Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

[Indenyllithium·2(*N*,*N*,*N*′-trimethylethylenediamine)]$_\infty$: N–H hydrogen bridges to the indenyl anion

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.003 Å
Disorder in solvent or counterion
R factor = 0.040
wR factor = 0.114
Data-to-parameter ratio = 9.7

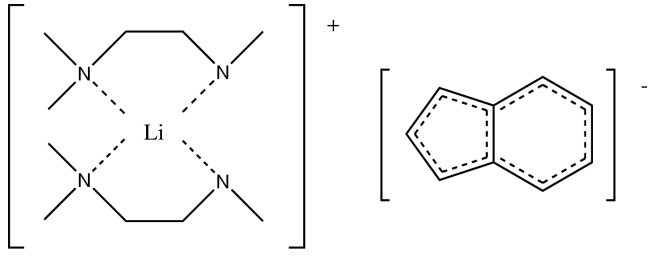
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 2 November 2001
Accepted 6 November 2001
Online 10 November 2001

The crystal structure of the title compound, bis(*N*,*N*,*N*′-trimethylethylenediamine)lithium indenide, [Li($C_5H_{14}N_2$)$_2$](C_9H_7), forms discrete layers of cations and anions, with N—H···C hydrogen-bond interactions between these layers. Both the cation and anion exhibit a crystallographic centre of inversion. This leads to a twofold disorder of the anion.

Comment

Although hydrogen-bond bridges to 'carbanions' have been extensively studied in solution (Cram, 1965; Ford, 1970; Pascault & Gole, 1971; Hogen-Esch, 1973; Hussénium *et al.*, 1989; Eliasson *et al.*, 1990; McEwen & Ahlberg, 1992; McEwen *et al.*, 1993), there are only a few cases of such bonds observed in the solid state (Laube *et al.*, 1985; Klebe *et al.*, 1987; Buchholz, Harms, Marsch *et al.*, 1989; Buchholz, Harms, Massa & Boche, 1989; Armstrong *et al.*, 1991; Lambert *et al.*, 1992). It was also recognized that the interaction of Li^+ with, *e.g.*, the N atom of an amine RNH_2 leads to better hydrogen-bonding properties for the amine (Buchholz, Harms, Marsch *et al.*, 1989). Here we report the crystal structure of [indenyllithium·2(*N*,*N*,*N*′-trimethylethylenediamine)]$_\infty$. The indenyl 'anion' has been of special interest for hydrogen bonding with a 'carbanion', and for mechanistic studies of H/D exchange reactions (Cram, 1965; Eliasson *et al.*, 1990; Hussénium *et al.*, 1989; McEwen & Ahlberg, 1992).



(I)

Experimental

0.49 mmol of LDA (lithium diisopropylamide) in 5 ml THF was treated with 0.46 mmol indene at 195 K. The yellow solution was warmed to room temperature and 3.14 mmol TriMEDA (trimethylethylendiamine) was added. After several days at room temperature, yellow–brown single crystals were obtained.

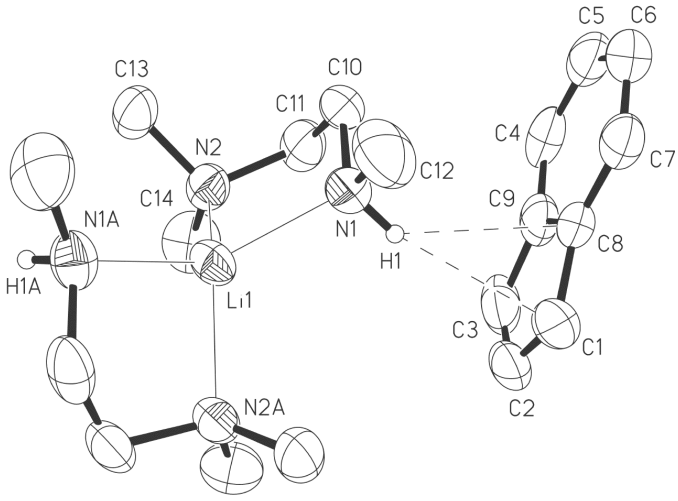


Figure 1
The structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. The disorder is not shown.

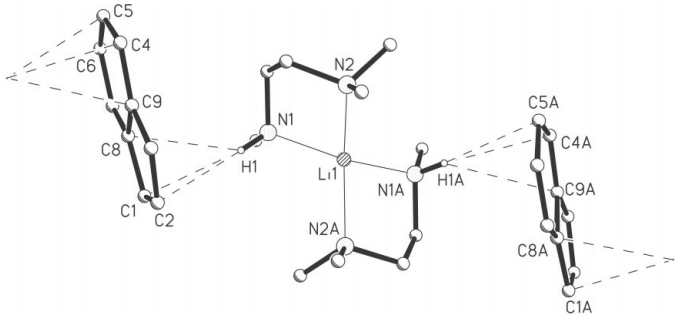


Figure 2
N—H···C interactions in the title compound.

