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1,4,7,8-Triazaborabicyclooctanes—First Examples of New Boron Heterocycles [1,2]

Antonio Rafael Tapia-Benavides and Rosalinda Contreras*

Departamento de Química, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Apartado Postal 14-740, México, D.F. 07000 México

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ABSTRACT

The first examples of 1,7,1,4,7,8-dialkyltriazaborabicyclo[3.3.0]octanes ***1–3*** *[R = isopropyl (**1**), R = 1-phenylbenzyl (**2**), R = 1-methylbenzyl (**3**)] are reported. The bulky substituents prevent dimerization and make the syntheses feasible. The structures and conformations of the new compounds were studied by NMR spectroscopy. A chiral bicycle* ***3*** *(R,R) was also prepared.*

RESULTS AND DISCUSSION

A few examples of triazaborabicycles have been known for a long time, triazaboradecalin (**4**) and its derivatives being the most studied [3,4]. Triazaborahydrindane [5] (**5**) has also been reported as well as 1,6,10,11-triazaborabicyclo-[5.4.0]undecane [6] **6** (Figure 1).

To our knowledge, the bicycle formed with two five-membered rings has not been described in the literature. In compounds **4–6**, the ring size allows a planar boron atom and a strong retrocoordination from nitrogen to boron that stabilizes these molecules [3–6]. An attempt to obtain the parent compound (R = H) of **1–3** was unsuccessful [5]. An explanation of this fact could be that the presence of two five-membered rings causes the boron atom to lose its planar structure, the strong cyclic strain forcing the boron to be in a tetrahedral arrangement, thus losing the back donation from nitrogen and making it acidic and reactive. The phosphabicyclooctanes dimerize very easily [7], and a similar behavior for the boron heterocycles is known [5]. We have achieved the syntheses of the triazaborabicyclooctanes **1–3** using bulky substituents at the N-1 and N-7 atoms that inhibit the approach of other molecules to the boron atom and a subsequent reaction.

Compounds **1–3** were synthesized by the transamination reaction of the corresponding triamines **7–9** with *tris*-dimethylaminoborane [3–6] (Fig. 2) The reaction products were liquids purified by distillation, with the exception of compound **2** which is a glassy solid. The structures of all compounds were established by NMR spectroscopy. They are very reactive toward oxygen and moisture. The syntheses of amines **7** and **9** are known [8,9], but, herein, we report a simpler method that affords better yields [10,11]. The amine **7** was prepared directly from the reaction of 2-propanone, diethylenetriamine, and BH_3-THF. The amines **8** and an isomeric mixture of compounds **9** were obtained by BH_3-THF reduction of the imines which, in turn, were prepared from the corresponding ketone and diethylenetriamine (Fig. 3). The amine **9** was obtained as a mixture of the *dl* and *meso* isomers. The chiral triamine **9** (R,R) was obtained by BH_3-THF reduction of the amide resulting from the reaction of the iminodiacetic acid with chiral (R) methylbenzylamine (Fig. 3).

The δ ^{11}B values of **1–3** (+29.0, +30.0, and +30.4, respectively) are similar to those of the *tris*-aminoborazines and *tris*aminoboranes, [12] indicating the presence of planar boron atoms for **1–3**, the expected ring strain actually being reflected in the ^{11}B chemical shifts. Strain free systems show δ around 21 [12]. The IR spectra of compounds **1–3** have absorption bands near 1514 and 1440 cm^{-1} that are similar to those of triazaborabicyclic compounds [3,5].

*To whom correspondence should be addressed.

