Crystal structure of \(N,N,N',N'-\text{tetramethylethanediamine} \)

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The title compound \(N,N,N',N'-\text{tetramethylethanediamine}, \text{C}_6\text{H}_{16}\text{N}_2, \text{I} \) 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 \(\text{H}\cdot\cdot\cdot\text{H} \) (van der Waals) interactions dominate with a contact percentage of 92.3%.

1. Chemical context

\(N,N,N',N'-\text{tetramethylethanediamine} \) (TMEDA, \(\text{C}_6\text{H}_{16}\text{N}_2, \text{I} \)) 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 dimethyltin 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 I 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 disopropylamide forms a polymeric structure with I 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
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 $N1—C3—C3′—N1′$ [symmetry code: (i) $-x, 1-y, 1-z$] $= 180.0^\circ$ by symmetry. The conformations of the $C1—N1—C3—C3′$ and $C2—N1—C3—C3′$ 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 Table 1. The angles of $C2—N1—C1$ and $C2—N1—C3$ differ by about $1^\circ$ 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,
a Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) was carried out: Fig. 4 illustrates the Hirshfeld surface mapped over \(d_{\text{norm}}\) 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⋯H contacts are the largest region (92.3%). The remaining 6.7% are generated by N⋯H contacts, whereby C⋯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 \(\textbf{I}\) 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 \(\text{N}_2\text{N}_2\text{N}_2\text{N}_2\)-tetramethylethanediamine (BITNEX; Köster & Weiss, 1982), tetrasodium tetraakis(tetramethylethanediamine) octachloroditungsten (BORZUD; Cotton et al., 1982), sodium \((2,2,6,6\text{-tetramethylpiperidin-1-ide})\text{ferrocenyl-t-butyldimethyl-N,N,N,N\prime,chloride} (Spackman et al., 2007), hexakis(\(\mu_2\text{-methyl})\text{-tris(tetramethylethanediamine-lithium)methylthiorubin(IV)}\) tetrabromotetramethylethanediamine (COSZOH; Lauke et al., 1984), dilithium tribenzylidene-methane bis(tetramethylethanediamine) (COZJUW; Wilhelm et al., 1984), cyclopentadienyl sodium tetrabromotetramethylethanediamine (CPNATM10; Aoyagi et al., 1979).

Since \(\textbf{I}\) 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 \(\text{N}_2\text{N}_2\text{N}_2\text{N}_2\)-tetramethylethanediamine (Gessner & Strohmann, 2008), isopropyl lithium \(\text{N}_2\text{N}_2\text{N}_2\text{N}_2\)-tetramethylethanediamine (Strohmann et al., 2008), (diethylamino)diphenylsilyl \(\text{N}_2\text{N}_2\text{N}_2\text{N}_2\)-tetramethylethanediamine (Strohmann et al., 2006), \([{(R)-(S\text{-2})\text{-methoxyethyl}]\text{pyrrolidin-1-yl}[methyl]}\text{dimethylsilyl)}([\text{phenyl}]\text{methyl})\text{lithium} \(\text{N}_2\text{N}_2\text{N}_2\text{N}_2\)-tetramethylethanediamine (Strohmann et al., 2003), methyl lithium \(\text{N}_2\text{N}_2\text{N}_2\text{N}_2\)-tetramethylethanediamine (Gessner et al., 2011) and zinc bromide \(\text{N}_2\text{N}_2\text{N}_2\text{N}_2\)-tetramethylethanediamine (Eckert et al., 2013).

