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1-METHYLBOREPIN, ITS AROMATICITY AND THERMAL DECOMPOSITION

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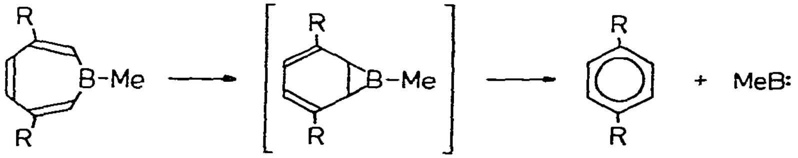
Summary

1-Methylborepin (I) is judged to be aromatic on the basis of a) the value of its Hückel MO resonance energy, b) the ring-current effect on its ^{1}H NMR spectrum, and c) its degree of aromaticity based on Julg's criterion. The thermal stabilities of hetero-conjugated monocyclic ring systems containing 5, 7, 9, and 11 ring atoms and B or N as the hetero atom are assessed to the basis of orbital symmetry considerations. Hetero-conjugated ring systems containing $2n + 1$ ring atoms ($2n$ being the number of ring carbon atoms) are predicted to be thermally stable when n is even, and thermally unstable when n is odd.

Introduction

In the preceding paper [1] we reported the formation of 1-methylborepin (I) and of 1-methyl-3,6-dideuteroborepin (II). Compounds I and II were found to be thermally unstable, yielding benzene and 1,4-dideuterobenzene, respectively, on decomposition. The following mechanism was proposed for this decomposition:



I R=H
II R=D

IIIa R=H
IIIb R=D

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The presence of the 7-methyl-7-borabicyclo[4.1.0]heptadiene (or methylboranorcaradiene) derivatives IIIa and IIIb was indicated by complex olefinic ^{1}H NMR signals.

In this paper the aromaticity of 1-methylborepin (I) and the feasibility of the reaction mechanism indicated above are considered.

Discussion

Criteria for aromaticity

The criteria that will be used in assessing the aromaticity of 1-methylborepin (I) (out of the many available criteria for aromaticity [2—4]) are the following:

1. The value of its Hückel MO (HMO) resonance energy, E_R [5].
2. The effect of the so-called ring-current (i.e. the free movement of the π-electrons over the ring) on the chemical shifts in its ^{1}H NMR spectra (paramagnetic deshielding).
3. The value obtained for the so-called degree of aromaticity, using the formula given by Julg [6]:

$$A = \left[1 - \frac{225}{n} \sum_{(ij)}^{n} \left(1 - \frac{r_{ij}}{r}\right)^2\right] \prod_{(kl)}^{n} \left[1 - \left(\frac{\Delta q_{kl}}{r_{kl}}\right)^2\right]$$

with A = degree of aromaticity

n = number of peripheral C-C bonds (ij,kl)

r = mean length of the peripheral C-C bonds

r_{ij} = length of peripheral C-C bond ij

$\frac{\Delta q_{kl}}{r_{kl}} = \frac{q_k - q_l}{r_{kl}}$ = charge gradient over the bond kl

This formula is based on the uniformization of the lengths of the peripheral carbon—carbon bonds and on minimization of the charge gradient around the ring(s) (or minimization of the resistance to the circulation of electrons around the ring(s)). For benzene the degree of aromaticity is 1; the constant 225 has been chosen in order to obtain a value of zero for the degree of aromaticity for the Kekulé form of benzene (cyclohexatriene).

These criteria are in no way blurred by other properties of borepins, and thus should give a reasonably fair impression of the aromaticity.

The structure of 1-methylborepin (I).

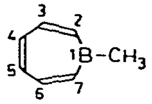
It was considered that insight into the question of the aromaticity of I might be obtained by forming an impression of its structure. To this end the geometry of I was optimized in two ways, the first of which was the following.

For a number of configurations of 1-methylborepin the energy of the molecule was calculated by means of the CNDO/2 method [7—9]. The bond lengths were varied between calculations, while each geometry had to meet the following requirements:

1. The ring would have to be planar and have C_{2v} symmetry.

2. The geometry of the ring would have to approach that of a regular heptagon as closely as possible at given bond lengths.

