Notes

Synthesis, Crystal Structure,† and Gas-phase Photoelectron Spectroscopic Study of *B*,*B*′-Bis(1,3-dicyclohexyl-1,3,2-diazaborolidin-2-yl)

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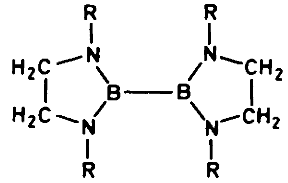
The highly sterically hindered compound *B*,*B*′-bis(1,3-dicyclohexyl-1,3,2-diazaborolidin-2-yl) (**1**) was prepared by transamination of $B_2(NMe_2)_4$. It is unreactive towards air or moisture. Crystals of (**1**) are monoclinic, a = 16.829(3), b = 12.021(2), c = 14.744(3) Å, β = 95.06(2)°, Z = 4, and space group $C2/c$. The structure was solved by direct methods and refined by full-matrix least-squares calculations to R = 0.097 for 1 247 reflections with $I > 3\sigma(I)$. The molecule has crystallographic two-fold symmetry and the two halves of the molecule are linked through boron atoms, with B–B 1.721(12) Å. Other ring distances are: mean B–N 1.393(7), mean C–N 1.454(6), and mean C–C 1.494(9) Å. The five-membered ring BN_2C_2 planes form a dihedral angle of 80.7°. Both cyclohexyl rings are in chair conformations. A comparison of the photoelectron spectrum of compound (**1**) with that of $B_2(NMe_2)_4$ suggests that both compounds are in a staggered conformation in the gas phase; a reassignment of the $B_2(NMe_2)_4$ spectrum is proposed.

Compounds of the type $X_2B–BX_2$ (X = halide, OR, or NR_2) are well known.[1] The halides (X = F or Cl) are structurally interesting because they appear to adopt planar (D_{2h}) configurations in the solid state and either planar (X = F) or non-planar (D_{2d}) configurations (X = Cl) in the liquid or gas phase. Dialkylamino derivatives, $B_2(NMe_2)_4$,[2] and *B*,*B*′-bis(1,3-dimethyl-1,3,2-diazaborolidin-2-yl) (I; R = Me)[3] are reported to be non-planar in the liquid and solid state respectively. The two BN_2 groups are not mutually perpendicular, but have interplane (BN_2)–$(BN_2)'$ angles of *ca.* 30 and *ca.* 60° respectively. The gas-phase photoelectron (p.e.) spectrum of $B_2(NMe_2)_4$ has been interpreted in terms of a planar model.[4] In view of the possible variation of interplane angle with phase, we decided to prepare sterically rigid B_2N_4 systems which would be non-planar in both the solid and gas phase and to investigate their electronic structure in the gas phase by p.e. spectroscopy and MNDO molecular-orbital (m.o.) calculations. The results are compared to data for $B_2(NMe_2)_4$.



(I)

Results and Discussion

In order to achieve a sterically rigid non-planar structure the compounds (I) [R = cyclohexyl (**1**) or Pr^i (**2**)[5]] were prepared. Compound (**1**) was obtained in 47% yield by the transamination of $B_2(NMe_2)_4$ with *N*,*N*′-dicyclohexylethylenediamine. It is stable to atmospheric hydrolysis for at least 6 months. Crystals suitable for an *X*-ray diffraction study were grown from isopropyl alcohol.

The molecular structure of compound (**1**) and the atom numbering are shown in the Figure, with selected interatomic distances and angles in Table 1. The structure contains discrete well separated molecules with the two C_2N_2B rings related by crystallographic two-fold symmetry and linked through boron atoms with B–B′ 1.721(12) Å. A B–B distance of 1.693(9) Å was previously reported for (I; R = Me).[3] Intercage B–B distances in 1,1′-$(B_5H_8)_2$[6] and the 2,2′-,[7] 2,6′-,[8] and 1,5′-[9] isomers of $(B_{10}H_{13})_2$ are 1.74(6), 1.692(3), 1.679(3), and 1.698(3) Å