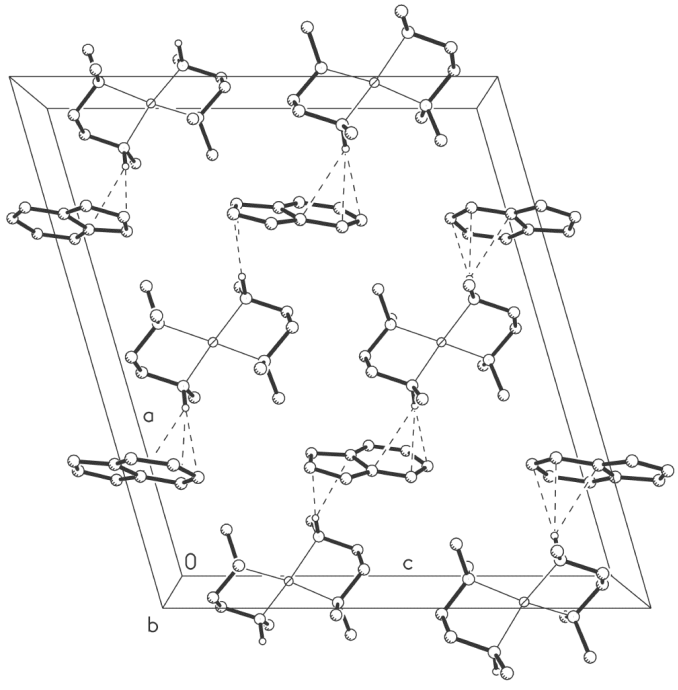


Figure 3
Packing diagram, viewed down the *b* axis.

Crystal data

$[Li(C_5H_{14}N_2)_2](C_9H_7)$	D_x = 1.034 Mg m^{-3}
M_r = 326.45	Cu $K\alpha$ radiation
Monoclinic, *C*2/*c*	Cell parameters from 25 reflections
a = 17.669 (8) Å	θ = 39.8–46.9°
b = 7.921 (2) Å	μ = 0.46 mm^{-1}
c = 15.598 (4) Å	*T* = 173 (2) K
β = 106.10 (1)°	Prism, colourless
V = 2097.4 (12) Å^3	0.40 × 0.25 × 0.20 mm
Z = 4	

Data collection

Enraf–Nonius CAD-4 diffractometer	θ_{max} = 55.0°
ω scans	$h = -18 \rightarrow 18$
2624 measured reflections	$k = -8 \rightarrow 8$
1323 independent reflections	$l = 0 \rightarrow 16$
1111 reflections with $I > 2\sigma(I)$	3 standard reflections
R_{int} = 0.058	frequency: 60 min
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 0.8262P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.040	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.114	$\Delta\rho_{max}$ = 0.11 e Å^{-3}
S = 1.07	$\Delta\rho_{min}$ = −0.14 e Å^{-3}
1323 reflections	Extinction correction: *SHELXL*97
137 parameters	Extinction coefficient: 0.0016 (2)
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···C1	0.892 (19)	2.522 (19)	3.386 (7)	163.0 (15)
N1—H1···C4^{i}	0.892 (19)	2.553 (19)	3.373 (6)	153.0 (14)
N1—H1···C5^{i}	0.892 (19)	2.830 (18)	3.721 (9)	176.5 (14)
N1—H1···C8	0.892 (19)	2.648 (18)	3.359 (5)	137.3 (13)
N1—H1···C9^{i}	0.892 (19)	2.738 (18)	3.400 (5)	131.9 (13)

Symmetry code: (i) $\frac{3}{2} - x, \frac{1}{2} - y, -z$.

The structure was initially solved in space group *Cc*. Displacement-ellipsoid plots after the anisotropic refinement indicated clearly a disorder of the indenyl anion due to inversion symmetry. The refinement was continued in space group *C*2/*c*, in which the anion adopts crystallographic inversion symmetry leading to a twofold disorder. A complete indenyl anion (occupancy factor 0.5) has been modelled using restraints for bond distances, planarity and displacement parameters. The derived geometry (C—C bond distances 1.37–1.43 Å) has been fixed as a rigid group in the final stage of the refinement. A similiar disorder of an indenyl anion has been found in the crystal structure of bis[bis(dimethylphosphino)ethane-*P*,*P*′]-rhodium indenide (Marder & Williams, 1987). The N-bonded H atom was located and allowed to refine isotropically.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1996); software used to prepare material for publication: *SHELXTL*.

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