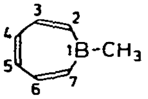
In this way the bond lengths were optimized (criterion: minimal energy) along with the geometry. The following values for the bond lengths (r), bond angles (ϕ), π charges (q), and π bond orders (p) were obtained:



bond angles ϕ	bond lengths r (Å)	π charges q	π bond orders p
$\phi_1=126.9°$	$r_{12}=1.496$	$q_1=0.5604$	$p_{12}=0.5086$
$\phi_2=126.7°$	$r_{23}=1.363$	$q_2=0.9109$	$p_{23}=0.7549$
$\phi_3=130.1°$	$r_{34}=1.402$	$q_3=0.8936$	$p_{34}=0.5329$
$\phi_4=129.8°$	$r_{45}=1.363$	$q_4=0.9535$	$p_{45}=0.7621$

From the values given above, it follows that the B—C bond length in 1-methylborepin is considerably shorter than that in e.g. trimethylboron (1.496 Å vs. 1.56 Å [10]). The B—C π bond order ($p_{12} = 0.5086$) also indicates a strong π interaction between the boron atom and the conjugated system, and thus the possibility of a ring-current. The latter is substantiated by ^{1}H NMR evidence [1]. The carbon—carbon bonds still alternate, though not strongly. It is also clear that the boron atom bears a fair amount of π-electron density.

The second way in which the geometry of 1-methylborepin was optimized was by the MINDO/3 method * [11]. The only a priori condition used here was that the ring had to be planar. In the optimized structure the molecule had C_{2v} symmetry. The values obtained were as follows:

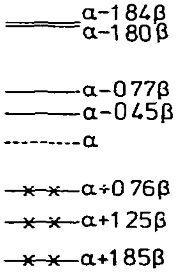


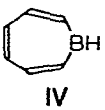
bond angles ϕ	bond lengths r (Å)	π charges q	π bond orders p
$\phi_1=124.0°$	$r_{12}=1.516$	$q_1=0.5101$	$p_{12}=0.4832$
$\phi_2=128.4°$	$r_{23}=1.357$	$q_2=0.8938$	$p_{23}=0.7987$
$\phi_3=130.8°$	$r_{34}=1.432$	$q_3=0.9063$	$p_{34}=0.4655$
$\phi_4=128.8°$	$r_{45}=1.369$	$q_4=0.9666$	$p_{45}=0.8144$

These values give 1-methylborepin a somewhat smaller degree of aromaticity than do the CNDO/2 results; the bond lengths alternate a little more.

HMO calculations on borepin (IV)

HMO calculations [12] were performed on borepin (IV). The parameters used first were those of Matteson [13] as mentioned by Streitwieser [14]: $\alpha_B = \alpha - \beta$ and $\beta_{B-C} = 0.7\beta$. The following HMO energy diagram was obtained:





IV

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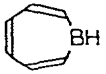
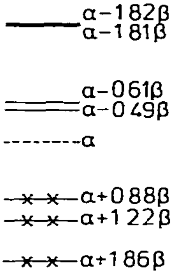
* These calculations were carried out by Mr. P.H.M. Budzelaar to whom the author expresses his gratitude.

This yielded a resonance energy E_R of 1.71β (cf. E_R (benzene) = 2.00β) for borepin.

The HMO parameters used above were felt not to be optimal, in view of the lack of correspondence between the HMO and CNDO/2 charges and bond orders. By adapting the Matteson parameters to the results (i.e. the charges and bond orders) of the CNDO/2 calculations, the following set was obtained: $\alpha_B = \alpha - 0.60\beta$, $\beta_{B-C} = 0.80\beta$, and $\alpha'_C = \alpha - 0.09\beta$, in which α'_C is the Coulomb integral for carbon atoms bound directly to boron. With these parameters the following HMO energy diagram was obtained for borepin:



IV



This results in a resonance energy $E_R = 1.92\beta$.

The degree of aromaticity of 1-methylborepin (I)

Julg's formula has not yet found wide application in organic chemistry. However, the values obtained with this equation for a number of compounds (see Table 1) agree very well with accumulated experience. Since experimental values for the bond lengths in I were not available, in the application of Julg's formula to I the values (for bond lengths and π-electron charges) from the CNDO/2 calculation on the optimized geometry and from the MINDO/3 optimization were used. The values thus obtained are also listed in Table 1.

Considering the available evidence (HMO resonance energy, ^{1}H NMR spectrum [1], and degree of aromaticity) it can be stated that 1-methylborepin meets the criteria of aromaticity mentioned earlier. Consequently, in these respects, 1-methylborepin may be considered to be fairly aromatic.

