J. Chem. Research (S),
1999, 264–265†

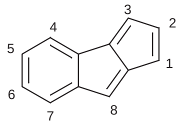
8-Mesityl-8-borafluorazene: A BN-heterocyclic Benzopentalene†

Karsten Albrecht and Dieter E. Kaufmann*

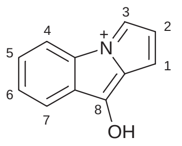
*Institut für Organische Chemie, Technische Universität Clausthal, Leibnizstr. 6, 38678
Clausthal-Zellerfeld, Germany*

8-Mesityl-8-borafluorazene, a formally anti-aromatic benzopentalene, is prepared by cyclization of 2,2′-dilithio-1-phenylpyrrole with dimethoxymesitylborane.

Boron containing heterocyles which are isoelectronic and isolobal to known aromatic carbon cycles play an increasingly important role as ligands in organometallic chemistry, *i.e.*, those replacing the cyclopentadienide anion, the benzene ring or the tropylium ion.[1] Furthermore, much attention has been focused on pyrrolo- or thieno-borepines which are isoelectronic to the 10π electron system azulene.[2] However, with the exception of boroles,[3] only little is known about anti-aromatic boron containing heterocycles. The parent carbobicyclic anti-aromatic 8π electron pentalene has been detected in an argon matrix very recently,[4] whereas the 12π anti-aromatic benzopentalene **1** could be characterized by NMR spectroscopy at low temperatures.[5] Early studies on the existence of a nitrogen containing hetero benzopentalene, the protonated fluorazone **2**, also indicate its anti-aromatic character.[6] Consequently, the combination of nitrogen and boron within the benzopentalene skeleton should lead to an uncharged, anti-aromatic heterocycle **3**. We now report on the synthesis of the first 8-borafluorazene derivative **3a** (R = mesityl) and *ab initio* calculations for the parent compound **3b** (R = H).



1



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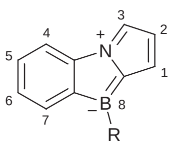
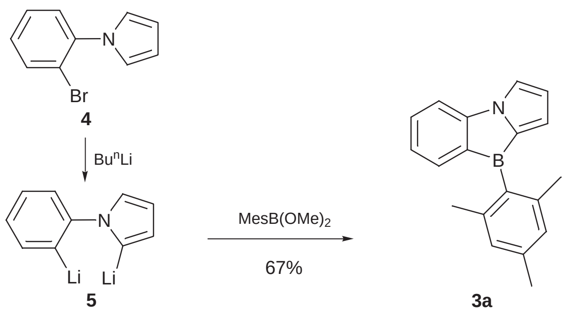


3

Experimentally, treatment of 1-(2′-bromophenyl)pyrrole **4** with *n*-butyllithium leads to 2,2′-dilithio-1-phenylpyrrole **5**.[7] Subsequent reaction with dimethoxymesitylborane **6** gives **3a** accompanied by complexes of **3a** with various nucleophiles (Scheme 1). Purification could be achieved by distillation of the mixture of products at 140 °C in high vacuum to give **3a** as a yellow air and moisture sensitive oil which becomes semi-solid on standing.



Scheme 1

In order to evaluate whether **3** can be best described as a tricyclic phenylpyrrole bridged by a boron atom **3bI** or by the conjugated anti-aromatic benzopentalene type structure **3bII**, we carried out spectroscopic studies for **3a** and *ab initio* calculations for **1**, **2** and **3b**. Systematic studies by Wrackmeyer and Nöth on boron substituted five-membered heterocycles based on NMR measurements suggested an intramolecular interaction between boron and the donor atom *via* the aromatic ring.[8] The ^{11}B NMR chemical shift of **3a** in benzene (δ58.4) excludes intermolecular donor–acceptor complexes and is in the same area as pentaphenylborole (δ55).[3b,c] However, the ^{11}B NMR chemical shifts of triorganoboranes as well as of zwitterionic type structures are in the range of δ50–60.[9] A bathochromic shift in the UV spectra should be expected for the pentalene type structure **3a**. In fact, **3a** shows maxima of absorption at 226, 265, 328 and 410 nm compared to only two maxima at 226 and 322 nm for dimesityl(2-pyrrolyl)borane.[10]

Additionally, we carried out *ab initio* calculations for **1**, **2** and **3b** at high level of theory including electron correlation.[11] All geometries were optimized at C_s symmetry and confirmed to be minima on the potential energy surface by vibrational analysis. The bond distances in **1**, **2** and **3b** are summarized in Table 1. The alternation between single and double bond, *i.e.*, 1.36 and 1.49 Å is expected, as has been calculated for the parent pentalene.[4] By contrast, the C–C bond distances within the pyrrole ring of **2** and **3b** are very similar at about 1.40 Å, which indicates strong conjugation. In particular, the C(3)–N(3a) as well as the $B_{(8)}-C_{(8a)}$ distance are significantly shortened to 1.34 Å compared to a single bond (1.52 Å), whereas the $N_{(3a)}-C_{(3b)}$, $C_{(8a)}-N_{(3a)}$ and $C_{(7a)}-B_{(8)}$ distances are lengthened almost to a normal single bond length, suggesting a partial contribution of structure type **3bII**.

