*
H11	0.332065	0.104265	0.877298	0.076*
C2	0.5449 (8)	0.1627 (6)	0.7081 (12)	0.055 (3)
H22	0.683900	0.167532	0.728087	0.066*
H21	0.522184	0.138989	0.551947	0.066*
C3	0.4591 (6)	0.2410 (7)	0.7031 (12)	0.062 (3)
H32	0.480115	0.264728	0.859597	0.075*
H31	0.320307	0.236485	0.679769	0.075*
C4	0.5394 (8)	0.2926 (5)	0.5096 (13)	0.061 (3)
H42	0.678221	0.297005	0.532398	0.074*
H41	0.517725	0.269072	0.352958	0.074*
C5	0.4533 (8)	0.3714 (5)	0.5061 (12)	0.070 (3)
H52	0.470541	0.394238	0.664685	0.084*
H51	0.315124	0.367130	0.477184	0.084*
C6	0.5390 (8)	0.4243 (5)	0.3177 (16)	0.088 (3)
H63	0.476617	0.473119	0.327290	0.132*
H62	0.675190	0.430265	0.347089	0.132*
H61	0.519522	0.403112	0.159285	0.132*

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

Atomic displacement parameters  $(Å^2)$ 

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.073 (3)	0.079 (7)	0.055 (5)	0.004 (3)	0.001 (4)	0.003 (3)
C1	0.059 (3)	0.076 (10)	0.054 (7)	-0.003 (5)	0.000 (5)	0.003 (5)
C2	0.053 (3)	0.055 (11)	0.057 (7)	-0.001 (5)	-0.007(5)	-0.002(5)
C3	0.048 (3)	0.085 (12)	0.054 (7)	0.005 (5)	0.001 (5)	-0.004(5)
C4	0.056 (3)	0.078 (11)	0.051 (7)	-0.002 (4)	-0.002(5)	0.004 (4)
C5	0.071 (4)	0.082 (10)	0.057 (7)	-0.004 (5)	0.001 (5)	0.005 (5)
C6	0.088 (4)	0.099 (12)	0.076 (9)	0.008 (5)	-0.005 (6)	0.012 (5)

### *Geometric parameters (Å, °)*

N1_H2	0.9000	C3—C4	1.507 (8)
N1—H1	0.9001	C4—H42	0.9700
N1—C1	1.449 (9)	C4—H41	0.9700

C1 1110	0.0500	C4 C5	1 50 ( (0)
C1—H12	0.9700	C4—C5	1.506 (8)
C1—H11	0.9700	C5—H52	0.9700
C1—C2	1.498 (10)	C5—H51	0.9700
С2—Н22	0.9700	C5—C6	1.515 (11)
C2—H21	0.9700	С6—Н63	0.9600
C2—C3	1.497 (12)	С6—Н62	0.9600
С3—Н32	0.9700	C6—H61	0.9600
C3—H31	0.9700		
U2 N1 U1	100 5	C4 C2 H21	108.6
$\Pi_2 = \Pi_1 = \Pi_1$	109.5	$C_4 = C_5 = H_{31}$	108.0
CI = NI = H2	109.0	$C_3 = C_4 = H_{42}$	108.0
CI-NI-HI	109.4	$C_3 - C_4 - H_4$	108.0
NI-CI-HI2	108.0	H42 - C4 - H41	10/.6
NI-CI-HII	108.0	$C_{5}$ $C_{4}$ $C_{3}$	114.6 (/)
NI—CI—C2	117.3 (7)	C5—C4—H42	108.6
H12—C1—H11	107.2	C5—C4—H41	108.6
C2—C1—H12	108.0	C4—C5—H52	108.6
C2—C1—H11	108.0	C4—C5—H51	108.6
C1—C2—H22	108.2	C4—C5—C6	114.7 (6)
C1—C2—H21	108.2	H52—C5—H51	107.6
H22—C2—H21	107.4	C6—C5—H52	108.6
C3—C2—C1	116.2 (7)	C6—C5—H51	108.6
C3—C2—H22	108.2	С5—С6—Н63	109.5
C3—C2—H21	108.2	С5—С6—Н62	109.5
С2—С3—Н32	108.6	С5—С6—Н61	109.5
C2—C3—H31	108.6	Н63—С6—Н62	109.5
C2—C3—C4	114.8 (6)	H63—C6—H61	109.5
H32—C3—H31	107.5	H62—C6—H61	109.5
С4—С3—Н32	108.6		
N1	-178 1 (6)	C2—C3—C4—C5	-1797(6)
$C_1 = C_2 = C_3$	170.1 (6)	$C_2 = C_1 = C_2$	177.9 (6)
01-02-03-04	1/9.1 (0)	$C_{J} = C_{T} = C_{J} = C_{U}$	177.9 (0)

