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Theoretical Studies of Borepin and Cycloheptatriene

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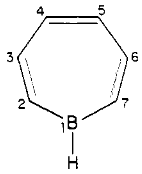
Abstract: Borepin and cycloheptatriene were studied by ab initio molecular orbital theory with use of STO-3G and 4-31G basis sets, with correlation energies calculated in the latter. When geometry optimization was used, cycloheptatriene was shown to have a boat equilibrium structure. A planar structure was found to be ca. 6 kcal/mol higher in energy and to be a transition state on the C_7H_8 energy surface, probably for interconversion of boat structures. Geometry optimization of borepin furnished a planar structure which, through analysis of bond lengths and electronic populations, is shown to be a weakly conjugated system.

I. Introduction

The borepin molecule (I) is a 6π-electron "aromatic" system whose synthesis has not yet been achieved. From the viewpoint of resonance stabilization,[1] borepin, with boron's smaller electronegativity than carbon and its poorer carbon–boron π–π overlap, is intermediate between the tropylium cation (II),[2] with cyclic conjugation involving seven equivalent carbons, and 1,3,5-cycloheptatriene (CHT) (III),[3] in which cyclic conjugation over seven centers is precluded by the saturated methylene carbon, C_7.



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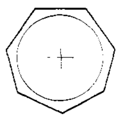

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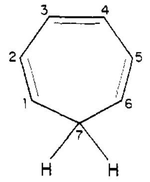
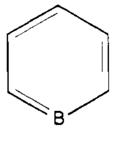


III

The tropylium cation is presumed to have a planar (D_{7h}) geometry.[4] It is remarkably stable, even in water, where it acts as a weak Lewis acid. This stability undoubtedly arises from its large π delocalization energy (0.77β) with respect to the acyclic heptatrienyl cation, enabling it to overcome both bond-angle and bond-stretching strain energies associated with its planar, symmetric structure.

In contrast to the tropylium cation, CHT adopts a boat conformation, as shown by electron diffraction,[5] microwave,[6] infrared,[7] and NMR[8] measurements as well as by X-ray structure determination of a derivative of 7,7-dimethylcycloheptatriene-3-carboxylic acid.[9] A planar conformer of CHT has been suggested as the transition state for interconversion of boat structures; the present work shows this to be quite likely the case.

In order to determine whether borepin would adopt a boat or planar geometry and to assess the extent of electron delocalization onto the boron, we have performed ab initio calculations on boat and planar CHT and boat and planar borepin, minimizing the total energies with respect to all but the most trivial geometric parameters under the constraints of C_s (boat) and C_{2v} (planar) symmetries. In addition, we studied the following related systems: borabenzene (IV), for which we optimized the geometry of the C_{2v} structure; substituted borepins (V), where X = F, OH, CH_3, and NH_3^+; and several aminoborepins.



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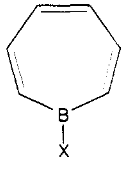

V

Although the literature on borepin derivatives is scant, several of the relevant systems should be mentioned. Eisch and Galle[10] have reported the synthesis of two heptaphenylborepins. Their studies suggest the occurrence of valence isomerism involving norcaradiene-like structures; however, the pertinence of this result to the parent borepin is not clear. Halpern and Axelrad[11] have reported the synthesis of 3-hydroxy-3-cyclohexenoborepin and have

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Table I. Geometrical Parameters of Boat Cycloheptatriene Optimized in the STO-3G Basis Set[a]

bond lengths, Å		bond angles, deg		torsional angles, deg	
C_1C_7	1.526	$C_7C_1C_2$	123.3	$C_1C_2C_3C_4$	33.3
C_1C_2	1.318	$C_1C_2C_3$	125.3	$C_2C_3C_4C_5$	0.0
C_2C_3	1.483	$C_2C_3C_4$	125.9	$C_2C_1C_7C_6$	−60.0
C_3C_4	1.325	$C_1C_7C_6$	110.3	$C_7C_1C_2C_3$	3.3
C_1H_1	1.084	$H_1C_1C_2$	119.9	$H_1C_1C_2C_3$	−176.7
C_2H_2	1.084	$H_2C_2C_3$	115.2	$H_1C_1C_2H_2$	0.0
C_3H_3	1.085	$H_3C_3C_4$	118.5	$H_4C_4C_3C_2$	175.2
C_7H_{7n}	1.089[b]	$H_nC_7C_1$	109.4	$H_xC_7C_1H_1$	−1.7
C_7H_{7x}	1.089[b]	$H_xC_7C_1$	110.1	$H_nC_7C_1H_1$	−120.0
		$H_nC_7H_x$	107.6		
		bow elevation	47.7		
		stern elevation	27.3		

[a] The total energy was minimized to within 0.2 kcal/mol. [b] The endo hydrogen, denoted as H_n, points towards the stern. The exo and endo CH bond lengths were constrained to equality.

inferred some degree of "aromatic character" from its UV and NMR spectra, which imply some electron delocalization onto boron. Several substituted benzoborepins have also been prepared and studied,[11,12] but unfortunately there are no structural data for these compounds.

