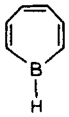
Tetrahedron Letters No.14, pp. 1263-1266, 1967. Pergamon Press Ltd. Printed in Great Britain.

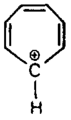
3-PHENYL-3-BENZOBOREPIN; A CARBON-BORON HETEROCYCLE WITH AROMATIC CHARACTER

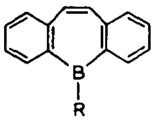
A.J.Leusink, W.Drenth, J.G.Noltes and G.J.M.van der Kerk
Institute for Organic Chemistry TNO, Utrecht, The Netherlands

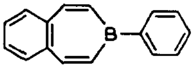
(Received 26 January 1967)

Hückel's $(4n+2)\pi$-electron rule predicts that borepin (I), which is isoelectronic with the tropylium ion (II), will be aromatic. However, all attempts to prepare borepin have failed (1-3). The dibenzo derivative (III) has been synthesized by Van Tamelen et al.(4), but these authors do not make clear the extent of aromatic stabilization in the central ring.

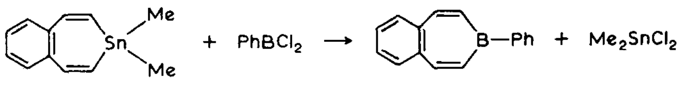

I


II

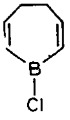

III


IV

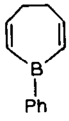
We wish to report on the synthesis of 3-phenyl-3-benzoborepin (IV). A study of its properties has revealed that this compound does display aromatic character. IV was obtained in approximately 50% yield (after crystallization from benzene) from the reaction of 3,3-dimethyl-3-benzostannepin (5) (V) with phenylboron dichloride:


V
IV

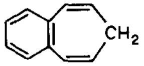
3-Phenyl-3-benzoborepin, a colourless compound melting at 134-137° (found: C 89.2, H 6.0, MW 215; calc.: C 88.93, H 6.06, MW 216.1), has unusual oxidative stability for an organoboron compound. After exposure of the solid to air for some days its UV spectrum (in cyclohexane) had remained largely unchanged. The half-life time of a very dilute solution in cyclohexane (2 mg of IV in 10 ml of C_6H_{12}) at room temperature is seven days (UV spectroscopy). In contrast, 1-chloro- and 1-phenyl-4,5-dihydroborepin (VI and VII, respectively) are rapidly air-oxidized (2).



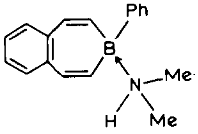
VI



VII



VIII



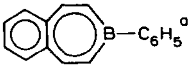
IX

These observations suggest that the seven-membered heterocycle of IV is stabilized by resonance. Further evidence for the aromatic character of the heterocycle was obtained from UV and PMR spectra (Tables 1 and 2).

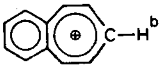
In contrast with the UV spectra of trivinylboron (XIII, λ_{max} = 234 nm, log ϵ = 4.28 (6)), 3,3-dimethyl-3-benzostannepin (V, λ_{max} = 227 nm, log ϵ = 4.51 (7)) and benzocycloheptatriene (VIII, λ_{max} = 224 and 255 nm, log ϵ = 4.60 and 3.90, respectively (8)) which fail to show maxima in the absorption curve above 260 nm, the UV spectrum of IV shows absorption bands up to 352 nm. In fact, the spectrum of IV shows a great similarity with the spectra of the benzotropylium ions X and XI (Table 1). The long wave length absorption band at ~ 420 nm present in the electronic spectra of X and XI is shifted to lower wave length in the spectrum

TABLE 1

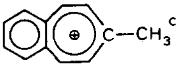
Ultraviolet Data of IV, X and XI



(IV)



(X)



(XI)

(IV)		(X)		(XI)	
λ(nm)	log ε	λ(nm)	log ε	λ(nm)	log ε
232	4.50	234	4.25		
285	4.68	282	4.70	285	5.02
301	4.45	-	-	-	-
322	3.98	-	-	-	-
336	4.22	338	3.50	340	3.69
352	4.21	-	-	354	3.60
-	-	425	3.25	415	3.37

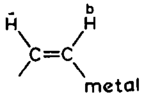
[a] In cyclohexane [b] In 60% H_2SO_4(ref.10) [c] In conc. H_2SO_4(ref.11)

