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BOREPIN AND ITS VALENCE ISOMERS

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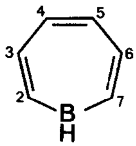
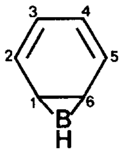
Summary: *Ab initio* calculations show borepin to be planar and more stable than its valence isomers boranorbornadiene and boranorcaradiene by a considerable amount; the latter have C_s symmetry.

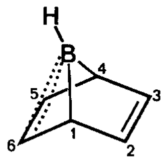
Borepin (I) is perhaps the most conspicuously absent member of the family of monocyclic 4n+2 pi-electron systems. In contrast to the isoelectronic tropylium cation, which is stable in aqueous solution, even alkylborepins are quite unstable.[1-3] Stable heptaarylborepins are known[4], however, as are benzo-fused borepins.[5-7] In order to understand the energetics of the borepin system we have undertaken *ab initio* theoretical studies of borepin and its valence isomers 7-borabicyclo[4.1.0]hepta-2,4-diene (II) and 7-borabicyclo[2.2.1]hepta-2,5-diene (III).



I



II



III

The geometries have been optimized at the STO-3G SCF level of calculation. Results for borepin have been reported previously[8], while those for II and

III are given in Table I. Borepin has a (planar) C_{2v} structure with alternating CC bond lengths: C_2C_3 = 1.345 Å; C_4C_5 = 1.344 Å, and C_3C_4 = 1.451 Å. There is a modest delocalization of 0.28e into the boron p-pi atomic orbital. For II we obtained a tub-shaped C_s structure with bow and stern elevation angles of 69.1° and 4.7°, respectively, quite similar to the structure we found for norcaradiene[9]. The extent of bond alternation in II is greater than in I: C_2C_3 = 1.321 Å and C_3C_4 = 1.481 Å. The bond lengths BC_1 = 1.529 Å and C_1C_6 = 1.548 Å are in reasonable agreement with their counterparts in borirane[10], 1.521 Å and 1.526 Å, respectively. The local geometry at B in II is nearly planar.

For III we obtained a C_s structure with boron canted toward C_5=C_6. The angle BPQ, where P and Q are the respective midpoints of C_1C_4 and C_5C_6, is 87.8°. The angle H_7BP is 177.4° with the hydrogen pointed toward C_5C_6. The canting of boron furnishes a homoaromatic counterpart to borirene and an isoelectronic counterpart to the 7-norbornadienyl cation, a subject of both nmr[11] and theoretical[12] studies. Concommitant with back-donation of electrons to the nearly pure boron p orbital, the C_5C_6 bond length of 1.353 Å is 0.041 Å larger than that of C_2C_3. The distances BC_5 and BC_6 are relatively short, 1.88 Å, compared with the BC_2 and BC_3 value, 2.48 Å; however, the boron remains firmly bonded to C_1 and C_4 since BC_1 = 1.588 Å, almost exactly the carbon-boron bond length in dimethylborane[8].

Examination of the relative energies of I, II, and III given in Table II for the (a) STO-3G(SCF); (b) 4-31G(SCF); (c) 4-31G(RMP2) and (d) 6-31G*(SCF) levels allows several conclusions to be drawn. Discounting the energetics at level (a), which is known to be erroneous for strained-ring compounds, it is clear that borepin is more stable than II by at least ca. 37 kcal/mol. This argues against the proposed conversion (I→II) suggested for 1-methylborepin[3]. Borepin is markedly more stable than II when compared with tropilidene, which is only ca. 7 kcal/mol more stable than norcaradiene. However, we have found that tropylium cation is more stable than the

Table I. Geometrical Parameters of 7-borabicyclo[4.1.0]-heptadiene (II) and 7-borabicyclo[2.2.1]heptadiene (III)

II		III	
Bond Length (Å)			
C_1B	1.529	C_1B	1.588
C_1C_2	1.503	C_1C_2	1.520
C_2C_3	1.321	C_1C_6	1.522
C_3C_4	1.481	C_2C_3	1.312
C_1C_6	1.548	C_5C_6	1.353
C_1H_1	1.084	C_1H_1	1.082
C_2H_2	1.084	C_2H_2	1.082
C_3H_3	1.082	C_5H_5	1.084
BH_7	1.149	BH_7	1.152
Bond Angle (Degrees)			
BC_1C_2	119.7	BC_1C_2	106.4
$C_1C_2C_3$	122.5	$C_1C_2C_3$	110.3
$C_2C_3C_4$	121.5	$C_4C_5C_6$	109.4
C_1BC_6	60.9	BC_1C_6	74.2
$H_1C_1C_2$	114.8	C_1BC_4	96.3
$H_2C_2C_3$	120.9	$H_2C_2C_3$	127.2
$H_3C_3C_4$	117.8	$H_5C_5C_4$	124.3
H_7BC_1	149.3	H_7BC_1	131.8
$C_1C_6C_5$	115.9	$H_1C_1C_2$	118.2
		$C_3C_4C_5$	110.9
Torsion Angle (Degrees)			
$C_1C_2C_3C_4$	4.8	$C_1C_2C_3C_4$	0.0
$C_2C_3C_4C_5$	0.0	$C_4C_5C_6C_1$	0.0
$C_2C_1BC_6$	-104.3	$C_2C_3C_4C_5$	-58.6
$BC_1C_2C_3$	63.6	$C_2C_1BC_4$	29.3
$H_1C_1C_2C_3$	-147.2	$BC_1C_6C_5$	43.8
$H_1C_1C_2H_2$	32.1	$BC_1C_2C_3$	-20.4
$H_4C_4C_3C_2$	175.9	$H_1C_1C_2C_3$	-166.6
$H_7BC_1H_1$	-71.9	$H_1C_1C_2H_2$	17.1
		$H_5C_5C_4H_4$	2.2
		$C_3C_4C_5C_6$	58.1
		$H_7BC_1C_6$	98.1

hypothetical bicyclo[4.1.0]hepta-2,4-dien-7-yl cation (the analog of II) by 101.5 kcal/mol and 112.7 kcal/mol at levels (b) and (c), respectively. This suggests that borepin has 40-43% of the delocalization energy of tropylium, a conclusion consistent with that found in our earlier study.[8]

While the gap between I and II is unlikely to change substantially at higher levels of approximation, that between I and III undoubtedly would decrease further; this is because inclusion of d-orbitals and electron correlation work in tandem to diminish the relative energy of III. Finally, the asymmetric structure of III due to canting of the boron bridge probably adds somewhat to the complexity of the nmr of p-tolyl derivatives of III observed by Eisch and Galle[13].

Table II. Relative Energies of Borepin and its Valence Isomers (kcal/mol)

molecule	STO-3G(SCF)	4-31G(SCF)	4-31G(RMP2)	6-31G*(SCF)
I	0.0	0.0	0.0	0.0
II	25.7	43.7	44.8	37.7
III	1.6	37.4	26.9	23.6

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