Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A variable-temperature study of 1,2-bis(dimethylamino)-1,2-bis(2,6-dimethylanilino)diborane

Andrei S. Batsanov,[a]* George Bramham,[b] Nicholas C. Norman[b] and Christopher A. Russell[b]

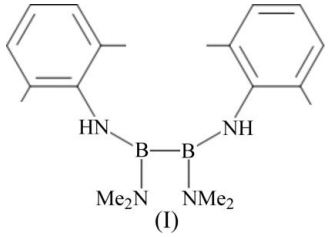
[a]Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England, and [b]School of Chemistry, University of Bristol, Bristol BS8 1TS, England
Correspondence e-mail: a.s.batsanov@durham.ac.uk

Received 17 August 2011
Accepted 24 September 2011
Online 28 September 2011

The title compound, $C_{20}H_{32}B_2N_4$, is monoclinic at ambient temperature but triclinic (pseudo-monoclinic) below 150 K. The structures of the two phases, determined at 200 and 120 K, respectively, are very similar, the molecular symmetry being crystallographic C_2 and approximate (local) C_2, respectively. There is significant π conjugation within each N—B—N moiety, but none between them or between the N—B—N and arene moieties.

Comment

Tetra(amido)diborane(4) derivatives are important as precursors in diborane(4) chemistry (Brotherton, 1964), especially since the Suzuki reaction became widely used in the synthesis of complex molecular species (Miyaura & Suzuki, 1995). The title compound, (I), was first reported by Patton *et al.* (2001). In the course of our studies of substitution reactions in diboranes (Baber *et al.*, 2005), we reproduced the synthesis of (I) and structurally characterized it by X-ray diffraction, which revealed a phase transition.



(I)

Under ambient conditions, (I) is monoclinic. On slow cooling, this α form (fully studied at 200 K) persisted to 160 K, as was indicated by express lattice parameter determinations at 292, 274, 250, 230, 200, 180 and 160 K. The phase transition was observed between 160 and 150 K, at which point the peaks of most reflections became split, but the separations between the maxima were not wide enough to index the components separately. If flash-cooled below 150 K, the crystals shattered. After several unsuccessful attempts, we obtained just one crystal of the low-temperature phase, β-(I), by annealing a crystal with three cycles of cooling–heating above the phase transition (230 to 160 K) before finally cooling it to 120 K. On warming to 230 K, the crystal remained triclinic, but cracked on warming to room temperature. We tried the annealing procedure on other samples but without success.

The structure of β-(I), determined from the data set collected at 120 K, is triclinic, although the actual difference from α-(I) is small. To simplify the comparison, β-(I) is presented here in the (nonstandard) pseudo-monoclinic lattice setting analogous to that of α-(I). Interestingly, this lattice of β-(I) can be transformed by the operation $(10\bar{1}/101/0\bar{1}0)$ to a C-centred pseudo-monoclinic lattice with a = 15.844, b = 13.702 and c = 9.645 Å, and α = 89.91, β = 93.46 and γ = 89.66°, and V = 2090 Å^3. However, we found no approximate structural or Laue symmetry (R_{int} = 0.51) associated with this cell.

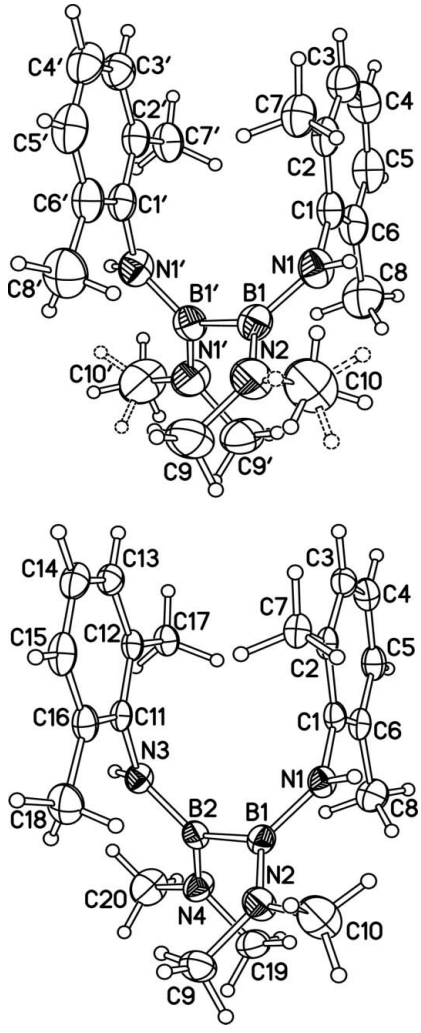


Figure 1
The molecular structure of (I) in the α (top) and β (bottom) forms. Displacement ellipsoids are drawn at the 50% probability level and dashed lines indicate the minor disordered components of the methyl groups. Primed atoms are generated by the crystallographic twofold axis (symmetry code: $-x+\frac{1}{2}, y, -z+\frac{1}{2}$).