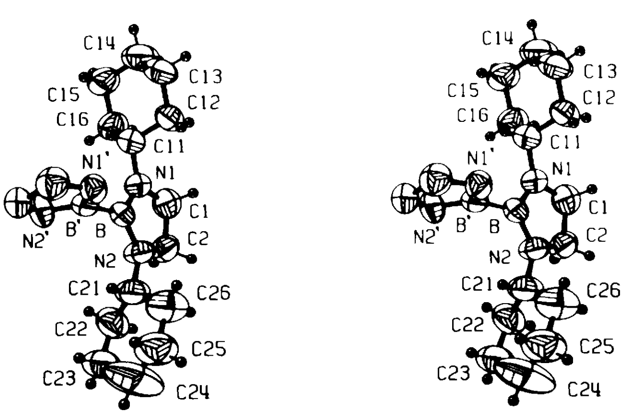


Figure. Stereoview of compound (**1**). The crystallographic two-fold axis passes through the midpoint of the B–B bond; for clarity, the cyclohexyl rings bonded to N(1′) and N(2′) have been omitted

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† *Supplementary data available* (No. SUP 56611, 3 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Molecular dimensions (distances in Å, angles in °) for $C_{28}H_{52}B_2N_4$, (**1**), with estimated standard deviations (e.s.d.s) in parentheses

B–B′	1.721(12)	N(2)–C(2)	1.435(6)	C(12)–C(13)	1.535(7)	C(21)–C(26)	1.422(9)
B–N(1)	1.402(7)	N(2)–C(21)	1.467(7)	C(13)–C(14)	1.449(10)	C(22)–C(23)	1.533(8)
B–N(2)	1.383(7)	C(1)–C(2)	1.555(8)	C(14)–C(15)	1.504(9)	C(23)–C(24)	1.384(13)
N(1)–C(1)	1.439(6)	C(11)–C(12)	1.505(7)	C(15)–C(16)	1.535(8)	C(24)–C(25)	1.491(11)
N(1)–C(11)	1.476(6)	C(11)–C(16)	1.450(8)	C(21)–C(22)	1.501(8)	C(25)–C(26)	1.557(9)

B′–B–N(1)	125.2(7)	B–N(2)–C(21)	127.5(5)	C(11)–C(12)–C(13)	109.9(5)	C(22)–C(21)–C(26)	117.7(6)
B′–B–N(2)	125.9(7)	C(2)–N(2)–C(21)	121.4(5)	C(12)–C(13)–C(14)	112.6(6)	C(21)–C(22)–C(23)	111.2(6)
N(1)–B–N(2)	109.0(5)	N(1)–C(1)–C(2)	103.8(4)	C(13)–C(14)–C(15)	113.1(6)	C(22)–C(23)–C(24)	113.2(7)
B–N(1)–C(1)	111.0(4)	N(2)–C(2)–C(1)	104.6(4)	C(14)–C(15)–C(16)	110.2(5)	C(23)–C(24)–C(25)	120.1(9)
B–N(1)–C(11)	126.5(5)	N(1)–C(11)–C(12)	108.8(3)	C(11)–C(16)–C(15)	111.9(5)	C(24)–C(25)–C(26)	110.9(7)
C(1)–C(1)–C(11)	122.1(5)	N(1)–C(11)–C(16)	114.7(5)	N(2)–C(21)–C(22)	112.6(5)	C(21)–C(26)–C(25)	112.3(6)
B–N(2)–C(2)	111.2(4)	C(12)–C(11)–C(16)	111.9(5)	N(2)–C(21)–C(26)	115.5(6)		

Torsion angles*

C(16)C(11)–C(12)C(13)	55.4	C(26)C(21)–C(22)C(23)	48.1	N(2)B–N(1)C(1)	−1.7	BN(1)–C(11)C(12)	110.0
C(11)C(12)–C(13)C(14)	−53.4	C(21)C(22)–C(23)C(24)	−44.4	N(1)B–N(2)C(2)	−3.0	BN(2)–C(21)C(22)	117.4
C(12)C(13)–C(14)C(15)	53.5	C(22)C(23)–C(24)C(25)	46.6	BN(1)–C(1)C(2)	5.2	N(1)B–B′N(1′)	−85.0
C(13)C(14)–C(15)C(16)	−52.7	C(23)C(24)–C(25)C(26)	−45.2	BN(2)–C(2)C(1)	6.0	N(2)B–B′N(2′)	−81.6
C(14)C(15)–C(16)C(11)	54.3	C(24)C(25)–C(26)C(21)	43.0	N(1)C(1)–C(2)N(2)	−6.6		
C(12)C(11)–C(16)C(15)	−57.0	C(22)C(21)–C(26)C(25)	−48.2				

* Average e.s.d. of torsion angles is 0.8°. Primed atoms are related to unprimed atoms by the symmetry operation: $-x, y, \frac{1}{2}-z$. The equation of the best plane through the atoms of the BN_2C_2 ring is $10.8727x + 7.7798y + 5.1028z = 2.0892$. Deviations (Å × 10^3) of the atoms from this plane are: B, −3; N(1), −23; N(2), 28; C(1), 36; C(2), −38.