n-Hexylamine (hexylamine\_0\_65GPa)

Crystal data

C<sub>6</sub>H<sub>15</sub>N  $M_r = 101.19$ Orthorhombic,  $Pca2_1$  a = 6.8591 (9) Å b = 17.494 (5) Å c = 5.4892 (4) Å V = 658.7 (2) Å<sup>3</sup> Z = 4F(000) = 232  $D_{\rm x} = 1.020 \text{ Mg m}^{-3}$ Mo K $\alpha$  radiation,  $\lambda = 0.71073 \text{ Å}$ Cell parameters from 1173 reflections  $\theta = 3.2-23.5^{\circ}$  $\mu = 0.06 \text{ mm}^{-1}$ T = 295 KDisc, colourless  $0.27 \times 0.27 \times 0.26 \text{ mm}$  Data collection

Rigaku Xcalibur Atlas diffractometer Detector resolution: 10.5384 pixels mm <sup>-1</sup> $\varphi$ - and $\omega$ -scans Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2022) $T_{\min} = 0.600, T_{\max} = 1.000$ 5447 measured reflections <i>Refinement</i>	1085 independent reflections 527 reflections with $I > 2\sigma(I)$ $R_{int} = 0.063$ $\theta_{max} = 31.4^{\circ}, \ \theta_{min} = 3.2^{\circ}$ $h = -8 \rightarrow 8$ $k = -15 \rightarrow 15$ $l = -7 \rightarrow 7$
Refinement on $F^2$ Least-squares matrix: full $R[F^2 > 2\sigma(F^2)] = 0.047$ $wR(F^2) = 0.131$ S = 0.98 1085 reflections 64 parameters 1 restraint Primary atom site location: dual Hydrogen site location: mixed	H-atom parameters constrained $w = 1/[\sigma^{2}(F_{o}^{2}) + (0.0573P)^{2}]$ where $P = (F_{o}^{2} + 2F_{c}^{2})/3$ $(\Delta/\sigma)_{max} < 0.001$ $\Delta\rho_{max} = 0.10 \text{ e } \text{Å}^{-3}$ $\Delta\rho_{min} = -0.10 \text{ e } \text{Å}^{-3}$ Absolute structure: Flack <i>x</i> determined using 181 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons <i>et</i> <i>al.</i> , 2013) Absolute structure parameter: 0.7 (10)

### 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.

**Refinement**. Rigaku Xcalibur EOS and Xcalibur ATLAS diffractometers were used for the high-pressure studies. The X-ray wavelength used in all experiments was 0.71073 Å. The DAC was centred by the gasket-shadow method (Budzianowski & Katrusiak, 2004). The *CrysAlis PRO* program suite was used for data collection, determination of the *UB* matrices and data reductions. All data were accounted for the Lorentz, polarization and absorption effects. *OLEX2* (Dolomanov *et al.*, 2009), *SHELXT* (Sheldrick, 2015a) and *SHELXL* (Sheldrick, 2015b) were used to solve the structures by direct methods, and then to the full-matrix least-squares refinement.