The thermal decomposition of 1-methylborepin

In this section the thermal decompositions of free and coordinated 1-methyl-

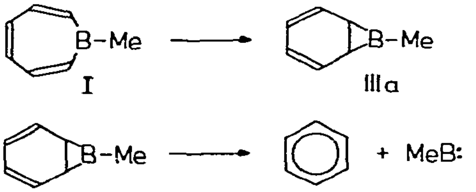
TABLE 1

DEGREE OF AROMATICITY ACCORDING TO JULG [6] FOR A NUMBER OF COMPOUNDS

benzene	1.00
thiophene	0.67
pyrrole	0.38
furan	0.06
pyridine	0.97
tropylium cation	1.00
naphthalene	0.90
1-methylborepin (CNDO/2)	0.85
1-methylborepin (MINDO/3)	0.75

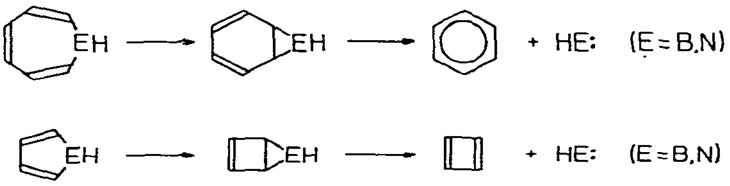
borepin are discussed, using orbital symmetry considerations [15—18].

In the introduction it was stated that 1-methylborepin (I) is thermally unstable, yielding benzene on decomposition. The following route involving two successive concerted reactions is suggested:



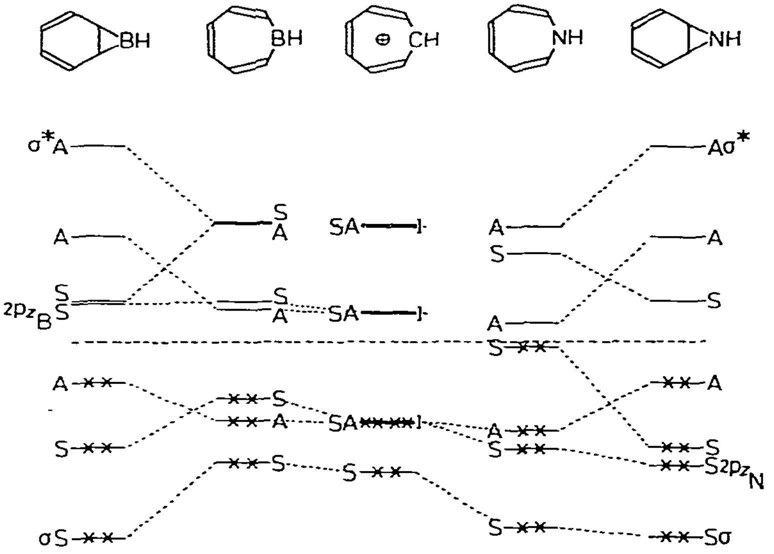
The first reaction, the formation of 7-methyl-7-borabicyclo[4.1.0]heptadiene (methylboranorcaradiene, IIIa) is a disrotatory electrocyclic ring closure: a new σ bond is formed from the π system. In the second reaction methylborylene, MeB:, is eliminated from IIIa, to yield benzene. This is a cheletropic reaction. The feasibility of these reactions can be judged by orbital symmetry considerations.

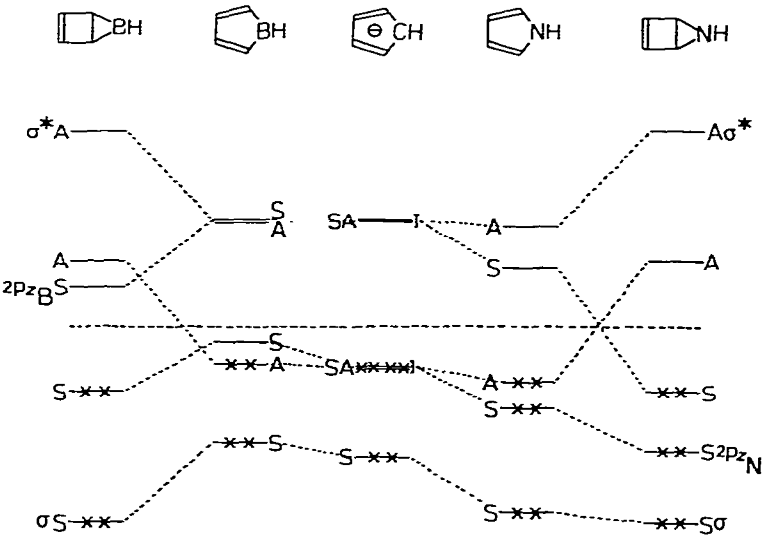
To obtain a more general picture, the reactions of eleven-, nine-, seven-, and five-membered ring systems, containing one hetero atom, either boron or nitrogen have been considered. The results for the seven- and five-membered systems are shown below. (The five-ring containing boron is called borole, and the seven-ring containing nitrogen azepin).