Table 2. Ionisation energies (eV) of the four highest-occupied orbitals in $B_2(NMe_2)_4$, (**1**), and (**2**)

$B_2(NMe_2)_4$			
Exptl.[4]	Calc. (MNDO)	(**1**)	(**2**)
(Π_4) 7.3	8.84	7.4	7.3
(Π_3) 7.6	9.11		
(Π_2) 9.0	10.40, 10.53	8.9	9.0
(Π_1) 9.5 (sh)	11.66		

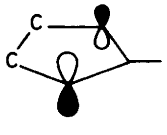
sh = Shoulder, designation Π_1—Π_4 as in ref. 4. The ionisation Π_1 is reassigned in the text.

respectively. For B_2F_4 and B_2Cl_4 the values for the gas phase and solid state were 1.720 and 1.67 and 1.702 and 1.75 Å respectively.[1] The mean distances B–N 1.393(7), C–N 1.454(6), and C–C 1.494(9) Å in compound (**1**) are unexceptional (Table 1) and agree well with the corresponding bond lengths reported for (**I**; R = Me) [mean B–N 1.413(8), mean ring C–N 1.461(7), C–C 1.520(9) Å][3] and 3,6-bis(dimethylamino)-1,2,4,5-tetramethyl-1,2,4,5,3,6-tetra-azadiborinane, $C_8H_{24}B_2N_6$ [mean B–N 1.428(3) Å].[10]

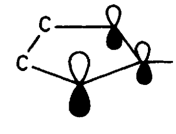
The five-membered BN_2C_2 ring has close to two-fold symmetry, with the non-crystallographic axis passing through B and the midpoint of the C(1)–C(2) bond. The five-membered rings in the two halves are inclined at an angle of 80.7° thereby relieving steric interactions of the cyclohexyl groups. The corresponding interplanar angles in the two independent molecules of (**I**; R = Me) in the crystal structure are 61.6 and 56.7°.[3]

The two independent cyclohexyl rings adopt chair conformations with the ring substituent equatorial. Both rings showed marked anisotropy (or slight disorder) with one ring [C(21)—C(26)] much more affected than the other. Thus the unsigned values of torsion angles in ring C(11)—C(16) are 52.7—57.0°, whereas in ring C(21)—C(26) the corresponding values are 43.0—48.2°. The C–C bond lengths in the cyclohexyl rings reflect this anisotropy/disorder with values in the range 1.384(13)—1.557(9)°.

Noting the structural trends in B–B and B–N bond distances above, it appears that the electronic structure of compound (**1**) contains two almost identical but isolated BN_2 systems. The highest-lying occupied orbitals of these BN_2 systems are shown schematically as (**II**) and (**III**); (**II**) is N localised by symmetry



(**II**)



(**III**)

but the N components of (**III**) can π donate to the nominally empty B 2*p* orbital. The interaction of these two systems across the B–B bond depends on the interplanar angle (θ), and as θ approaches 0° a splitting of the energies of the Π_1 and Π_2 orbitals[4] arising from (**III**) would be expected. The He I p.e. spectrum of $B_2(NMe_2)_4$ has been interpreted[4] on the assumption of θ = 0°, and the apparent Π_2/Π_1 split of the third and fourth ionisation (Table 2) is about 0.5 eV. However, our MNDO calculations[11] on this molecule indicate a staggered conformation with minimum energy at θ = 73°, and a Π_1/Π_2 split of only 0.13 eV (Table 2), which could not be resolved on a broad ionisation band; in D_{2d} symmetry (θ = 90°) the orbitals become degenerate. The other π-energy separations in the calculation are in excellent agreement with experiment if it is assumed that the third ionisation at 9.0 eV corresponds to both Π_1 and Π_2, and the observed intensity of the third band[4] is fully consistent with this. Such an interpretation requires a reassignment of the ionisation at *ca.* 9.5 eV: we believe that this is due to the B 2*p*–B 2*p* σ-bonding orbital. Corresponding orbitals ionise at 13.3 eV in B_2F_4 and at 11.0 eV in B_2Cl_4,[12] so it is very unlikely that the B–B σ orbital in $B_2(NMe_2)_4$ would have a higher ionisation energy (i.e.) than 11 eV. Furthermore, there is no band in this region of the spectrum other than that at *ca.* 9.5 eV to which the B–B ionisation can be assigned. Thus a very satisfactory reassignment of the $B_2(NMe_2)_4$ spectrum can be made if the staggered conformation with θ *ca.* 70° is assumed. The splitting pattern of the corresponding π orbitals in B_2Cl_4, which is known to have a staggered conformation, supports this. In B_2Cl_4, the $1a_2$ and $1b$ orbitals equivalent to (**II**) ionise at

