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Isomeric icosaboranes $B_{20}H_{26}$: the synchrotron structure of 1,1′-bis(*nido*-decaboranyl)

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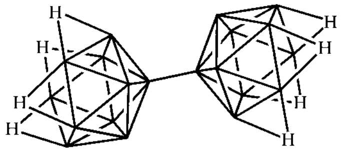
An isomer of $B_{20}H_{26}$, isolated from the autolysis of *nido*-$B_{10}H_{14}$ in a silent electrical discharge, is shown to be the title compound 1,1′-bis(*nido*-decaboranyl). The molecule has crystallographic inversion symmetry and a long intercage B—B bond of 1.704 (3) Å.

Comment

Some time ago, the synthesis of the globular macropolyhedral megaloborane $B_{20}H_{26}$, from the passage of $B_{10}H_{14}$ through a silent electrical discharge, was reported, although precise reaction conditions were unspecified (Friedman *et al.*, 1963). An alternative Me_2BNHMe-catalysed thermolytic preparation was also reported (Miller & Muetterties, 1963; Miller *et al.*, 1964). Since then (Miller & Muetterties, 1963, Enemark *et al.*, 1966), this very interesting compound has been essentially unexamined. We have now developed an interest in $B_{20}H_{26}$ and in the possibilities of synthesizing other globular boranes (Kaur *et al.*, 1997; Bould *et al.*, 1999, 2000; Yao *et al.*, 1999), and have consequently sought to duplicate the original synthesis, which used a silent electrical discharge. A 1500 V AC silent discharge through a glass tube containing decaborane(14) yielded predominantly a yellow material which is a main focus of our investigations and which we have yet to identify. However, dichloromethane extraction of the material followed by high-performance liquid chromatographic (HPLC) separation yielded very small quantities of several substances, shown by NMR spectroscopy to be a variety of boron hydride species. Predominant among these was a series of compounds identified by NMR spectroscopy [compare with Boocock *et al.* (1980)] as being in the bis(*nido*-decaboranyl) family, $(B_{10}H_{13})_2$. Two of these were identified as the known compounds 2,2′- and 1,2′-(*nido*-$B_{10}H_{13}$)$_2$ [after Boocock *et al.* (1981)]. A further previously unobserved bis(*nido*-decaboranyl) isomer was isolated and crystallized by slow sublimation in an evacuated tube. We report here its structure determination as the 1,1′-(*nido*-$B_{10}H_{13}$)$_2$ isomer, *i.e.* the title compound, (I). Crystals were small (0.03 mm cubes) and the single-crystal work required synchrotron-generated X-irradiation for sufficient diffraction intensity (Cernik *et al.*, 1997, 2000; Clegg *et al.*, 1998).



(I)

There are 15 possible isomers of (*nido*-$B_{10}H_{13}$)$_2$, of which eight are four enantiomeric pairs (Boocock *et al.*, 1980). Those previously characterized structurally by single-crystal X-ray work are the 1,2′- (Barrett *et al.*, 1985), the 1,5′- (Brown *et al.*, 1979), the 2,2′- and the 2,6′- species (Boocock *et al.*, 1980). The 6,6′- (Boocock *et al.*, 1979), 2,5′- and 5,5′-isomers (Boocock *et al.*, 1981) have been characterized by NMR spectroscopy. The 1,1′-isomer (Fig. 1) contains an inversion centre at the midpoint of the intercage B—B linkage. The B—B linkage distance [B1—B1^{i}; symmetry code: (i) $1 - x, 1 - y, 1 - z$] of 1.704 (3) Å is at the top end of the range of values reported for bis(decaboranyl) isomers, which range from 1.698 (2) (1,5′-isomer; Brown *et al.*, 1979) to 1.679 (3) Å (2,2′-isomer; Barrett *et al.*, 1985). The basal intracluster B—B distances associated with the linkage B1 atom show small but significant lengthenings of *ca* 0.017 (2) Å compared to those around the unsubstituted B3 atom and are similar in magnitude to those noted previously (0.015 Å; Boocock *et al.*, 1980). Other distances on the substituted side of the decaborane subcluster do not differ significantly from those on the unsubstituted side with the exception of the long B5—B10 ‘gunwale’ interboron vector in the *nido*-decaboronyl ‘boat’, which, at 1.955 (2) Å, is 0.016 (2) Å shorter than the opposing B7—B8 distance.