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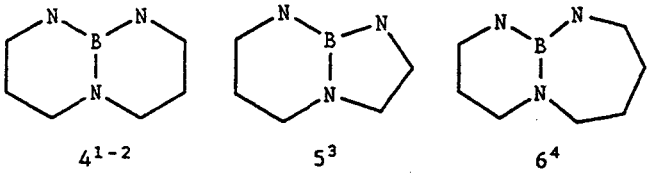

4^{1-2} 5^{3} 6^{4}

FIGURE 1

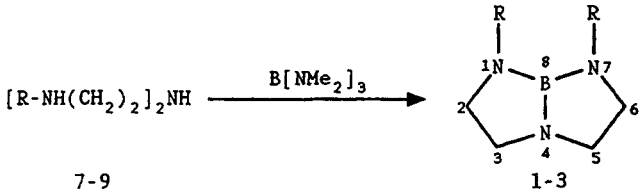

FIGURE 2

The large N-substituents of compounds **1–3** are joined to the ring, by two nearly parallel σ bonds, and, from Dreiding and molecular mechanics models, it is apparent that the *exo*-C–N bonds cannot undergo free rotation. Frozen rotamers are favored, as shown for **3** in Fig. 4.

The NMR signals of the methylene protons of amines **7–9** are singlets, while the same protons in the triazaborabicycles **1–3** give a more complex coupling pattern. The dynamic inversion of the ring conformation was established from the ^{1}H NMR spectra measured at 270 MHz at room temperature. In the spectra, the methylene groups of compounds **1** and **2** appear as two triplets with $^{3}J(H–H) = 6.6$ Hz. The assignment of the coupling constants for compound **3** (R,R), verified by use of the program Laocoön [13], showed the same vicinal coupling constant as in **1** and **2**, indicating a ring conformational equilibrium for the three compounds. The ring inversion makes both groups equivalent on the exocyclic carbon despite the fact that they are contained in frozen rotamers. In compound **3**, the rotamers make different both ring faces and all hydrogen atoms, in spite of the ring conformational equilibrium of the molecule. The ^{1}H NMR data assignment of compound **1** was supported by a NOESY experiment.

The ^{13}C NMR assignment was effected by the use of correlated heteronuclear $^{13}C/^{1}H$ spectra. Comparison of the ^{13}C NMR spectra of amines **7–9** and their corresponding bicyclic derivatives **1–3** shows that, in the heterocycles **1–3**, the C-2 and C-6 resonances are shifted to low field, attributable to the inductive effect of the planar N-1 and N-7. Resonances of C-3 and C-5 are slightly shifted to high field, which suggests the presence of a tetrahedral N-4 atom.

When compound **3** was synthesized from a mixture of the *meso* and the *dl* amine, the signals of two diasteromers were observed in their ^{1}H and ^{13}C NMR spectra, viz those of the R,R and S,S pair,