Table 3. Final fractional co-ordinates ($\times 10^4$) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
B	250(4)	1 010(5)	2 015(4)
N(1)	81(2)	1 713(4)	1 265(3)
N(2)	867(3)	304(4)	1 839(3)
C(1)	613(4)	1 500(5)	572(4)
C(2)	1 105(3)	475(5)	939(4)
C(11)	−484(4)	2 655(4)	1 204(4)
C(12)	−48(3)	3 747(4)	1 194(4)
C(13)	−643(4)	4 714(5)	1 214(5)
C(14)	−1 289(5)	4 633(6)	500(5)
C(15)	−1 714(3)	3 531(5)	491(5)
C(16)	−1 112(3)	2 575(5)	467(4)
C(21)	1 257(4)	−534(5)	2 451(5)
C(22)	1 151(5)	−1 694(5)	2 084(5)
C(23)	1 484(4)	−2 556(5)	2 784(6)
C(24)	2 221(8)	−2 266(8)	3 209(7)
C(25)	2 360(5)	−1 118(6)	3 571(6)
C(26)	2 021(4)	−234(6)	2 869(5)

12.3 and 12.5 eV, and 3*e*, equivalent to (**III**), ionises at 13.6 eV.[12] The smaller spacings in the chloride can be attributed to the π bonding being weaker for B–Cl than for B–N.

Further support for a near-D_{2d} gas-phase structure of $B_2(NMe_2)_4$ comes from the He I p.e. spectra of compounds (**1**) and (**2**) (Table 2). The substantial steric hindrance in these molecules makes it very unlikely that either would take up a conformation in the gas phase which was far removed from that of (**1**) in the solid. It is seen in Table 2 that the ionisation energies are almost exactly the same as for $B_2(NMe_2)_4$ except that the Π_3/Π_4 splitting [type (**II**) orbitals] is not resolved; this is not surprising given the greater complexity of the molecules. The region beyond 10 eV is unresolved, but for (**1**) a shoulder can be picked out at 10.1 eV, very close to the B–B ionisation of $B_2(NMe_2)_4$ at 9.5 eV, and we assign this to the B–B bond in (**1**). Thus the spectra, and hence the conformations, of all three molecules are very similar. We conclude that in the gas phase all the $B_2(NR_2)_4$ compounds examined adopt a conformation with θ approaching 90°; those most sterically hindered are closest to this condition. Compound (**1**) is the most sterically demanding reported to date.

Experimental

Infrared spectra were recorded on Perkin-Elmer 1310 and 457 spectrophotometers using KBr discs or thin films. N.m.r. spectra were recorded on Perkin-Elmer R20A (^1H) and Bruker WH400 (^{11}B) spectrometers. Chemical shifts are relative to $SiMe_4$ (^1H) and $BF_3 \cdot OEt_2$ (external) (^{11}B), positive values representing shifts to high frequency of the reference. Melting points are uncorrected. Analyses were carried out by the Microanalytical Laboratory, University College, Cork. Mass spectra were recorded on an AEI-Kratos MS 30DB instrument at 70 eV (1.12×10^{-17} J), in electron-impact (e.i.) mode. Photoelectron spectra were recorded on a Perkin-Elmer PS16 spectrometer.

Solvents were dried and distilled before use. Experiments were carried out under dry, oxygen-free nitrogen. The compounds $B_2(NMe_2)_4$,[13] (**2**),[5] and *N,N′*-dicyclohexylethylenediamine[14] were prepared by literature methods.