5. Synthesis and crystallization

\(\text{N}_2\text{N}_2\text{N}_2\text{N}_2\)-Tetramethylethanediamine \((\text{C}_6\text{H}_{16}\text{N}_2\text{N}_2, \textbf{I})\) 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 I 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 Å) and refined using a riding model, with $U_{iso}$(H) = 1.2$U_{eq}$(C) for CH$_2$ and CH hydrogen atoms and $U_{iso}$(H) = 1.5$U_{eq}$(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). Acta Cryst. B72, 171–179.
Knauer, L., Wattenberg, J., Kroesen, U. & Strohmann, 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. 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.
Schrimpf, M. A. & Jayatilaka, D. (2009). CrystEngComm, 11, 19–32.
Spackman, P. R., Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimmwood, D. J., Jayatilaka, D. & Spackman, M. A. (2021). J. Appl. Cryst. 54, 1006–1011.
Strohmann, C., Buchold, D. H. M., Seibel, T., Wild, K. & Schildbach, D. (2003). Chem. Ber. pp. 3453–3463.
Strohmann, C., Däschlein, C. & Auer, D. (2006). J. Am. Chem. Soc. 128, 704–705.
Strohmann, C., Gessner, V. H. & Damme, A. (2008). Chem. Commun. pp. 3381–3383.
Walker, M., Harvey, A. J. A., Sen, A. & Dessert, C. E. H. (2013). J. Phys. Chem. A, 117, 12590–12600.
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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).

\(N,N,N',N'\text{-Tetramethylethane-1,2-diamine}\)

Crystal data

\(C_6H_{16}N_2\)

\(Mr = 116.21\)

Monoclinic, \(P2_1/c\)

\(a = 5.6987 (13)\) Å

\(b = 8.311 (2)\) Å

\(c = 8.453 (2)\) Å

\(\beta = 106.954 (9)°\)

\(V = 382.92 (18)\) Å³

\(Z = 2\)

\(F(000) = 132\)

\(D_x = 1.008\) Mg m⁻³

Mo \(K\alpha\) radiation, \(\lambda = 0.71073\) Å

Cell parameters from 352 reflections

\(\theta = 3.5–22.8°\)

\(\mu = 0.06\) mm⁻¹

\(T = 100\) K

Block, colourless

\(0.56 \times 0.35 \times 0.30\) mm

Data collection

Bruker Venture D8 diffractometer

Radiation source: microfocus sealed X-ray tube, Incoatec \(\mu\)S

HELOS mirror optics monochromator

Detector resolution: 10.4167 pixels mm⁻¹

\(\varphi\) and \(\omega\) scans

Absorption correction: multi-scan

(SADABS; Krause et al., 2015)

Refinement

Refinement on \(F^2\)

Least-squares matrix: full

\(R(F^2 > 2\sigma(F^2)) = 0.038\)

\(wR(F^2) = 0.110\)

\(S = 1.05\)

1720 reflections

39 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

\(w = 1/[\sigma(F_c^2) + (0.0452P)^2 + 0.073P]\)

where \(P = (F_c^2 + 2F_c^2)/3\)

\((\Delta\sigma)_{\text{max}} < 0.001\)

\(\Delta\rho_{\text{max}} = 0.41\) e Å⁻³

\(\Delta\rho_{\text{min}} = -0.15\) 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           | Uiso*/Ueq    |
|----|-------------|-------------|-------------|--------------|
| 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 (Å²)**

|    | U₁₁   | U₂₂   | U₃₃   | U₁₂   | U₁₃   | U₂₃   |
|----|-------|-------|-------|-------|-------|-------|
| 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 (Å, °)**

|        |          |          |          |          |          |          |
|--------|----------|----------|----------|----------|----------|----------|
| 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—C3i   | 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)| C1—H1A  | 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—C3i| 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   | C3i—C3—H3A| 109.1  |          |          |          |
| H1B—C1—H1C| 109.5   | C3i—C3—H3B| 109.1  |          |          |          |
| Bond                  |   | Bond                  |   |
|----------------------|---|----------------------|---|
| N1—C2—H2A           | 109.5 | H3A—C3—H3B          | 107.9 |
| N1—C2—H2B           | 109.5 |                       |   |
| C1—N1—C3—C3\textsuperscript{i} | 167.33 (6) | N1—C3—C3\textsuperscript{i}—N1\textsuperscript{i} | 180.0 |
| C2—N1—C3—C3\textsuperscript{i} | −71.17 (8) |                       |   |

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