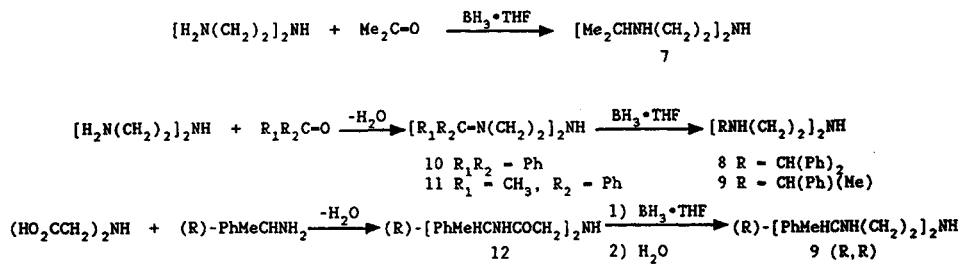

FIGURE 3

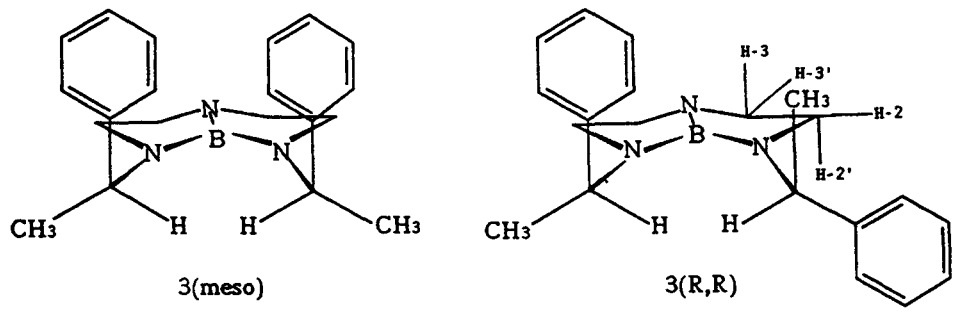

FIGURE 4

and the *meso* compound. The diasteromers of compound **3** are evident by their NMR spectra, whereas, for the free amine **9**, they are not. The explanation is that, in **3**, both chiral carbon atoms of each molecule are constrained to be close to each other, and the strong diastereomeric interaction established between them in the chiral and *meso* heterocycles can be observed by NMR spectroscopy. The same interaction in the respective free amine **9** is not apparent, because the two chiral carbon atoms are far apart.

The bicycle **3**-*meso* has the two aromatic rings in the same face. Conversely, **3**-*dl* molecules present the aromatic rings in opposite faces. The assignment of the different signals of ^1H and ^{13}C NMR spectra of each isomer is difficult. Fortunately, the chiral bicyclic **3** (R,R) synthesis allowed us to establish the chemical shifts and coupling constant for each diastereoisomer. Due to the presence of chiral centers, the methylenic hydrogen atoms of **3** (R,R) are diastereotopic [^2J(H–H) = −8.9 for CH_2-2) and −6 and −14.2 Hz for CH_2-3 and −5]. The difference in the coupling constant is explained by the different electronegativity of the nitrogen atoms [14]. N-1 and N-7 are more electronegative, as they have the sp^2 hybridization, whereas N-4 has the sp^3 hybridization.

EXPERIMENTAL

The NMR spectra were recorded with JEOL-FX90Q (90 MHz) and JEOL-GSX-270 (270 MHz) instruments. Chemical shifts are relative to $BF_3 \cdot OEt_2$ or TMS. The IR spectra were obtained with a Nicolet MX-1 FT spectrometer. The optical rotation was determined by use of a Perkin-Elmer 241 polarimeter. Borane·THF was prepared, as described elsewhere [15]. The solvents were dried and freshly distilled. Reactions were carried out under a nitrogen atmosphere.

Effectively, all of our compounds were checked by detailed NMR analyses, but we were unable to purify completely (100%) the bicyclic compounds **1–3** in order to obtain elemental analyses. We have achieved about 95% purity in order to obtain reasonable NMR spectra. These compounds are very unstable when subjected to almost any purification method.

We have also tried to obtain mass spectra, but the molecules were completely fragmented and we have not observed the molecular ion in any instance.

2,10-Dimethyl-3,6,9-triazaundecane (**7**)

The synthesis of **7** is reported [8,9], but we have used a simpler method. A cold (0°C) magnetically stirred solution of diethylenetriamine (5.51 g, 53.37 mmol) and acetone (12.48 mL, 213.48 mmol) in THF (170 mL) was treated dropwise with 2.3 M $BH_3 \cdot THF$ (46.21 mL, 106.74 mmol). The mixture was stirred for 24 hours at room temperature and then washed with 100 mL of water and extracted three times with 50 mL of CH_2Cl_2, dried, and concentrated. The amine **7** was purified by distillation (69–72°C; 0.03 mmHg), affording a colorless liquid (6.938 g, 69.38%): IR ($CHCl_3$, ν_{max}/cm^{-1}) 3188 (N–H), 2971 and 2831 (C–H), 1471 (CH_2), 1179 and 1129 (C–N); δ ^1H (90 MHz, $CDCl_3$) 1.06 (d, 12H, J = 7.0 Hz, CH_3), 1.50 (s, 3H, NH), 2.71 (s, 8H, CH_2), 2.76 (m, 2H, J = 7.0 Hz, CH); δ ^{13}C (22.49 MHz, $CDCl_3$) 22.7 (CH_3), 46.8 (C-4 and C-8), 48.4 (CH), 49.4 (C-5 and C-7).

