N-Methyl-*B*-mesityldibenzo-1,4-azaborinine: the First Experimental Structure of a 1,4-Azaborinine Derivative

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The structure of the 1,4-azaborinine ring in the title compound, a representative of a novel class of potentially aromatic compounds that are isoelectronic with arenes, confirms conclusions of earlier *ab initio* calculations that cyclic conjugation in 1,4-azaborinines is interrupted by the boron atom.

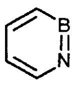
The azaborinines **1–3**, benzene analogues in which two carbon atoms have been replaced by a boron and a nitrogen, have aroused considerable theoretical[1–4] and experimental[5,6] interest, both because they may be aromatic and because of their possible use in radiotherapy.[7]

Of the three possible azaborinine isomers, many derivatives of 1,2-azaborinine **1** are known, none of the 1,3-isomer **2** and only a few of 1,4-azaborinine **3**. In particular, we known of no experimental structure of a derivative of **3**, although calculated structures abound.[1–4] We now report the first X-ray structure determination of a derivative of 1,4-azaborinine, the title compound **4**. To our knowledge, our structure is also the first that has been determined for an azaborinine derivative without heteroatom substituents.

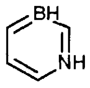
Small quantities of **4** were obtained by reacting *o,o*′-dilithiodiphenylmethylamine **5** with $BF_3 \cdot Et_2O$ followed by mesityl lithium. Column chromatography over kieselgel and recrystallisation from diethyl ether–light petroleum yielded colourless crystals that were neither air nor moisture sensitive. The ^{13}C and ^{11}B chemical shifts are shown in parentheses in Scheme 1.

X-ray analysis† of **4** gave the structure shown in Fig. 1. The azaborinine ring deviates slightly from planarity towards a twist boat conformation, but the mean deviation from a plane is only 0.03 Å. The mesityl ring is, as expected, perpendicular to the azaborinine system.

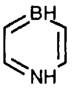
Of particular interest are the bond lengths in the 1,4-azaborinine ring. Our MP2/6-31G* calculated structure[4] for the parent compound **3** suggested that the ring conjugation extends over the four carbons and the nitrogen, but is interrupted by the boron. The observed bond lengths (CC = 1.42; CN = 1.38; CB = 1.54 Å) confirm this conclusion. The MP2/6-31G* calculated values for **3** (1.37, 1.37 and 1.52 Å, respectively) agree well with the crystal structure except for the benzo-fused CC-bonds, which should be longer in **4** than in **3**. MNDO[8] and AM1[9] structures have also been calculated for **4**. The results are compared with the experimental structure in Table 1. Generally, AM1 gives slightly better agreement with experiment than MNDO. Both methods fail to predict the short C(2)–C(3) and C(8)–C(9) distances and calculate the CN-ring bonds to be too long. AM1 finds the C–Me bonds to be drastically too short.



1



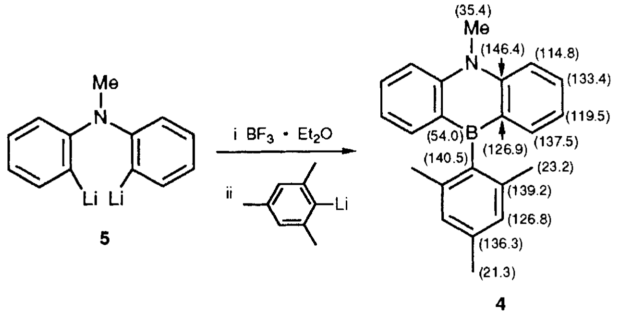
2



3

A comparison of the geometry of **4** with related compounds shows that the CN bonds are slightly longer than those in pyridine (1.34 Å)[10] and pyridinium ions (1.31–1.35 Å).[11] The ring CB-bonds are slightly shorter than the B–phenyl bonds in triphenylborane (1.57–1.59 Å)[12] and the azaborinine CC-distances are within the range observed for normal arenes. In general, however, the azaborinine ring geometry is consistent with the results of the *ab initio* calculations.

The ^{13}C and ^{11}B chemical shifts also support our interpretation. The boron shift is comparable to that (δ 60.0–60.2)[13] found for triphenylborane or the δ 58.0[14] found for a 9-phenyl-9,10-dihydro-9-boraanthracene. The mesityl group ^{13}C chemical shifts of **4** are all in the range expected from compounds like tris(mesityl)borane[15] and the shifts found for C1/C7 and C6/C12 are close to those calculated[4] for the parent heterocycle **3** (δ 141.0 and 115.8, respectively).