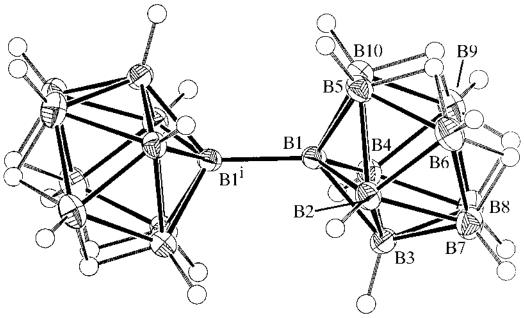


Figure 1
The crystallographically determined molecular structure of 1,1′-(*nido*-$B_{10}H_{13}$)$_2$ drawn with 40% probability ellipsoids and with H atoms shown as small circles of arbitrary radii. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

Experimental

Decaborane(14) (0.472 g), contained in a small sample vial, was placed in a glass high-voltage silent-discharge reaction tube [constructed in a similar manner to the one used by Friedman *et al.* (1963)]. Silent electrical discharge under dynamic vacuum (1500 V

AC, *ca* 10^{-3} mm Hg) for 90 min resulted in a substantial amount of yellow material being deposited on the sides of the tube. The reaction vessel was opened to air and the material extracted with dichloromethane. The extract was filtered through silica gel and the filtrate subjected to preparative HPLC separation (25 × 2.12 cm column, Lichosorb SI 60, 15:85 CH_2Cl_2/*n*-hexane, 20 ml min^{-1}) giving three products with R_T 6.9 (component A), 7.3 (component B) and 7.7 m (component C). Components A and B were identified by ^{11}B NMR spectroscopy as 2,2′- and 1,2′-(*nido*-$B_{10}H_{13}$)$_2$, respectively, by comparison with previously characterized samples (Boocock *et al.*, 1981). The ^{11}B NMR spectroscopic characterization of component C suggested the previously unreported 1,1′-bis(decaboranyl) isomer; $CDCl_3$ solution 300 K, cluster resonances ordered as assignment, $\delta(^{11}B)$/p.p.m. [$^2J(^{11}B–^1H)$/Hz in brackets]: B2,4 −34.5 [156]; B5,7,8,10 +0.8 [148]; B6,9 +9.5 [165]; B3 +12.8 [151]; B1 +19.8 [site of conjuncto linkage]. Single crystals were grown over a period of two months by sublimation in a sealed evacuated glass tube placed on a warm oven.

Crystal data

$B_{20}H_{26}$
$M_r = 242.41$
Orthorhombic, *Pbca*
$a = 10.6601$ (5) Å
$b = 10.5515$ (5) Å
$c = 14.5604$ (6) Å
$V = 1637.75$ (13) Å^3
$Z = 4$
$D_x = 0.983$ Mg m^{-3}

Synchrotron radiation
$\lambda = 0.6890$ Å
Cell parameters from 5421 reflections
$\theta = 2.7–29.4°$
$\mu = 0.04$ mm^{-1}
$T = 150$ (2) K
Cuboid, colourless
0.03 × 0.03 × 0.03 mm

Data collection

Siemens SMART CCD diffractometer
ω rotation scans with narrow frames
10 589 measured reflections
2301 independent reflections
1746 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.056$
$\theta_{\rm max} = 29.4°$
$h = -14 \rightarrow 14$
$k = -14 \rightarrow 7$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.150$
$S = 1.09$
2301 reflections
143 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0740P)^2 + 0.3725P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.38$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.18$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

B1—B1$^{\rm i}$	1.704 (3)	B3—B8	1.759 (2)
B1—B10	1.7620 (19)	B3—B4	1.773 (2)
B1—B5	1.7628 (19)	B4—B9	1.717 (2)
B1—B3	1.7836 (19)	B4—B10	1.777 (2)
B1—B2	1.788 (2)	B4—B8	1.786 (2)
B1—B4	1.7910 (19)	B5—B6	1.790 (2)
B2—B6	1.715 (2)	B5—B10	1.955 (2)
B2—B3	1.772 (2)	B6—B7	1.796 (2)
B2—B5	1.787 (2)	B7—B8	1.972 (2)
B2—B7	1.787 (2)	B8—B9	1.784 (2)
B3—B7	1.758 (2)	B9—B10	1.786 (2)
B1$^{\rm i}$—B1—B10	116.40 (12)	B1$^{\rm i}$—B1—B2	119.14 (13)
B1$^{\rm i}$—B1—B5	115.71 (12)	B1$^{\rm i}$—B1—B4	120.14 (13)
B1$^{\rm i}$—B1—B3	128.32 (12)		

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

Data collection procedures are described by Clegg *et al.* (1998). The data set, derived from several series of exposures, is complete to $\theta = 26°$. Corrections were applied for the decay in the synchrotron primary beam intensity. All H atoms were refined freely [B—H range 1.051 (16)–1.329 (17) Å].