1,1,9,9-Tetraphenyl-2,5,8-triazanonane (**8**)

Diethylenetriamine (0.956 g, 9.27 mmol) and benzophenone (3.378 g, 18.54 mmol) were dissolved in toluene (75 mL). A catalytic amount of *p*-toluensulfonic acid was added, and the reaction mixture heated under reflux for 8 hours. The toluene was evaporated under vacuum. A yellow viscous liquid was obtained (3.94 g, 98.4%) and identified as the diimine (1,1,9,9-tetraphenyl-2,5,8-triaza-1,8-nonadiene, **10**): IR ($CHCl_3$, ν_{max}/cm^{-1}) 3186, 2928, and 2834 (C–H), 1659 (C=C), 1623 (C=N), 1446 (CH_2), 1315 and 1282 (C–N); δ ^1H (60 MHz, $CDCl_3$) 2.20 (s, 1H, NH), 3.00 (t, 4H, J = 6.0 Hz, CH_2-4 and CH_2-6), 3.58 (t, 4H, J = 6.0 Hz, CH_2-3 and CH_2-7), 7.16–7.90 (m, 20H, Ph); δ ^{13}C (67.8 MHz, $CDCl_3$) 50.5 (C-4 and C-6), 53.4 (C-3 and C-7), 169.0 (C=N), phenyl group *trans* to the lone pair (128.0 *m*, 128.2 *p*, 128.5 *o*, 136.8 *i*), phenyl group *cis* to the lone pair (127.7 *m*, 128.3 *o*, 129.8 *p*, 139.7 *i*). Compound **10** (3.768 g, 14.46 mmol) was dissolved in THF (15 mL) and 3.4 M $BH_3 \cdot THF$ (5.18 mL, 17.46 mmol) was added dropwise at room temperature. The mixture was stirred 1 hour. The solvent was evaporated, xylene (150 mL) added, and the solution heated under reflux for 20 hours. The reaction mixture was hydrolyzed with 15% HCl (125 mL), heated again under reflux for 2 hours, and extracted three times with water (100 mL). The aqueous phase was treated with NaOH until pH = 8 and extracted three times with CH_2Cl_2 (50 mL). The organic solvent was evaporated under vacuum to give a pale yellow oil (3.19 g, 83.0%): IR ($CHCl_3$, ν_{max}/cm^{-1}) 3325 and 3299 (N–H), 2956, 2889, and 2826 (C–H), 1453 (CH_2), 1260, 1100, and 1025 (C–N). δ ^{-1}H (60 MHz, $CDCl_3$) 1.83 (s, 3H, NH), 2.73 (b s, 8H, CH_2), 4.9 (s, 2H, CH), 7.1–7.8 (m, 20H, Ph); δ ^{13}C (22.49 MHz, $CDCl_3$) 47.7 (C-3 and C-7), 49.4 (C-4 and C-6), 67.5 (CH), 126.9 (*p*-Ph), 127.3 (*o*-Ph), 128.4 (*m*-Ph), 144.2 (*i*-Ph).

2,10-Diphenyl-3,6,9-triazaundecane (dl and meso compounds) (**9**)

The same procedure used for the preparation of compound **8** was followed to give the diimine 1,9,1,9-dimethyldiphenyl-2,5,8-triaza-1,8-nonadiene **11** [(97.54%) as a yellow viscous liquid:

IR ($CHCl_3$, ν_{max}/cm^{-1}) 2927 and 2832 (C–H), 1634 (C=N), 1446 (CH_2), 1348, 1284, 1181, and 1126 (C–N); δ ^1H (90 MHz, $CDCl_3$) 2.25 (s, 6H, CH_3), 2.55 (s, 1H, NH), 3.13 (t, 4H, J = 6.0 Hz, CH_2-4 and CH_2-6), 3.65 (t, 4H, J = 6.0 Hz, CH_2)-3 and C-7), 7.5–7.93 (m, 10H, Ph); δ ^{13}C (22.49 MHz, $CDCl_3$) 14.7 (CH_3), 49.7 (C-4 and C-6), 51.0 (C-3 and C-7), 125.7 (*p*-Ph), 127.6 (*o*-Ph), 128.4 (*m*-Ph), 140.0 (*i*-Ph), 164.7 (C=N)]. And the amine **9** [(95.5%): IR ($CHCl_3$, ν_{max}/cm^{-1}) 3185 (N–H) 2960, 2827 (C–H), 1674 (C=C), 1452 (CH_2), 1304, 1276, 1150, and 1109 (C–N) δ ^1H (60 MHz, $CDCl_3$) 1.35 (d, 6H, J = 7.0 Hz, CH_3), 1.71 (s, 3H, NH), 2.61 (s, 8H, CH_2), 3.78 (c, 2H, J = 7.0 Hz, CH), 7.38 (s, 10H, Ph); δ ^{13}C (67.8 MHz, $CDCl_3$) 24.3 (CH_3), 47.2 (C-3 and C-7), 49.4 (C-4 and C-6), 58.4 (CH), 126.6 (*o*-Ph), 126.9 (*p*-Ph), 128.4 (*m*-Ph), 145.8 (*i*-Ph).

(2R,10R)-4,8-Dioxo-2,10-diphenyl-3,6,9-triazaundecane (**12**)

A mixture of iminodiacetic acid (4.14 g, 31.12 mmol) and R-(+)-α-methylbenzylamine (11.31 g, 93.36 mmol) was heated under reflux for 3 days. The reaction mixture was extracted with CH_2Cl_2 (50 mL) and treatment with hexane afforded a crystalline precipitate (75%, p.f. 80–82°C), IR (KBr, ν_{max}/cm^{-1}) 3413 (N–H), 3000 and 2988 (C–H), 1662.8 (C=O), 1622, and 1598 (C=C), 1494 (CH_2); δ ^1H (60 MHz, $CDCl_3$) 1.47 (d, 6H, J = 7.0 Hz, CH_3), 1.98 (s, 1H, NH), 3.2 (s, 4H, CH_2), 5.18 (q, 2H, J = 7.0 Hz, CH), 7.17 (d, 2H, J = 7.0 Hz, NH), 7.38 (s, 10H, Ph); δ ^{13}C (22.49 MHz, $CDCl_3$) 21.8 (CH_3), 48.4 (CH_2), 52.5 (CH), 126.0 (*o*-Ph), 127.3 (*p*-Ph), 128.6 (*m*-Ph), 143.1 (*i*-Ph), 169.9 (C=O).

(2R, 10R)-2,10-Diphenyl-3,6,9-triazaundecane (**9**)

The diamide **12** (3.95 g, 11.62 mmol) was dissolved in THF (75 mL). A solution of 3.4 M $BH_3 \cdot$ THF (27.59 mL, 93.00 mol) was added dropwise at room temperature and the mixture stirred for 1 hour. Xylene (200 mL) was added and the solution heated under reflux for 24 hours. The reaction product was hydrolyzed with 15% HCl (200 mL). The aqueous layer was treated with NaOH until pH = 8 and extracted three times with CH_2Cl_2 (50 mL). Evaporation of the solvent afforded a pale yellow viscous liquid (3.07 g, 84.77%). The reaction product has the same spectral data as **9** (*dl* and *meso*).

1,7-Bis-(isopropyl)-1,4,7,8-triazaborabicyclo[3.3.0]octane (**1**)

The amine **7** (1.30 g, 6.93 mmol) was dissolved in benzene (50 mL) and $B[N(CH_3)_2]_3$ (1.3 mL, 7.63 mmol) was added at room temperature and the mixture heated 4 hours under reflux. The solvent was evaporated and compound **1** distilled under vacuum at 51–55°C, 0.2 mm/Hg. A moisture-sensitive colorless liquid was obtained (0.484 g, 36.5%). IR ($CHCl_3$, ν_{max}/cm^{-1}) 2968, 2902, and 2829 (C–H), 1556 and 1510 (B–N), 1475 CH_2, 1442 (B–N); δ ^1H (270 MHz, $CDCl_3$) 1.11 (d, 12H, J = 6.6 Hz, CH_3), 2.80 (t, 4H, J = 6.6 Hz, CH_2-2 and CH_2-6), 3.36 (t, 4H, J = 6.6 Hz, CH_2-3 and CH_2-5), 3.59 (m, 2H, J = 6.6 Hz, CH); δ ^{11}B (28.69 MHz, $CDCl_3$) δ + 29.0 (s, BN_3), δ ^{13}C (67.8 MHz, $CDCl_3$) 22.1 (CH_3), 44.9 (CH), 47.6 (C-3 and C-5), 49.0 (C-2 and C-6).