II. Ab Initio Studies on 1,3,5-Cycloheptatriene

Before undertaking ab initio calculations on borepin it was important to establish whether the present level of calculation is capable of producing a reasonable geometry and inversion barrier for CHT. This proved to be so. For the boat structure a complete geometry optimization within C_s symmetry was performed with the STO-3G Gaussian basis,[13] the only constraint being that of equal lengths for the two methylene CH bonds. Nineteen parameters were varied in all, using a combination of hand optimization and the automated analytic first-derivative option of the Gaussian 80 package.[14] The final geometry, which should be accurate to 1° for the bond angles and 0.03 Å for the bond lengths, is given in Table I. The geometry differs somewhat from the electron diffraction values[5] but is quite reasonable. The bow and stern elevation angles α and β (cf. ref 5) found here are 47.7° and 27.3°, which are in fair agreement with those of Traetteberg,[5] 40.5 ± 2° and 36.5 ± 2°, respectively; in better agreement with the microwave values of Butcher,[6] 50° ± 5° and 29.5 ± 4°; and in good agreement with the X-ray values for a 7,7-dimethylcycloheptatriene-3-carboxylic acid derivative,[9] 49.7° and 23.7°, respectively. The torsional angles $\angle C_2C_1C_7C_6 = 60.0°$, $\angle C_7C_1C_2C_3 = 3.3°$, and $\angle C_1C_2C_3C_4 = 33.3°$ are in good agreement with the π SCF force field calculated values of Lindner,[15] 60.7°, 6.4°, and 29.3°, respectively.

Using the STO-3G optimized geometry we next performed calculations on CHT in the 4-31G basis set[16] at the SCF and second-order Møller–Plesset levels (in the frozen core approximation).[17] The total energies obtained are given in Table II, which also contains the dipole moments at the SCF level. The value furnished by the 4-31G basis was 0.30 D, which is in good agreement with the microwave value, 0.25 D.[6] The dipole moment vector points in the direction of the methylene group.

We next optimized the geometry of planar CHT in the STO-3G basis, subject to the constraint of C_{2v} symmetry. The final geometrical parameters are given in Table III. The bond lengths are quite similar to the corresponding values for the boat conformer; however, the bond angles changed appreciably, particularly $\angle C_1C_7C_6$, which increased from 110.3° in the boat to 125.9° in the planar structure and, to a lesser extent, $\angle H_nC_7H_x$, which decreased slightly. It is interesting to note that apart from the methylene hydrogens the atoms of planar CHT are nearly superimposable on those of planar borepin, which is described in the next section. This suggests that the bond angle strain is distributed over the seven vertices in a rather similar manner in the two molecules.

Table II. Total Energies (hartrees) and Dipole Moments (D) of CHT and Borepin[a]

	energy		dipole moment
	Cycloheptatriene (Planar)		
STO-3G (SCF)	−266.39827	STO-3G	0.40[b]
4-31G (SCF)	−269.28426	4-31G	0.51[b]
4-31G (E_2)	−0.61288		
4-31G (RMP2)	−269.89714		
	Cycloheptatriene (Boat)		
STO-3G (SCF)	−266.40636	STO-3G	0.26[b]
4-31G (SCF)	−269.29407	4-31G	0.30[b]
4-31G (E_2)	−0.61668		
4-31G (RMP2)	−269.91075		
	Borepin (Planar)		
STO-3G (SCF)	−252.81158	STO-3G	1.74[c]
4-31G (SCF)	−255.57184	4-31G	2.01[c]
4-31G (E_2)	−0.57223		
4-31G (RMP2)	−256.14407		

[a] Energy and dipole moments were calculated at the STO-3G optimized geometries. [b] The positive end of the dipole is toward the methylene end of the molecule. [c] The positive end of the dipole is away from boron.