Table 1 Selected bond distances (Å) for **1**, **2**, and **3b** fully optimized at B3LYP/6-31G*[a]

	1	**2**	**3b**
C(1)–C(2)	1.36	1.38	1.40
C(2)–C(3)	1.49	1.41	1.39
C(3)–C(3a)	1.36		
C(3)–N(3a)		1.34	1.35
C(3a)–C(3b)	1.47		
N(3a)–C(3b)		1.42	1.41
C(7a)–C(8)	1.48	1.44	
C(7a)–B(8)			1.56
C(8)–C(8a)	1.36	1.38	
B(8)–C(8a)			1.52
C(8a)–C(1)	1.47	1.42	1.40
C(8a)–C(3a)	1.47		
C(8a)–N(3a)		1.40	1.40

[a] Calculated bond distances (Å) for reference molecules fully optimized at B3LYP/6-31G*: $H_2C=CH_2$ 1.33, H_3C-CH_3 1.49, $HN=CH_2$ 1.28, H_2N-CH_3 1.46, $HB=CH_2$ 1.39, H_2B-CH_3 1.56.

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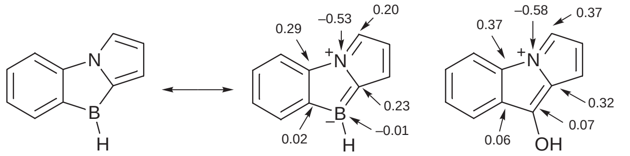
* To receive any correspondence.

† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.



I II 2
3b

Fig 1 Mullikan charges with charges summed into heavy atoms

Selected Mullikan charge distributions in **2** and **3b** are shown in Fig 1. Surprisingly, in both structures the nitrogen atom is negatively charged, and the positive charge is mostly located at the neighbouring quaternary carbon atoms C(3), C(3b) and C(8a).

In conclusion, the calculated bond distances and charge distributions as well as the spectroscopic data suggest that the benzopentalene type structure **II** is participating in the novel 8-borafluorazene **3** and that therefore an electron delocalization *via* the boron atom is a possible description.

We gratefully acknowledge the support of this work by the *Fonds der Chemischen Industrie*. We are indebted to Dr G. Remberg (Universität Göttingen) for high-resolution MS measurements.

Experimental

To 1.34 g (6.0 mmol) of 1-(2′-bromophenyl)pyrrole **4** in 20 ml diethyl ether, 7.8 ml (12.6 mmol) of a 1.6 M solution of Bu^{n}Li in hexane were added at 0 °C. After stirring for 2 h, 1.16 g (6.0 mmol) of dimethoxymesitylborane **6** were added and the resulting solution was stirred at room temperature for 12 h. Afterwards, the mixture was evaporated to dryness, the residue washed with 10 ml hexane and dissolved in 30 ml diethyl ether. The solution was separated from the precipitated LiOMe and evaporated to dryness. Purification was achieved by distillation at 140 °C (10^{-5} Torr) to give 1.1 g (67%) **3a** as a yellow oil which becomes semi-solid after standing without change of the spectroscopical data. δ_H (200 MHz, C_6D_6): 2.22 (s, 3H, $C^{8'}H$), 2.28 (s, 6H, $C^{7'}$, $C^{9'}H$), 6.04 (dd, $^3J = 3.5$, $^3J = 2.2$ Hz, 1H, C^2H), 6.47 (ddd, $^3J = 7.5$, $^4J = 1.5$, $^5J = 0.8$ Hz, 1H, C^4H), 6.63 (dd, $^3J = 2.2$, $^4J = 1.0$ Hz, 1H, C^3H), 6.66–6.73 (m, 2H, C^1H, C^6H), 6.92 (ddd, $^3J = 7.5$, $^3J = 7.5$, $^4J = 1.5$ Hz, 1H, C^5H), 7.16 (s, 2H, $C^{3'}H$, $C^{5'}H$), 7.22 (ddd, $^3J = 7.5$, $^4J = 1.5$, $^5J = 0.8$ Hz, 1H, $C^{7'}H$). δ_C (100.6 MHz, C_6D_6), 21.7 ($C^{8'}$), 23.5 ($C^{7'}$, $C^{9'}$), 110.5 (C^4), 116.6 (C^2), 122.9 (C^3), 125.5 (C^6), 127.7 (C^1), 128.2 ($C^{3'}$, $C^{5'}$), 134.2 (C^5), 135.3 (C^7), 136.2 (br, $C^{1'}$), 137.9 (br, C^{7a}), 138.7 ($C^{4'}$), 140.0 ($C^{2'}$, $C^{6'}$), 142.5 (br, C^{8a}), 151.6 (C^{3b}). δ_B(128.4 MHz, C_6D_6) 58.4. UV (hexane): $\lambda_{max}(\log\varepsilon) = 226$ nm (4.518), 265 (4.531), 328 (4.548), 410 (3.562). MS (70 eV); *m/z* (%): 271 (100) [M$^+$], 256 (70), 161 (15), 105 (10). HRMS (calc. and found): 271.1532.

Received, 28th September 1998; Accepted, 13th January 1999
Paper E/8/07519K

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