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Structural Characterization of "Frozen" Intermediates in the Transition from an Eight-Membered Monocyclic System to a Bridged Ring Bicyclo[3.3.0]Octane

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TRANSANNULAR N→B BOND FORMATION IN 1,3,5-TRIOXA-6,8-DIAZA-2,4-DIBORACYCLOOCTANES: STRUCTURAL CHARACTERIZATION OF "FROZEN" INTERMEDIATES IN THE TRANSITION FROM AN EIGHT-MEMBERED MONOCYCLIC SYSTEM TO A BRIDGED RING BICYCLO[3.3.0]OCTANE

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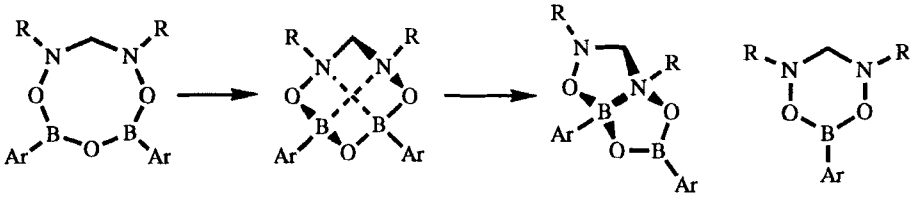
Abstract The strength of the transannular N→B interaction in the substituted cycloboronate 1,3,5-trioxa-6,8-diaza-2,4-diboracyclooctane **1** can be controlled both by varying the Lewis basicity of the ring nitrogen atoms and by modifying the steric factors dependent on the nature of the nitrogen substituents (by changing R). Examples of the structural types displaying varying degrees of transannular bonding have been prepared and characterized by X-ray analysis. A simple six-membered cycloboronate structure **4** containing one boron atom is formed when the basicity of the aminal nitrogen atom is reduced and the boronic acid residue is sterically hindered [R = $C(CH_3)_2CN$ and Ar = 2,4,6-$(CH_3)_3C_6H_2$]. The bicyclo[3.3.0]octane structure **3** is obtained when R = simple alkyl and Ar = phenyl. A structural type between **1** and **2** is realized when R = $C(CH_3)_2CN$ and Ar = Ph.

Keywords: Transannular N→B bonds, Organoboron compounds, Boron compounds, Crystal structure analysis

The substituted cycloboronate 1,3,5-trioxa-6,8-diaza-2,4-diboracyclooctane **1** can be prepared by reacting an *N,N'*-dihydroxy-*N,N'*-dialkylaminal, $[HO(R)N]_2CH_2$, with an arylboronic acid, $ArB(OH)_2$. Eight-membered 1:2 cyclocondensates **1** are produced when the boronic acid is not sterically hindered by *ortho*-substitution of the aryl group.The strength of the transannular N→B interaction in **1** which leads to the bicyclo[3.3.0]octane structure **3** via the intermediate **2** can be controlled both by varying the Lewis basicity of the ring nitrogen atoms (by changing R) and by modifying the steric factors dependent on the natures of both the nitrogen and boron substituents (R and Ar)[1]. In cases where a sterically hindered boronic acid is reacted with a weakly basic aminal [e.g. R = $C(CH_3)_2CN$, Ar = 2,4,6-$(CH_3)_3C_6H_2$], a simple six-membered 1:1 cyclocondensate **4** is formed[2]. One compound having a structure between **1** and **2** (I[1]), another having a structure intermediate between **2** and **3** (II[3]), and one of type **3** (III[4]) have been prepared and characterized by X-ray analysis. The bicyclo[3.3.0]octane structure **3** is obtained when R = simple alkyl and Ar = Ph[5]. The structure I is realized

when R = $C(CH_3)_2CN$ and Ar = Ph and the intermediate structure II results when R = $C(CH_3)_3$ and Ar = phenyl. The R = $C(CH_3)_2COOEt$, Ar = Ph derivative is type **2**.



1 **2** **3** **4**

The geometries of I and III (see Table I) are analogous to those reported by Dunitz *et al.*[6] for eight-membered cyclic aminoketones (with incipient nucleophilic addition of the amino group to the carbonyl function) and their transannular reaction products. The transannular N···C(O) distances in the starting materials range from 2.46 to 2.76 Å and the N^+-C distances in the reaction products are 1.64 Å. No analog to compound II was reported in this earlier study. The structures of I-III are shown in Figure 1.

There is substantial evidence for the significance of the B(1)→N(2) interaction in I. The eight-membered ring adopts a boat-boat ("saddle") conformation, known to be stabilized by transannular interactions[7]. The boron atom is displaced 0.098(2) Å from the OOC plane toward the nitrogen atom, significantly greater than the maximum of about 0.03 Å arising from packing effects for trigonal planar boron atoms in related structures. Correspondingly, the mean O-B(1)-O/C bond angle is reduced to 119.5° from the 120° expected for a planar system. An increase in the mean O-B, and the intra-annular N-C(1) distances are also noted. The overall geometry of I is consistent with a system at the beginning of the transition from an eight-membered monocyclic structure to a bridged ring structure.

The structure of II is intermediate in this transition, with a N→B bond length of 1.953(3) Å corresponding to a bond order of about 0.3. This is the first such transitional structure involving only first-row elements to be characterized by an X-ray diffraction study. The structural parameters for this compound are in general intermediate between those observed for compounds I and III, the exceptions being some nitrogen atom parameters not involving the boron atom.