Scheme 1

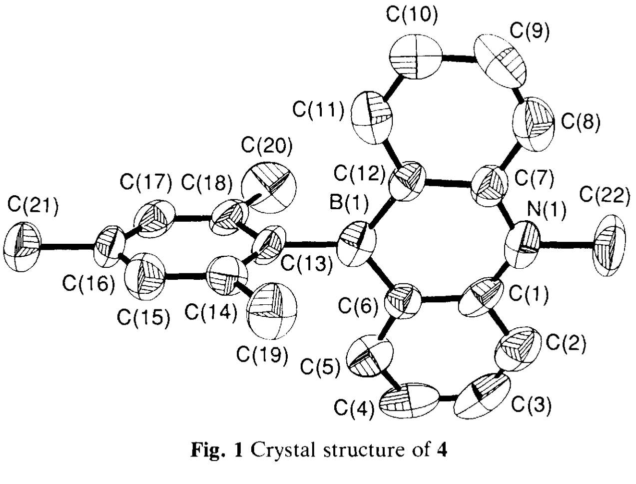


Fig. 1 Crystal structure of **4**

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† *Crystal data* for **4**: $C_{22}H_{22}BN$, $M = 311.2$, orthorhombic system, space group *Pbca*, $a = 8.189(2)$, $b = 15.039(3)$, $c = 29.166(6)$ Å, $V = 3592(11)$ Å^3, $Z = 8$, $D_c = 1.51$ g cm^{-3}, $F(000) = 1328$, $\lambda = 0.71073$ (Mo-Kα), $T = 298 \pm 1$ K, graphite monochromator. Data were collected on a Nicolet R3m/V diffractometer using a crystal of dimensions 0.3 × 0.3 × 0.4 mm by the ω-scan method ($3.0 < 2\theta < 54°$). Three standard reflections were measured every 100 reflections. From 3917 unique measured data 744 reflections with $F > 3.0\sigma(F)$ were used in structure solution (direct methods) and subsequent full-matrix least-squares refinement (SHELXTL PLUS). Final $R = 6.66\%$, final $R_w = 5.19\%$. Hydrogen atoms were refined isotropically in idealised positions using the riding model with common isotropic *U*. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Table 1 Experimental and calculated bond lengths (Å) for 1,4-azaborinines

Bond	Experiment (4)	MNDO (4)	AM1 (4)	MP2/6-31G* (3)[a]
N(1)–C(1)	1.371(18)	1.418	1.401	1.366
N(1)–C(7)	1.378(16)	1.418	1.401	1.366
N(1)–C(22)	1.518(14)	1.474	1.440	
C(1)–C(2)	1.443(20)	1.430	1.422	
C(1)–C(6)	1.412(15)	1.434	1.420	1.371
C(2)–C(3)	1.329(25)	1.395	1.385	
C(3)–C(4)	1.389(21)	1.411	1.398	
C(4)–C(5)	1.386(19)	1.396	1.387	
C(5)–C(6)	1.413(16)	1.426	1.401	
B(1)–C(6)	1.531(16)	1.525	1.530	1.517
B(1)–C(12)	1.543(17)	1.525	1.530	1.517
B(1)–C(13)	1.555(15)	1.558	1.546	
C(7)–C(8)	1.402(19)	1.430	1.422	
C(7)–C(12)	1.417(15)	1.434	1.420	1.371
C(8)–C(9)	1.340(19)	1.395	1.385	
C(9)–C(10)	1.381(19)	1.411	1.398	
C(10)–C(11)	1.360(19)	1.396	1.387	
C(11)–C(12)	1.406(17)	1.426	1.401	

[a] See ref. 4.

We conclude that 1,4-azaborinines are best represented as conjugated C=C–N–C=C systems that are bridged by a boron atom that contributes little to cyclic conjugation. This conclusion is supported both by *ab initio* calculations on the parent azaborinine and by the current experimental investigation.

This work was supported by the Fonds der Chemischen Industrie, the Volkswagen Stiftung and Convex Computer GmbH. We thank Dr W. Bauer for the assignment of the NMR spectrum and Professor P. v. R. Schleyer for his interest and for useful discussions.

Received, 19th May 1992; Com. 2/02621J

References

1 J. J. Kaufman and J. R. Hamann, *Adv. Chem. Ser.*, 1964, **42**, 273.

2 R. Carbó, M. S. DeGiambiagi and M. Giambiagi, *Theor. Chim. Acta*, 1969, **14**, 147.

3 S. T. Massey and R. W. Zoellner, *Int. J. Quantum Chem.*, 1991, **39**, 787.

4 M. Kranz and T. Clark, *J. Org. Chem.*, 1992, **57**, in the press.

5 A. J. Fritsch, *Chem. Heterocycl. Compd.*, 1977, **30**, 381.

6 I. Ander, in *Comprehensive Heterocyclic Chemistry*, ed. A. R. Katritzky and C. W. Rees, Pergamon Press, Oxford, 1984, vol. 1, p. 629.

7 A. H. Soloway, in *Progress in Boron Chemistry*, ed. H. Steinberg and A. L. McCloskey, Pergamon Press, Oxford, 1964, vol. 1, p. 203.

8 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899; M. J. S. Dewar and M. L. McKee, *J. Am. Chem. Soc.*, 1977, **99**, 5231.

9 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902; M. J. S. Dewar, C. Jie and E. G. Zoebisch, *Organometallics*, 1988, **7**, 513.

10 From microwave spectroscopy: F. Mata, M. J. Quintana and G. O. Sørensen, *J. Mol. Struct.*, 1977, **42**, 1.

11 From X-ray analyses: C. Rérat, *Acta Crystallogr.*, 1962, **15**, 427; A. J. Serewicz, B. K. Robertson and E. A. Meyers, *J. Phys. Chem.*, 1965, **69**, 1915.

12 F. Zettler, H. D. Hausen and H. Hess, *J. Organomet. Chem.*, 1974, **72**, 157.

13 H. Nöth and B. Wrackmeyer, in *NMR, Basic Principles and Progress*, ed. P. Diehl, E. Fluck and R. Kosfeld; Springer-Verlag, Berlin, 1978, vol. 14.

14 P. Jutzi, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 53.

15 N. M. D. Brown, F. Davidson, R. McMullan and J. W. Wilson, *J. Organomet. Chem.*, 1980, **193**, 271.