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

			-	II */II	
	$\lambda$	<u>J</u>	2	$U_{\rm iso} / U_{\rm eq}$	
N1	0.5563 (5)	0.0358 (3)	0.9205 (5)	0.0550 (14)	
H2	0.684017	0.040646	0.954979	0.066*	
H1	0.542127	0.011566	0.777019	0.066*	
C1	0.4676 (5)	0.1112 (3)	0.9056 (6)	0.0464 (17)	
H12	0.484199	0.136515	1.061406	0.056*	
H11	0.328753	0.104832	0.879059	0.056*	
C2	0.5472 (5)	0.1630 (3)	0.7083 (6)	0.0442 (17)	
H22	0.686689	0.168369	0.731413	0.053*	
H21	0.526551	0.138715	0.551522	0.053*	
C3	0.4575 (5)	0.2410 (4)	0.7023 (7)	0.0497 (17)	
H32	0.475565	0.264744	0.860355	0.060*	
H31	0.318406	0.235580	0.675689	0.060*	
C4	0.5404 (5)	0.2940 (3)	0.5071 (7)	0.0464 (15)	
H42	0.679673	0.299029	0.533055	0.056*	
H41	0.521480	0.270362	0.349076	0.056*	

C5	0.4517 (5)	0.3729 (4)	0.5013 (6)	0.0539 (16)	
H51	0.312578	0.368251	0.473613	0.065*	
H52	0.470200	0.396829	0.659017	0.065*	
C6	0.5376 (5)	0.4237 (3)	0.3078 (9)	0.0695 (17)	
H63	0.475481	0.472863	0.313277	0.104*	
H62	0.674870	0.429650	0.336080	0.104*	
H61	0.517151	0.401053	0.150563	0.104*	

Atomic displacement parameters  $(Å^2)$ 

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.065 (3)	0.055 (5)	0.0453 (17)	0.0000 (18)	-0.004 (2)	0.004 (2)
C1	0.051 (3)	0.045 (7)	0.043 (2)	-0.003 (2)	0.001 (3)	-0.003 (3)
C2	0.046 (3)	0.049 (7)	0.0372 (19)	0.001 (2)	0.000 (2)	0.001 (2)
C3	0.040 (3)	0.065 (7)	0.044 (2)	0.000(2)	0.000 (3)	0.002 (2)
C4	0.043 (3)	0.055 (6)	0.041 (2)	-0.002 (2)	-0.003 (3)	0.000(2)
C5	0.054 (3)	0.059 (6)	0.048 (2)	-0.002 (2)	0.004 (3)	0.001 (2)
C6	0.072 (3)	0.077 (6)	0.060 (3)	0.004 (2)	0.001 (3)	0.008 (3)

### Geometric parameters (Å, °)

N1—H2	0.9000	C3—C4	1.528 (6)	
N1—H1	0.9000	C4—H42	0.9700	
N1-C1	1.454 (6)	C4—H41	0.9700	
C1—H12	0.9700	C4—C5	1.508 (6)	
C1—H11	0.9700	C5—H51	0.9700	
C1—C2	1.514 (6)	С5—Н52	0.9700	
C2—H22	0.9700	C5—C6	1.505 (6)	
C2—H21	0.9700	C6—H63	0.9600	
С2—С3	1.496 (6)	C6—H62	0.9600	
С3—Н32	0.9700	C6—H61	0.9600	
С3—Н31	0.9700			
H2—N1—H1	109.5	C4—C3—H31	108.6	
C1—N1—H2	109.5	C3—C4—H42	108.5	
C1—N1—H1	109.4	C3—C4—H41	108.5	
N1-C1-H12	108.4	H42—C4—H41	107.5	
N1-C1-H11	108.4	C5—C4—C3	114.9 (4)	
N1-C1-C2	115.6 (3)	C5—C4—H42	108.5	
H12—C1—H11	107.4	C5—C4—H41	108.5	
C2-C1-H12	108.4	C4—C5—H51	108.9	
C2-C1-H11	108.4	C4—C5—H52	108.9	
C1—C2—H22	108.7	H51—C5—H52	107.7	
C1-C2-H21	108.7	C6—C5—C4	113.4 (4)	
H22—C2—H21	107.6	C6—C5—H51	108.9	
C3—C2—C1	114.4 (4)	C6—C5—H52	108.9	
С3—С2—Н22	108.7	С5—С6—Н63	109.5	
C3—C2—H21	108.7	С5—С6—Н62	109.5	