The N-B distance of 1.733 Å in the bicyclo[3.3.0]octane structure III (0.22 Å shorter than that in II) is similar to those reported for other bicyclic systems with essentially eclipsed configurations about transannular N-B bonds, and bearing *B*-phenyl and *N*-methyl substituents. It is, however, longer than those in analogous compounds

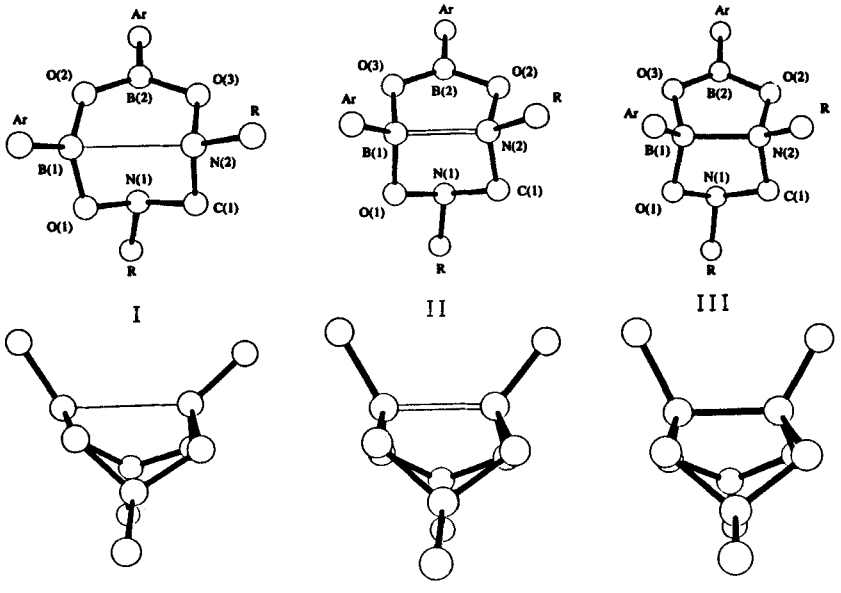


FIGURE 1 Perspective views of the structures of I (left), II (center), and III (right).

TABLE I Structural parameters for the N→B interactions in compounds I-III.[a]

Compound	I R = $C(CH_3)_2CN$ Ar = phenyl		II R = $C(CH_3)_3$ Ar = phenyl		III[b] R = CH_3 Ar = phenyl	
B-N Å	2.475(3)	2.755(3)	1.953(3)	2.897(4)	1.733	3.083
B-N bond order[c]	0.05		0.29		0.62	
mean B-O Å	1.382	1.371	1.424	1.366	1.452	1.370
B-C(ar) Å	1.545(3)	1.547(3)	1.573(4)	1.553(4)	1.581	1.546
N-C(1) Å	1.467(2)	1.454(3)	1.481(3)	1.450(3)	1.475	1.447
N-O Å	1.446(2)	1.452(2)	1.453(2)	1.462(2)	1.447	1.459
mean N-B-O/C°	94.3		102.0		103.9	
mean O-B-O/C°	119.5	120.0	115.8	120.0	114.4	120.0
mean B-N-O/C°	108.2		109.4		109.2	
mean C-N-O/C°	109.1	109.0	108.6	109.0	109.5	106.1
displacement of B from O_2C plane, Å	0.098(2)	0.017(2)	0.305(3)	0.026(3)	0.360(3)	0.007(3)

[a] For each compound figures in the the first and second columns refer to the interacting and non-interacting B, N pairs respectively. [b]Average parameters for the two crystallographically independent molecules. [c] Empirical, corrected for σ-hybridization and electronegativity effects.

with R = H which range from 1.666 to 1.692 Å. The N→B bonds in monocyclic compounds are even shorter, averaging about 1.65 Å. Both the calculated bond order for the N→B bond in III (0.62) and the degree of pyramidalization (0.36 Å from the OOC plane vs. an expected value of 0.50 Å for an ideal tetrahedral geometry) are consistent with an interaction weaker than a classical N(sp^3)-B(sp^3) single bond,which would be expected to have a bond length of around 1.61 Å.

One of the most interesting aspects of these three structures is that the degree of pyramidalization of the trigonal planar boron atom in its transition to a tetrahedral geometry is well ahead of the bond strength. The results of this study provide experimental evidence that rehybridization at the boron centre occurs before the N→B bond is formed. Examination of the data in Table I reveals that in I, where the bond is just beginning to form (bond order 0.05), the degree of pyramidalization is already about 20% of the value expected for an ideal tetrahedral geometry. In the intermediate structure II with a bond order of about 0.3, the degree of pyramidalization reaches 61%. Finally, in III (bond order 0.62), the pyramidalization is 72% complete.

Also noteworthy is the fact that while the bond lengths and angles involving the "soft" boron atom and, to a lesser extent, the N-O and N-C(1) bond lengths are sensitive to the strength of the transannular interaction, the bond angles at the nitrogen atom remain virtually unchanged. With an increasing degree of pyramidalization at the boron atom, a decrease in the strength of the O-B pp(π) interaction is indicated by the O-B bond lengths.

Full details of the preparation and crystal structure of II, along with a more detailed analysis of the data presented here, will be published later [3].

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