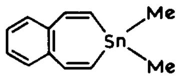
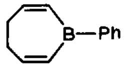
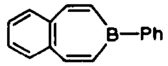
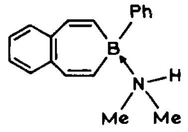
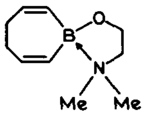
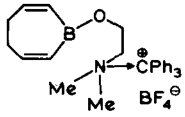
of IV. A calculation using an equation given by Coulson (9) showed that substitution of boron for the number 3-carbon in X will result in a downward shift of the 425 nm bond of approximately 80 nm. Thus, the UV spectral properties of IV are in accord with the view that the empty boron p_z-orbital participates in the π-electronic system of the ring, resulting in aromatic character. The electronic spectrum of the dimethylamine complex of IV (IX) which shows only one band at 237 nm (log ε = 4.66) supports this concept, since in this molecule the boron atom has no vacant p-orbital (sp^3hybridized boron).

In the PMR spectrum of IV (60 and 100 MHz, 4% by weight in CCl_4) the signals arising from the heterocyclic protons are found at lower field (8.22 and 7.72 ppm downfield from tetramethylsilane) than would be expected for an olefinic boron compound. In view of the values

TABLE 2

PMR Data of

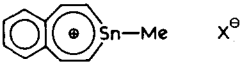


Compound		δH_a*	δH_b*	$J(H_a-H_b)$**	Ref.
$(CH_2=CH)_4Sn$	XII	6.1	6.3	13.2	12
	V	7.50	6.32	14	7
$(CH_2=CH)_3B$	XIII	~6.55		-	12
	VII	7.18	6.75	13	2
	IV	8.22	7.72	14	-
	IX	7.05	6.36	13.5	-
	XIV	6.33	5.53	-	2
	XV	~7.2	5.94	-	2

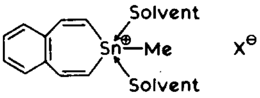
* ppm downfield from tetramethylsilane ** Hz

observed for V, VII, XII and XIII (Table 2) values of 7.8 and 6.9 ppm would seem to be a reasonable estimate for the chemical shifts of these protons if IV were olefinic. The shift to lower field of 0.4-0.8 ppm is in accord with the occurrence of a ring current, which can be sustained only if the boron p_z-orbital participates in the π-electronic system. This phenomenon is further substantiated by the PMR spectrum of IX showing signals due to the olefinic protons at 7.05 and 6.36 ppm. Of course, it must be expected that in the amine complex both protons will occur at higher field as a result of the larger electron density on the heterocycle. However, the shifts observed (1.15-1.35 ppm) are larger than those observed in similar compounds (0.4-0.9 ppm, compare XIV and XV, Table 2).

Attempts to demonstrate the occurrence of an aromatic benzo-stannatropylium ion (XVI) failed. Probably a structure involving sp^3d (XVII) instead of sp^2 hybridization of the tin atom is preferred.



XVI, $X^{\ominus}=Cl^{\ominus}$, $ClO_4^{\ominus}$, $BF_4^{\ominus}$



XVII

A full account of this work will be given elsewhere.

Acknowledgement

The authors are indebted to Mr.H.A.Budding for very able experimental assistence.

References

1. G.Brieger, Diss.Abstr. 22, 1824 (1961)
2. D.Sheehan, Ph.D.Thesis, Yale University, 1964.
3. P.K.Shenoy, Diss.Abstr. 26, 6381 (1966)
4. E.E.van Tamelen, G.Brieger and H.G.Untch, Tetrahedron Letters 1960, No. 8, 14.
5. A.J.Leusink, J.G.Noltes, H.A.Budding and G.J.M.van der Kerk, Rec.Trav.Chim. 83, 1036 (1964)
6. C.D.Good and D.M.Ritter, J.Am.Chem.Soc. 84, 1162 (1962)
7. A.J.Leusink, unpublished results.
8. J.Dale and A.J.Hubert, J.Chem.Soc. 1963, 5475.
9. C.A.Coulson, Proc.Phys.Soc. A 65, 933 (1952)
10. G.Naville, H.Strauss and E.Heilbronner, Helv.Chim.Acta 43, 1221 (1960)
11. D.J.Bertelli and Ching Ching Ong, J.Am.Chem.Soc. 87, 3719 (1965)
12. M.L.Maddox, S.L.Stafford and H.D.Kaesz, Adv. in Organometal.Chem. 3, 1 (1965)