1,7-Bis(α-Phenylbenzyl)-1,4,7,8-triazaborabicyclo[3.3.0]octane (**2**)

The same procedure used for the preparation of compound **1** was followed to give compound **2** from compound **8**. A dark yellow, glassy solid, moisture sensitive, was obtained (42.2%): IR ($CHCl_3$, ν_{max}/cm^{-1}) 2905 and 2840 (C–H), 1506 (B–N), 1452 (CH_2); δ ^1H (270 MHz, $CDCl_3$) 2.90 (t, 4H, J = 6.6 Hz, CH_2-2 and CH_2-6), 3.28 (t, 4H, J = 6.6 Hz, CH_2-3 and CH_3-5), 4.98 (s, 2H, CH), 7.03–7.37 (m, 20H, Ph); δ ^{11}B (86.55 MHz, $CDCl_3$) + 30.0; δ ^{13}C (67.8 MHz, $CDCl_3$) 52.9 (C-3 and C-5), 49.1 (C-2 and C-6), 62.5 (CH), 126.6 (*p*-Ph), 127.9 (*o*-Ph), 128.5 (*m*-Ph), 142.2 (*i*-Ph).

1,7-Bis[(1R)-1-methylbenzyl]-1,4,7,8-triazaborobicyclo[3.3.0]octane (**3**)

The same procedure used for the preparation of compound **1** was followed to give compound **3** from compound **9** (R,R), and **3** was distilled under vacuum. (74.89%, 160–170°C, 0.01 mm/Hg). Compound **3** is a colorless viscous liquid: $[\alpha]_D^{24}$ = + 119.68°, IR ($CHCl_3$, ν_{max}/cm^{-1}) 2969, 2897, and 2836 (C–H), 1515 (B–N), 1449 (CH_2), 1445 (B–N); δ ^1H (270 MHz, $CDCl_3$, see figure 4) 1.47 (d, 6H, J = 7.0 Hz, CH_3), 2.82 (m, 2H, $J_{3'2} = J_{42'} = 6.6$, $J_{3'3} = -14.2$ Hz, H-3'), 2.85 (m, 2H, $J_{32} = J_{32'} = 6.6$, $J_{33'} = -14.2$ Hz, H-3), 3.16 (m, 2H, $J_{22'}$, $= -8.9$, $J_{23} = J_{23'} = 6.6$ Hz, H-2'), 3.43 (m, 2H, $J_{22'} = -8.9$, $J_{23} = J_{23'} = 6.6$ Hz, H-2), 4.49 (c, 2H, J = 7.0 Hz, CH), 7.24–7.30 (m, 10H, Ph); δ ^{11}B (28.69 MHz, $CDCl_3$) +30.2; δ ^{13}C (67.8 MHz, $CDCl_3$) 19.64 (CH_3), 49.24 (C-3 and C-5), 49.71 (C-2 and C-6), 52.43 (CH), 126.35 (*p*-Ph), 126.61 (*o*-Ph), 128.15 (*m*-Ph), 144.56 (*i*-Ph). By comparison of **9** (R,R) with the isomeric mixture, the ^{13}C NMR data of **9** (*meso*) was obtained: δ ^{13}C (67.8 MHz, $CDCl_3$) 19.77 (CH_3), 49.30 (C-3 and C-5), 49.71 (C-2 and C-6), 50.00 (CH), 126.31 (*p*-Ph), 126.65 (*o*-Ph), 128.10 (*m*-Ph), 144.40 (*i*-Ph).

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