The π energy values for the diagrams shown below were calculated by the HMO method; the parameters for the boron compounds were those used previously. The parameters for the nitrogen compounds were: $\alpha_N = \alpha + 1.9\beta$, $\beta_{N-C} = \beta$, and $\alpha'_C = \alpha + 0.3\beta$. The parameters for the nitrogen compounds had been adapted to match the results (i.e. charges and bond orders) of CNDO/2 calculations on pyrrole. The form of the diagrams is as follows. In the middle column are depicted the π-electron energy levels of the tropylium ion (first diagram) and of the cyclopentadienylium ion (second diagram). On the left are shown the π energy levels of the corresponding boron compounds, and on the right those of the corresponding nitrogen compounds. This shows how the energy levels are shifted under the influence of the symmetry reduction resulting from the replacement of one carbon atom by a hetero atom of lower or higher electronegativity than carbon. Due to the reduction in symmetry (for the seven-rings from D_{7h} to C_{2v}, for the five-rings from D_{5h} to C_{2v}) the degeneracy is removed. The antisymmetrical MOs are little affected by the presence of the hetero atom, because these MOs have a nodal plane in which the hetero atom lies. Since they have considerable coefficients on the hetero atom the symmetrical MOs are influenced; when the hetero atom is less electronegative than carbon (in this case boron) the symmetrical MOs are shifted to higher energies;

when the hetero atom is more electronegative (as for nitrogen) the symmetrical MOs are shifted to lower energies. On the far left and far right of the drawings are depicted the energy levels (π and relevant σ) of the reaction products. In the diagrams the π levels are not marked, the σ levels (not on scale!) are marked σ or σ^*. The reaction geometry was assumed to have C_s symmetry; the monocyclic ring systems have a higher symmetry (C_{2v}), but in the course of the reaction the molecules become bent. The MOs marked with S are symmetric with respect to the mirror plane (perpendicular to the plane of drawing); MOs marked A are antisymmetric. The left and right parts of the diagrams are orbital correlation diagrams. It is seen that, both in the seven-membered and in the five-membered ring systems, low-lying unoccupied (π) MOs of the same symmetry as the highest occupied MO (HOMO) are present and, as a result, mixing is possible.

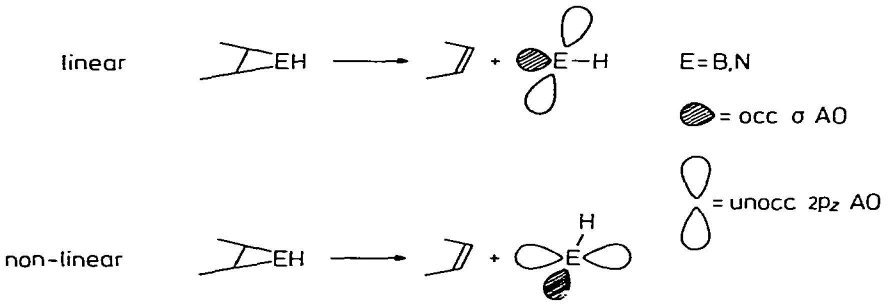




From the diagram it follows that both the conversion of borepin and azepin to the corresponding norcaradiene structure is symmetry-allowed in the ground-state, but that the conversion of both borole and pyrrole is forbidden in the ground state. In the same way it can be shown that the reaction of both nine-membered ring systems is symmetry-forbidden, while the reaction of both eleven-membered ring systems is allowed in the ground state.