C2—C3—H32 C2—C3—H31 C2—C3—C4 H32—C3—H31 C4—C3—H32	108.6 108.6 114.6 (3) 107.6 108.6	C5—C6—H61 H63—C6—H62 H63—C6—H61 H62—C6—H61	109.5 109.5 109.5 109.5
N1—C1—C2—C3	-178.2 (4)	C2—C3—C4—C5	-179.6 (4)
C1—C2—C3—C4	178.7 (3)	C3—C4—C5—C6	179.7 (3)

n-Hexylamine (hexylamine\_1\_40GPa)

Crystal data

 $C_6H_{15}N$  $D_{\rm x} = 1.098 {\rm Mg} {\rm m}^{-3}$  $M_r = 101.19$ Mo *K* $\alpha$  radiation,  $\lambda = 0.71073$  Å Orthorhombic,  $Pca2_1$ Cell parameters from 794 reflections  $\theta = 3.8 - 23.7^{\circ}$ a = 6.7241 (19) Åb = 17.052 (13) Å $\mu = 0.06 \text{ mm}^{-1}$ T = 295 Kc = 5.3367 (7) ÅV = 611.9 (5) Å<sup>3</sup> Disc, colourless Z = 4 $0.26 \times 0.26 \times 0.23$  mm F(000) = 232Data collection Rigaku Xcalibur Atlas 852 independent reflections diffractometer 401 reflections with  $I > 2\sigma(I)$ Detector resolution: 10.5384 pixels mm<sup>-1</sup>  $R_{\rm int} = 0.068$  $\theta_{\text{max}} = 30.4^{\circ}, \ \theta_{\text{min}} = 3.3^{\circ}$  $\varphi$ - and  $\omega$ -scans Absorption correction: multi-scan  $h = -8 \rightarrow 8$ (CrysAlis PRO; Rigaku OD, 2022)  $k = -14 \rightarrow 13$  $T_{\rm min} = 0.447, \ T_{\rm max} = 1.000$  $l = -7 \rightarrow 7$ 4114 measured reflections Refinement Refinement on  $F^2$ H-atom parameters constrained Least-squares matrix: full  $w = 1/[\sigma^2(F_o^2) + (0.0896P)^2]$  $R[F^2 > 2\sigma(F^2)] = 0.061$ where  $P = (F_0^2 + 2F_c^2)/3$  $wR(F^2) = 0.194$  $(\Delta/\sigma)_{\rm max} < 0.001$ S = 1.04 $\Delta \rho_{\rm max} = 0.17 \text{ e } \text{\AA}^{-3}$  $\Delta \rho_{\rm min} = -0.19 \text{ e} \text{ Å}^{-3}$ 852 reflections 64 parameters Absolute structure: Flack x determined using 1 restraint 130 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons et Primary atom site location: dual al., 2013) Hydrogen site location: mixed Absolute structure parameter: 3.1 (10)

### 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.

**Refinement**. Rigaku Xcalibur EOS and Xcalibur ATLAS diffractometers were used for the high-pressure studies. The X-ray wavelength used in all experiments was 0.71073 Å. The DAC was centred by the gasket-shadow method (Budzianowski & Katrusiak, 2004). The *CrysAlis PRO* program suite was used for data collection, determination of the *UB* matrices and data reductions. All data were accounted for the Lorentz, polarization and absorption effects. *OLEX2* (Dolomanov *et al.*, 2009), *SHELXT* (Sheldrick, 2015a) and *SHELXL* (Sheldrick, 2015b) were used to solve the structures by direct methods, and then to the full-matrix least-squares refinement.