 © 2011 International Union of Crystallography doi:10.1107/S0108270111039230

The molecular structure of (I) (Fig. 1) is very similar to that of its mesityl analogue, 1,2-bis(2,4,6-trimethylanilido)-1,2-bis-(dimethylamido)diborane, (II) (Fırıncı *et al.*, 2010). In the α-(I) form, the molecule possesses a crystallographic twofold axis passing through the mid-point of the B—B bond. In the β form, this twofold symmetry was noncrystallographic yet almost perfect. In fact, the structure of β-(I) can be solved and refined to $R_1 = 0.125$ ($R_{int} = 0.255$) in the space group $P2/n$ of the α phase, ignoring the deviation of the α and γ angles from 90°.

All B and N atoms have planar–trigonal geometry. In each case, the planes of a B atom and its two adjacent N atoms coincide within experimental error, and the B—N distances (Tables 1 and 3) indicate a degree of multiple bonding (Weber *et al.*, 2001). On the other hand, strong twists around the B—B bond [67.6 (2)° in α-(I) and 65.9 (2)° in β-(I)] and around the N—C(Ar) bonds [69.2 (2)° in α-(I), and 67.1 (2) and 68.8 (2)° in β-(I)] preclude any π-conjugation. Thus, the B—B bond is essentially single; its length falls within the usual range of 1.69–1.75 Å for tetramido-diborane derivatives (Weber *et al.*, 2001; Baber *et al.*, 2005) and is practically the same as in (II) [1.735 (6) Å].

The two dimethylaryl groups in molecule (I) are nearly parallel, the interplanar angle being 3.5 (1)° in both forms. These groups stack closely together in an offset face-to-face manner, with mean interplanar separations of 3.48 and 3.46 Å in the α and β forms, respectively. Similar stacking occurs between the dimethylaryl groups of adjacent molecules related by an inversion centre. In this case, the arene planes are rigorously parallel, with an interplanar separation of 3.4270 (5) Å in α-(I) and 3.2018 (7) Å in β-(I). Thus, the structure contains an infinite stacking motif, running parallel to the [011] direction.

Since the lone electron pairs of the N atoms are involved in π conjugation, the molecule of (I) contains no electronegative acceptors for strong hydrogen bonds. The N—H bonds point roughly towards the π orbitals of arene C atoms of adjacent molecules within the stack. In α-(I) there is one symmetrically-independent contact of this type, *viz.* N1—H1N···C3($-x$, $-y$, $-z$) (Table 2), whereas in β-(I) there are two, one with the same notation and the other N3—H3N···C13($-x + 1$, $-y$, $-z + 1$) (Table 4). These H···C distances are 2.77 (1), and 2.76 (2) and 2.76 (2) Å, respectively. Rowland & Taylor (1996) estimated the standard van der Waals H···C separation as 3.02 Å, using H-atom positions normalized by moving the H atom along the observed X—H bond until this bond length matched the neutron diffraction value (0.983 Å for N—H). Applying such normalization to (I) and (II) reduces the above-mentioned H···C distances to 2.67, and 2.68 and 2.66 Å, respectively, hence these contacts can be regarded as weak hydrogen bonds (Desiraju & Steiner, 1999).

Experimental

Compound (I) was prepared from the reaction between $B_2(NMe_2)_4$ and two equivalents of NH_2-2,6-$Me_2C_6H_3$ in toluene and crystals were isolated by slow cooling.