Table III. Ring Bond Lengths (Å) of Several Molecules Geometry Optimized in the STO-3G Basis Set

		Planar Cycloheptatriene[a] (C_{2v})			
C_1C_7	1.525	C_2C_3	1.485	C_3C_4	1.323
C_1C_2	1.317				
		Borepin (C_{2v})			
BC_1	1.523	C_3C_4	1.451	C_4C_5	1.344
C_2C_3	1.345				
		Borabenzene[b] (C_{2v})			
BC_1	1.420	C_3C_4	1.394	C_2C_3	1.391
		Tropylium Cation[c] (D_{7h})			
C_1C_2	1.386				
		Borirene[d] (C_{2v})			
BC	1.440	CC	1.340		

[a] The internal angles at C_1, C_2, C_3, and C_4 were 128.8°, 128.3°, 130.0°, and 125.9°, respectively. [b] The internal angles at B, C_2, C_3, and C_4 were 122.6°, 117.2°, 121.4°, and 120.2°, respectively. [c] Reference 18. [d] Reference 20.

Extended basis set 4-31G SCF and second-order Møller–Plesset calculations were performed on planar CHT, using the STO-3G optimized geometry. At each level of calculation the boat structure was more stable than the planar: by 5.1 kcal/mol in STO-3G, 6.2 kcal/mol in 4-31G, and 8.5 kcal/mol in (4-31G) Møller–Plesset, the last of these methods clearly lowering the energy of the boat structure by about 2.3 kcal/mol more than the planar structure. These results are given in Table II. They are in reasonable agreement with the CHT inversion barriers obtained from low-temperature NMR studies,[8] 5.7 and 6.3 kcal/mol, and they support the idea that inversion takes place through the planar structure. To determine whether planar CHT is indeed a transition state we diagonalized the STO-3G force-constant matrix in the manifold of the seven B_1 symmetry distortions (antisymmetric with respect to reflection in the plane of the molecule). The planar form is unstable with respect to one symmetry coordinate (F-matrix eigenvector) which is "boat forming"; the eigenvalue has the extremely small value −0.024 mdyn/Å. The other six eigenvalues are positive. Therefore, in the STO-3G basis, the planar

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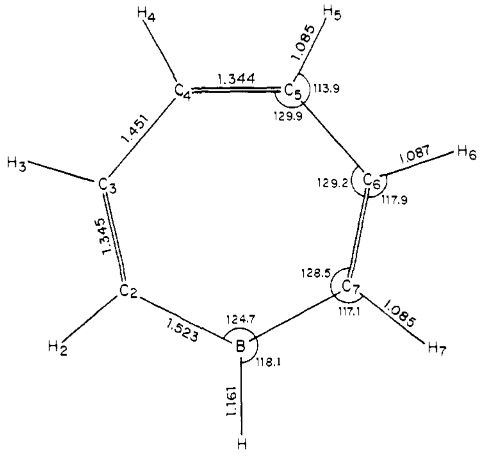


Figure 1. Bond lengths and bond angles of planar borepin obtained by geometry optimization in the STO-3G basis set.

form is a transition state between equivalent boat forms. On the other hand it must be said that the lowest of the positive eigenvalues is also quite small and the energy surface in the vicinity of the transition state is quite flat, perhaps containing complexities not apparent at this point.

III. Ab Initio Studies of Borepin and Related Systems

A. Considerations of Geometry and Total Energy. The geometry of borepin was optimized in the STO-3G basis set starting from a boat geometry based on the CHT equilibrium geometry of section II. Except for the dihedral angles $H_3C_3C_2B$, $H_4C_4C_5C_6$, and $H_3C_3C_2H_2$, which were fixed at 180°, 180°, and 0°, respectively, all geometrical parameters were varied within C_s symmetry—15 in all. In contrast to the case of CHT, no stable boat structure was found. Instead, the borepin energy decreased as the "bow" (C_7) and "stern" (C_3,C_4) elevation angles were lowered until the sole minimum energy configuration, the planar structure shown in Figure 1, was obtained. The STO-3G, 4-31G, and second-order Møller–Plesset energies of planar borepin are given in Table II. The energy of a hypothetical boat conformation of borepin, suggested by optimized cycloheptatriene, was computed to be 18.0 kcal/mol higher than the planar energy in the STO-3G basis (19.3 kcal/mol in the 4-31G basis). In contrast, the STO-3G energy of a tropylium cation in this geometry is 74.6 kcal/mol higher than that of its optimized D_{7h} structure.[18]