	x	У	Ζ	$U_{ m iso}$ */ $U_{ m eq}$
N1	0.5636 (8)	0.0353 (5)	0.9407 (9)	0.058 (2)
H2	0.694796	0.041899	0.966999	0.069*
H1	0.544766	0.009549	0.795479	0.069*
C1	0.4647 (9)	0.1130 (6)	0.9275 (12)	0.053 (3)
H12	0.484791	0.140747	1.084208	0.063*
H11	0.322777	0.105681	0.904622	0.063*
C2	0.5466 (9)	0.1622 (6)	0.7122 (11)	0.050 (3)
H22	0.689124	0.168003	0.733140	0.060*
H21	0.523657	0.134733	0.555654	0.060*
C3	0.4542 (8)	0.2414 (6)	0.6972 (12)	0.056 (3)
H32	0.470772	0.267628	0.857227	0.067*
H31	0.312710	0.235476	0.667628	0.067*
C4	0.5425 (9)	0.2932 (6)	0.4908 (10)	0.047 (3)
H42	0.684285	0.298718	0.519215	0.057*
H41	0.524514	0.267358	0.330484	0.057*
C5	0.4508 (9)	0.3733 (6)	0.4782 (11)	0.063 (3)
H52	0.467165	0.398929	0.639147	0.075*
H51	0.309275	0.367858	0.447405	0.075*
C6	0.5408 (8)	0.4251 (5)	0.2748 (12)	0.069 (3)
H63	0.476291	0.475376	0.275976	0.103*
H62	0.680310	0.431891	0.306105	0.103*
H61	0.522333	0.400803	0.114258	0.103*

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

Atomic displacement parameters  $(Å^2)$ 

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.067 (4)	0.064 (9)	0.042 (3)	-0.002 (3)	-0.009 (3)	0.005 (3)
C1	0.059 (5)	0.048 (13)	0.051 (4)	0.002 (4)	-0.002(4)	0.004 (4)
C2	0.048 (5)	0.064 (12)	0.038 (3)	0.002 (4)	-0.004(4)	0.002 (4)
C3	0.043 (5)	0.084 (12)	0.041 (3)	-0.007(4)	0.005 (4)	-0.005 (4)
C4	0.052 (5)	0.055 (11)	0.035 (3)	0.000 (4)	-0.003 (4)	0.006 (4)
C5	0.057 (6)	0.082 (13)	0.049 (4)	-0.002 (4)	0.006 (4)	-0.004 (5)
C6	0.068 (5)	0.095 (12)	0.043 (4)	0.006 (4)	0.006 (5)	0.008 (4)

### *Geometric parameters (Å, °)*

N1—H2	0.9000	C3—C4	1.532 (11)
N1—H1	0.8998	C4—H42	0.9700
N1—C1	1.485 (12)	C4—H41	0.9700

C1 H12	0.0700	C4 C5	1 400 (11)
C1 = H11	0.9700	C5 H52	0.0700
$C_1 = C_2$	1.526 (11)	C5 H51	0.9700
$C_1 = C_2$	0.0700	C5_C6	1 525 (10)
$C_2 = H_{21}$	0.9700	C6_H63	0.0600
$C_2 = C_3$	1 480 (11)	C6 H62	0.9000
$C_2 = C_3$	0.0700	C6 H61	0.9000
$C_{3} = H_{21}$	0.9700	0-1101	0.9000
Сэ—нэт	0.9700		
H2—N1—H1	109.5	С4—С3—Н31	108.8
C1—N1—H2	109.5	C3—C4—H42	108.9
C1—N1—H1	109.3	C3—C4—H41	108.9
N1—C1—H12	109.4	H42—C4—H41	107.7
N1—C1—H11	109.4	C5—C4—C3	113.4 (6)
N1—C1—C2	111.4 (6)	C5—C4—H42	108.9
H12—C1—H11	108.0	C5—C4—H41	108.9
C2—C1—H12	109.4	C4—C5—H52	108.9
C2—C1—H11	109.4	C4—C5—H51	108.9
C1—C2—H22	109.0	C4—C5—C6	113.4 (6)
C1—C2—H21	109.0	H52—C5—H51	107.7
H22—C2—H21	107.8	С6—С5—Н52	108.9
C3—C2—C1	112.9 (6)	C6—C5—H51	108.9
C3—C2—H22	109.0	С5—С6—Н63	109.5
C3—C2—H21	109.0	С5—С6—Н62	109.5
С2—С3—Н32	108.8	C5—C6—H61	109.5
C2—C3—H31	108.8	Н63—С6—Н62	109.5
C2—C3—C4	113.6 (5)	H63—C6—H61	109.5
H32—C3—H31	107.7	H62—C6—H61	109.5
С4—С3—Н32	108.8		
N1—C1—C2—C3	-178.5 (7)	C2—C3—C4—C5	-179.3 (7)
C1—C2—C3—C4	176.9 (6)	C3—C4—C5—C6	179.2 (5)