Data collection: *SMART* (Siemens, 1997); cell refinement: *SAINT* (Siemens, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1315). Services for accessing these data are described at the back of the journal.

References

Barrett, S. A., Greenwood, N. N., Kennedy, J. D. & Thornton-Pett, M. (1985). *Polyhedron*, **4**, 1981–1984.

Boocock, S. K., Cheek, Y. M., Greenwood, N. N. & Kennedy, J. D. (1981). *J. Chem. Soc. Dalton Trans.* pp. 1430–1437.

Boocock, S. K., Greenwood, N. N., Kennedy, J. D., McDonald, W. S. & Staves, J. (1980). *J. Chem. Soc. Dalton Trans.* pp. 790–796.

Boocock, S. K., Greenwood, N. N., Kennedy, J. D. & Taylorson, D. (1979). *J. Chem. Soc. Chem. Commun.* pp. 16–17.

Bould, J., Clegg, W., Teat, S. J., Barton, L., Rath, N. P., Thornton-Pett, M. & Kennedy, J. D. (1999). *Inorg. Chim. Acta*, **289**, 95–124.

Bould, J., Ormsby, D. L., Yao, H.-J., Hu, C.-H., Sun, J., Jin, R.-S., Shea, S. L., Clegg, W., Jelínek, T., Rath, N. P., Thornton-Pett, M., Greatrex, R., Zheng, P.-J., Barton, L., Štíbr, B. & Kennedy, J. D. (2000). *Contemporary Boron Chemistry*, edited by M. Davidson, A. K. Hughes, T. B. Marder & K. Wade, pp. 171–174. Cambridge: Royal Society of Chemistry.

Brown, G. M., Pinson, J. W. & Ingram, L. L. (1979). *Inorg. Chem.* **18**, 1951–1956.

Cernik, R. J., Clegg, W., Catlow, C. R. A., Bushnell-Wye, G., Flaherty, J. V., Greaves, G. N., Burrows, I., Taylor, D. J., Teat, S. J. & Hamichi, M. (1997). *J. Synchrotron Rad.* **4**, 279–286.

Cernik, R. J., Clegg, W., Catlow, C. R. A., Bushnell-Wye, G., Flaherty, J. V., Greaves, G. N., Burrows, I., Taylor, D. J., Teat, S. J. & Hamichi, M. (2000). *J. Synchrotron Rad.* **7**, 40.

Clegg, W., Elsegood, M. R. J., Teat, S. J., Redshaw, C. & Gibson, V. C. (1998). *J. Chem. Soc. Dalton Trans.* pp. 3037–3040.

Enemark, J. H., Friedman, L. B., Hartsuck, J. E. & Lipscomb, W. N. (1966). *J. Am. Chem. Soc.* **88**, 3659–3661.

Friedman, L. B., Dobrott, R. D. & Lipscomb, W. N. (1963). *J. Am. Chem. Soc.* **85**, 3505.

Kaur, P., Perera, S. D., Jelínek, T., Štíbr, B., Kennedy, J. D., Clegg, W. & Thornton-Pett, M. (1997). *J. Chem. Soc. Chem. Commun.* pp. 217–218.

Miller, N. E., Forstner, J. A. & Muetterties, E. L. (1964). *Inorg. Chem.* **3**, 1690–1694.

Miller, N. E. & Muetterties, E. L. (1963). *J. Am. Chem. Soc.* **85**, 3506.

Sheldrick, G. M. (1998). *SHELXTL.* Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Siemens (1997). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Yao, H.-J., Hu, C.-H., Sun, J., Jin, R.-S., Zheng, P.-J., Bould, J., Greatrex, R., Kennedy, J. D., Ormsby, D. & Thornton-Pett, M. (1999). *Collect. Czech. Chem. Commun.* **64**, 927–937.