The bond lengths of borepin, Table III and Figure 1, can be compared with those of planar cycloheptatriene on the one hand and those of the tropylium cation and borabenzene on the other. CHT is a model for a delocalized linear conjugated π system, whereas the latter are cyclic conjugated π systems. Borepin has two short carbon–carbon bonds, $C_2C_3 = C_6C_7$ (1.345 Å) and C_4C_5 (1.344 Å), and one longer bond, $C_3C_4 = C_5C_6$, (1.451 Å). The extent of bond alternation in borepin is similar to that in planar CHT, in which the STO-3G double bond lengths are 1.317 Å for C_1C_2 and 1.323 Å for C_3C_4 and the single-bond length is 1.485 Å for C_2C_3. On the other hand, borabenzene shows little or no bond alternation. Its bond lengths $C_2C_3 = C_5C_6$ and $C_3C_4 = C_4C_5$ have the nearly identical values of 1.391 Å and 1.394 Å, respectively, and these, in turn, are quite close to the STO-3G value for the tropylium cation, 1.386 Å.[18] The CB bond length in borepin, 1.523 Å, is similar to that expected for boron attached to an sp^3 carbon, since by optimizing the CB distance in dimethylborane we obtained 1.584 Å (the optimized CBC angle was 121.8°). On the other hand, the borabenzene CB bond length is 1.420 Å, significantly smaller than that of borepin. Thus, it is clear that from the standpoint of bond lengths borepin is closer to the noncyclic conjugated system, planar CHT, than it is to either of the cyclic systems, the tropylium cation or borabenzene.

Table IV. Mulliken π Overlap Populations (e) between Bonded Atoms in Borepin, Borabenzene, CHT, Vinylborane, and Borirene

Borepin[a]	
$BC_2 = 0.05$	$C_3C_4 = 0.05$
$C_2C_3 = 0.16$	$C_4C_5 = 0.16$
Borabenzene[a]	
$BC_1 = 0.12$	$C_3C_4 = 0.11$
$C_2C_3 = 0.11$	
Planar CHT[a]	
$C_1C_2 = 0.19$	$C_3C_4 = 0.18$
$C_2C_3 = 0.02$	
Vinylborane[b]	
$BC_1 = 0.05$	$C_1C_2 = 0.18$
Borirene	
$BC_1 = 0.08$	$CC = 0.14$

[a] STO-3G overlap populations for the STO-3G geometry-optimized structure. [b] Reference 19.

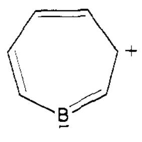
Table V. Gross Orbital Charges and Total Boron Populations in Several Borepin Derivatives (e). STO-3G Basis

molecule	boron π population	total charge on boron
borepin	0.28	4.76
hydroxyborepin[a,b]	0.46 (0.39)	4.59 (4.55)
fluoroborepin[a]	0.41	4.59
methylborepin[a]	0.30	4.76
ammoniumborepin[a]	0.43	4.60
2-aminoborepin[c]	0.30	4.76
3,6-diaminoborepin[c]	0.33	4.78

[a] The OH, F, Me, and NH_3 are the boron X substituents of V. [b] The hydroxyl hydrogen was in the plane of the ring; values obtained for the OH bond perpendicular to the ring are given in parentheses. [c] The amino groups are planar and are in the borepin plane.

B. Considerations of Electronic Structure. A conclusion similar to the above is reached by examination of Mulliken π overlap populations, Table IV. In planar CHT the π overlap populations of the double bonds are 0.18–0.19 e, while those of the single bonds are 0.02 e. In borepin the C_2C_3 and C_4C_5 bonds have overlap populations of 0.16 e, just slightly lower than the CHT double-bond values, and the C_3C_4 and BC_2 populations are 0.05 e, which is slightly higher than the CHT single-bond values by about the same amount. The view that the π conjugation in borepin is more nearly of the linear than the cyclic kind is also supported by the STO-3G populations of vinylborane:[19] C_1B 0.05 e and C_1C_2 0.18 e. These are very close to the borepin values.

Another measure of boron participation in the borepin π system is its pπ orbital population. The STO-3G value is 0.28 e, which while significantly different from zero is still only one third the value in the fully delocalized tropylium cation, 0.86 e. The π populations of the α, β, and δ carbons are 0.94 e, 0.94 e, and 0.98 e, respectively, suggesting contributions from structures Ia, Ib, and Ic in which boron has a negative charge. This idea is in accord with the increased BC_2 and C_3C_4 and decreased C_2C_3 and C_4C_5 π overlap populations compared to the planar CHT values. It should be noted that boron has a positive gross atomic charge due to a large transfer of electrons from boron to carbon in the σ system. The π population of boron is therefore due, in part, to back-donation tending to preserve electroneutrality.