Form α-(I)

Crystal data

$C_{20}H_{32}B_2N_4$
$M_r = 350.12$
Monoclinic, $P2/n$
$a = 10.4957$ (11) Å
$b = 9.6327$ (10) Å
$c = 10.5554$ (11) Å
$\beta = 98.06$ (2)°
$V = 1056.63$ (19) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.07$ mm^{-1}
$T = 200$ K
0.53 × 0.35 × 0.05 mm

Data collection

Siemens SMART 1000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2006)
$T_{min} = 0.924$, $T_{max} = 1.000$
10983 measured reflections
2436 independent reflections
1779 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.128$
$S = 1.05$
2436 reflections
124 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}

Form β-(I)

Crystal data

$C_{20}H_{32}B_2N_4$
$M_r = 350.12$
Triclinic, $P\overline{1}$
$a = 10.5043$ (13) Å
$b = 9.6449$ (11) Å
$c = 10.4428$ (14) Å
$\alpha = 92.69$ (3)°
$\beta = 98.29$ (3)°
$\gamma = 87.45$ (3)°
$V = 1045.0$ (2) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.07$ mm^{-1}
$T = 120$ K
0.52 × 0.21 × 0.02 mm

Data collection

Bruker SMART 6000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2006)
$T_{min} = 0.715$, $T_{max} = 0.862$
9870 measured reflections
3693 independent reflections
2774 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.150$
$S = 1.05$
3693 reflections
249 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

All H atoms were located in difference maps. Methyl groups were refined as rigid bodies rotating around C—C or N—C bonds, with C—H = 0.98 Å. The $C10H_3$ group in α-(I) was treated as ideally disordered over two conformations rotated from one another by 60°. The arene H atoms were treated as riding on their C atoms, with C—H = 0.95 Å. The amino H atoms were refined with N—H distances restrained to 0.88 (2) Å. The U_{iso} values of the methyl H atoms were constrained to 1.5 times, and those of other H atoms to 1.2 times, the U_{eq} value of the attached C or N atom.

Data collection: *SMART* (Bruker, 1998) for α-(I); *SMART* (Bruker, 2001) for β-(I). For both forms, cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXTL* (Version 6.12; Sheldrick, 2008);

Table 1
Selected bond lengths (Å) for α-(I).

N1—C1	1.4237 (16)	N2—B1	1.4197 (19)
N1—B1	1.4290 (19)	B1—B1^{i}	1.727 (3)

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

Table 2
Hydrogen-bond geometry (Å, °) for α-(I).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···C3^{ii}	0.87 (1)	2.77 (1)	3.5631 (18)	152 (1)

Symmetry code: (ii) $-x, -y, -z$.

Table 3
Selected bond lengths (Å) for β-(I).

N1—C1	1.422 (2)	N3—B2	1.428 (3)
N1—B1	1.433 (3)	N4—B2	1.424 (3)
N2—B1	1.423 (3)	B1—B2	1.726 (3)
N3—C11	1.424 (2)		

Table 4
Hydrogen-bond geometry (Å, °) for β-(I).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···C3^{i}	0.88 (2)	2.76 (2)	3.544 (2)	148 (2)
N3—H3N···C13^{ii}	0.87 (2)	2.76 (2)	3.528 (3)	148 (2)

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x+1, -y, -z+1$.

program(s) used to refine structure: *SHELXTL*; molecular graphics: *OLEX2* (Version 1.1-β+++; Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

The authors thank Professor J. A. K. Howard for helpful discussions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MX3055). Services for accessing these data are described at the back of the journal.

References

Baber, R. A., Charmant, J. P. H., Cook, A. J. R., Farthing, N. E., Haddow, M. F., Norman, N. C., Orpen, A. G., Russell, C. A. & Slattery, J. M. (2005). *Dalton Trans.* pp. 3137–3139.
Brotherton, R. J. (1964). *Progress in Boron Chemistry*, edited by H. Steinberg & A. L. McCloskey, ch. 1. New York: Macmillan.
Bruker (1998). *SMART*. Version 5.049. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2001). *SMART*. Version 5.625. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). *SAINT*. Version 7.46A. Bruker AXS Inc., Madison, Wisconsin, USA.
Desiraju, G. & Steiner, T. (1999). In *The Weak Hydrogen Bond*. Oxford University Press.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Fırıncı, E., Söyleyici, H. C., Gziroğlu, E., Temel, E., Büyükgüngör, O. & Şahin, Y. (2010). *Polyhedron*, **29**, 1465–1468.
Miyaura, N. & Suzuki, A. (1995). *Chem. Rev.* **95**, 2457–2483.
Patton, J. T., Feng, S. G. & Abboud, K. A. (2001). *Organometallics*, **20**, 3399–3405.
Rowland, R. S. & Taylor, R. (1996). *J. Phys. Chem.* **100**, 7384–7391.
Sheldrick, G. M. (2006). *SADABS*. Version 2006/1. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Weber, L., Schneider, M. & Lönnecke, P. (2001). *J. Chem. Soc. Dalton Trans.* pp. 3459–3464.