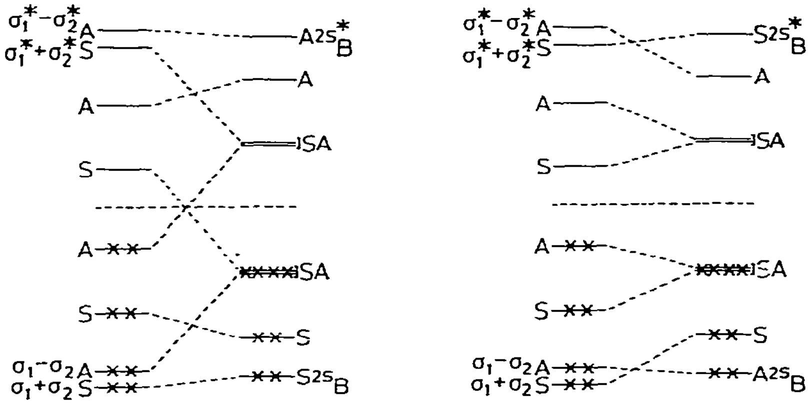
In the Woodward-Hoffmann rules the number of electrons is decisive for the course of a reaction; the number of atoms only serves to determine the number of MOs. In contrast with those rules, it appears in the cases considered here that the number of atoms is of prime importance. Let the number of atoms be $2n + 1$, in which n is an integer; then, if n is odd the reaction is symmetry-allowed in the ground state; if n is even the reaction is forbidden. It should be noted here that the nitrogen-containing systems always have two π-electrons more than the corresponding boron-containing systems (borepin for example has six π-electrons, azepin eight). The cause of this apparent discrepancy is the shifting of the energies of the symmetrical MOs under the influence of the hetero atom. MOs which are shifted upwards in energy in boron-containing systems are shifted downwards in nitrogen-containing systems. However, because nitrogen contributes two extra electrons to the π system, the HOMOs of corresponding boron- and nitrogen-containing ring systems always have the same symmetry.

The elimination of the hetero atom from the norcaradiene structures (a cheletropic reaction) can take place in two ways, linear and non-linear:



It should be noted that these reactions are the reverse of the addition of a carbene analogue to a conjugated system. As an example, the conversion of the boranorcaradiene system will be considered. The point group is C_s; S has the meaning of invariance under σ_h; a MO marked A is anti-symmetric under σ_h. For the boranorcaradiene system the following MOs are considered:

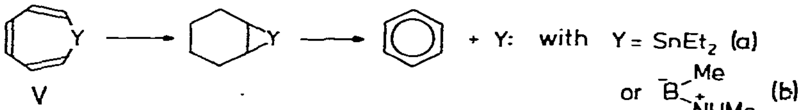
1. The symmetry-adapted linear combinations of the two σ bonds of the boron atom to the ring (σ_1 and σ_2): $\sigma_1 + \sigma_2$ (S), $\sigma_1 - \sigma_2$ (A), $\sigma_1^* + \sigma_2^*$ (S), and $\sigma_1^* - \sigma_2^*$ (A).
2. The four (butadiene) π MOs: π_1 (S), π_2 (A), π_3 (S), and π_4 (A). For the unit RB: the MOs are $2s_B$ and $2s_B^*$ (with symmetries S and A, and A and S for the linear and non-linear reaction, respectively). The π energy levels on the right in the diagrams are those of benzene. This gives the following correlation diagrams.



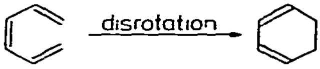
linear non-linear

It appears that in the ground state the non-linear reaction is symmetry-allowed. It should be noted that the other conceivable non-linear reaction geometry (the B—R bond perpendicular to the plane of the CCB triangle) is symmetry-forbidden under all circumstances. The thermal instability of 1-methylborepin (I) can thus be accounted for. The first reaction of the analogous decomposition scheme of the five-ring systems is symmetry-forbidden in the ground state. This is in accord with the observed thermal stability of borole [19,20] and pyrrole.

As was mentioned before [1], during the addition of diethylbromotin hydride to 1,5-hexadiyn-3-ene some benzene was formed. Further, 1-methylborepin complexed with dimethylamine proved to be thermally unstable, and the decomposition again yielded benzene. If the benzene formed in the reaction of 1,5-hexadiyn-3-ene with diethylbromotin hydride originated from the decomposition of traces of stannepin (Va), then the formation of benzene in these two cases might involve the same mechanism:



It should be noted that Y (i.e. the Sn atom or the four-coordinated B atom) does not take part in the π-electron system (no empty $2p_z$ AO available), so the system under consideration is:



According to the Woodward-Hoffmann rules this reaction is symmetry-allowed in the ground state, if it is disrotatory. Starting from a norcaradiene structure (point group C_s), the reaction must be disrotatory, so elimination of Y will always take place.

The $2n + 1$ ring-atoms rule derived here can be applied to monocyclic systems containing all kinds of suitable hetero atoms, since atoms more electronegative than carbon will always contribite two electrons to the π system, while those less electronegative than carbon contribute no π-electrons.

Conclusions

The experimental indications that 1-methylborepin (I) is aromatic [1], are corroborated by the calculations described.

The mechanism proposed for the observed thermal dissociation of I [1], via intermediate 7-methyl-7-borabicyclo[4.1.0]heptadiene, is confirmed by orbital symmetry considerations.

Acknowledgement

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