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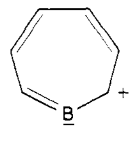

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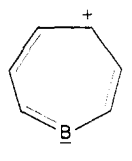

Ic

Several attempts were made to find borepin derivatives which might show more charge delocalization into the boron π orbital.

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Thus, we studied the one-substituted borepins (V) with X = OH, F, CH_3, NH_3^+, as well as 2-aminoborepin and 3,6-diaminoborepin. The NH_2 groups in the latter two molecules were oriented parallel to the borepin ring so as to enable maximum π overlap. It can be seen from the π populations given in Table V that in none of the substituted borepins is there any π delocalization onto boron approaching the statistical value, 6/7 e. In the case of hydroxyborepin, the 0.46 e is drawn largely from an oxygen p orbital. Moreover, a particularly telling case is the quaternary ammonium salt obtained for X = NH_3^+; even an adjacent positive charge fails to increase the boron π population.

IV. Discussion

It has been shown that molecular orbital SCF calculations at the STO-3G level are capable of adequately describing the geometry and energetics of cycloheptatriene and its planar transition state. Therefore, the results obtained for borepin are probably reliable. Borepin adopts a planar equilibrium geometry in preference to a boat conformation by some 18 kcal/mol (section III), which implies some π conjugation involving boron. Its tendency to do so, however, is much less than that of the tropylium cation, in which the planar–boat energy difference is on the order of 75 kcal/mol.

It is interesting to compare the 6π-electron borepin with the 2π-electron system borirene, which has recently been discussed from a theoretical point of view[20] and which also has yet to be synthesized. The gross π population of boron in borirene, 0.39 e, is 58% of the value of the cyclopropenyl cation, in contrast to the borepin value, 0.28 e, which is only 33% of the tropylium cation's 0.86 e. Similarly, borirene is closer in π overlap populations (Table IV) and bond lengths (Table III) to the cyclopropenyl cation, the tropylium cation, and borabenzene than it is to cyclopropane and planar cycloheptatriene.

In view of these results, it becomes clear that the existence of a strongly conjugated system of the cyclic kind depends not only on the presence of $4n + 2$ π electrons,[1] but also on the nature of the atoms and their interrelationships. This conclusion is also supported by the finding that the 2π-electron systems cyclobutadiene dication and 1,3-diboretene may be nonplanar.[20] The origin of the small extent of electron delocalization in borepin is the small electronegativity of boron, which makes it unable to obtain a π-electron density comparable to the carbons. From a valence bond point of view, the structures Ia–c make small contributions to the total wave function.

The delocalization energy of borepin has been estimated to be 70% of that in the cyclopropenyl cation. The present evidence suggests that the delocalization energy of borepin is ca. 35% of that of the tropylium cation. This conclusion is consistent with the small ring current effects found in various benzoborepins.[10]

Finally, borepin can be compared with the isoelectronic cycloheptatrienylidene molecule, which has been the subject of recent ab initio[21] and MNDO studies.[22] Both found a singlet tetraene ground state, a structure not available to borepin, as it would require weakening the BH bond. The cycloheptatrienylidene state analogous to planar borepin is a singlet (C_{2v}) excited state, which both calculations have found, albeit with rather different geometries. A σ lone pair corresponds to the borepin BH bond.

We have calculated the C_1 gross π population for this (C_{2v}) state, using the geometry of Radom et al.,[21] and found it to be 0.31 e (STO-3G); this is similar to the 0.28 e π population on boron in borepin. The reason for the low value in the former case may be the reduction in electron repulsion energy attendant upon a small occupation of the C_1 π orbital. Thus, neither cycloheptatrienylidene nor borepin has extensive delocalization on all seven π centers, although the reasons in the two cases are different.

It might be added that the MNDO study found the cycloheptatrienylidene (C_{2v}) state to be unstable with respect to a_2 distortions and a candidate for the transition state between ground-state tetraene enantiomers. Our study of the borepin force constant matrix showed no negative eigenvalues.

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Registry No. I, 291-62-3; III, 544-25-2; IV, 31029-61-5; V (X = OH), 81769-77-9; V (X = F), 81769-78-0; V (X = CH_3), 79010-91-6; V (X = NH_3), 81790-02-5; 2-aminoborepin, 81769-79-1; 3,6-diaminoborepin, 81769-80-4; borirene, 16488-40-7.

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