Synthesis of B,B′-*Bis*(1,3-*dicyclohexyl*-1,3,2-*diazaborolidin*-2-*yl*), (**1**).—Tetrakis(dimethylamino)diborane (0.50 g, 2.53 mmol) and *N,N′*-dicyclohexylethylenediamine (2.46 g, 5.28 mmol) were heated at 170 °C under N_2 for 40 h. On cooling to room temperature the mixture solidified. Recrystallisation from hot isopropyl alcohol afforded colourless crystals of (**1**) (0.55 g, 1.18 mmol, 47%) (Found: C, 71.95; H, 10.65; B, 4.15; N, 11.85. $C_{28}H_{52}B_2N_4$ requires C, 72.15; H, 11.15; B, 4.65; N, 12.05%), m.p. 188—190 °C; $\nu_{max.}$ at 2 920s, 2 847s, 2 657w, 1 463m, 1 460w, 1 444m, 1 409s, 1 368m, 1 340w, 1 269s, 1 240s, 1 192m, 1 180(sh), 1 162w, 1 131m, 1 112w, 1 048w, 1 075w, 1 068w, 1 028w, 1 002w, 975w, 920w, 894s, 843w, 805w, 702w, and 667m cm^{-1}. N.m.r. spectra (CD_2Cl_2, 35 °C): ^1H, δ 3.12 (s, 8 H), 2.90 (m, 4 H), and 0.4 (m, 40 H); ^{11}B, δ 31.1 p.p.m. Mass spectrum: *m/z* 466 (*M*, $^{12}C_{28}{}^1H_{52}{}^{11}B_2{}^{14}N_4$), 384 ($M - C_6H_{10}$), and 233 (*M*/2).

Molecular Structure Determination of Compound (**1**).—*Crystal data.* $C_{28}H_{52}B_2N_4$, $M = 466.4$, monoclinic, $a = 16.829(3)$, $b = 12.021(2)$, $c = 14.744(3)$ Å, $\beta = 95.06(2)°$, $U = 2\,971.1$ Å^3, $Z = 4$, $D_c = 1.04$ g cm^{-3}, $F(000) = 1\,032$, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 0.3 cm^{-1}, space group *C*2/*c* or *Cc* from systematic absences *hkl*, $h + k = 2n + 1$ and *h*0*l* both $h = 2n + 1$ and $l = 2n + 1$ (the former was chosen and confirmed by the successful analysis).

A colourless crystal of dimensions 0.50 × 0.40 × 0.32 mm was used for data collection with an Enraf-Nonius CAD4 diffractometer. Data were collected to a maximum θ of 24° by the ω—2θ scan method using monochromatised Mo-K_α radiation; 25 reflections in the range $10 < \theta < 15°$ were used to determine cell dimensions and the orientation matrix by least-squares refinement. The intensities of three standard reflections monitored every 2 h of exposure did not change significantly over the period of data collection. A total of 2 327 unique reflections were measured of which 1 247 had $I > 3\sigma(I)$ and were used in structure solution and refinement. Data were corrected for Lorentz and polarisation factors; absorption correction was not considered necessary.

The structure was solved by direct methods using SHELX 76.[15] An *E* map calculated with reflections with $E > 1.2$ revealed the positions of all non-hydrogen atoms. Initial refinement was by full-matrix least-squares calculations with isotropic thermal parameters for the non-hydrogen atoms. A difference map calculated at the conclusion of this isotropic refinement revealed maxima at positions corresponding to the hydrogen atoms which were then included in the subsequent refinement in geometrically idealised positions (C–H 0.95 Å); an overall isotropic thermal parameter was refined for these hydrogen atoms. Refinement allowing anisotropic thermal parameters for the non-hydrogen atoms converged with $R = 0.097$ and $R' = (\Sigma\Delta w^2/\Sigma w F_o^2)^{\frac{1}{2}} = 0.119$. The *R* value was relatively high because of large thermal motion and/or disorder in the cyclohexyl rings. In the final cycles of refinement a weighting scheme of the form $w = 1/(\sigma^2 F + pF^2)$ was employed where the final parameter *p* was 0.000 16. The number of parameters refined in the final refinement was 154. Scattering factors used in the structure-factor calculations were taken from ref. 16 for non-hydrogen atoms and ref. 17 for hydrogen atoms. A difference map calculated at the conclusion of the refinement showed no significant electron density. The final fractional co-ordinates for non-hydrogen atoms (with estimated standard deviations in parentheses) are given in Table 3.

Molecular-orbital Calculations.—The MNDO program was used as supplied.[11] Calculations were run with complete free variation of all geometry parameters.

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