Generation of iodobenzoborirene, a boraaromatic cyclopropabenzene derivative†

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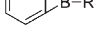
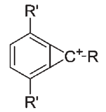
Iodobenzoborirene is obtained photochemically (λ = 308 nm) from diiodophenylborane by elimination of HI in solid argon at 10 K.

Two fundamental principles of chemistry, aromaticity and strain, are closely intertwined in the cyclopropabenzenes **1**.[1] Derivatives of **1** with a heteroatom replacing the methylene bridge in the three-membered ring have been postulated (BD,[2] NH,[3]) or isolated (SiR_2,[4] GeR_2,[5] S,[6] and Se[6]). The boron derivative, benzoborirene **2**, is of particular interest: the BH unit allows delocalization of the six π electrons over the entire molecule while the small boron atom should be well suited to bridge the formal benzyne triple bond. It has received some theoretical interest as a model system for studying the reversed Mills–Nixon effect.[7] Benzoborirene is isoelectronic to the cycloproparenyl cation **3a**, first observed as the 2,5-diphenyl-7-chloro substituted compound **3b** by Halton *et al.*,[8] without carrying its positive charge, thereby extending the idea of isoelectronic heteroaromatics (CH^+ *vs.* BH) to bicyclic systems.[9]

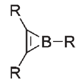
1



2a: R = H
2b: R = I



3a: R, R' = H
3b: R = Cl, R' = C_6H_5



4a: R = H
4b: R = C_6H_5

[D_5]-Benzoborirene [D_5]-**2a** has only been detected recently for the first time by time-of-flight MS as the product of the boron atom-[D_6]-benzene molecule crossed-beams reaction.[3]

The *monocyclic* borirenes **4** are highly reactive species: early experiments based on haloboration of alkynes and dehalogenation with active metals resulted in polymeric materials.[10] Photochemical trapping studies by Eisch *et al.* produced evidence for the intermediate existence of triphenylborirene **4b** in 1982.[11] Only a few years later several isolations of borirenes with bulky substituents had been described,[12–15] culminating in the report by Eisch *et al.* of the X-ray structure of trimesitylborirene.[16] More recently, the parent borirene **4a** was observed by matrix isolation[17] and by gas-phase crossed-beams experiments[18] as the product of reaction of boron atom with ethylene.

We here report on the first direct IR spectroscopic characterization of a benzoborirene derivative **2b** (R = I). In view of its expected reactivity, we generated **2b** in a solid argon matrix at 10 K from diiodophenylborane (**5**). The latter is readily available,[19] and its reported instability[20] towards irradiation encouraged us to investigate its photochemical reactivity. The IR spectrum of diiodophenylborane isolated in an argon matrix at 10 K is in very good agreement with the one previously reported for a neat sample at room temperature.[20] Upon irradiation with 308 nm light of a XeCl laser (1 Hz, ~150 mJ/pulse) a decrease of the signals of **5** is accompanied by the growing of IR bands (Fig. 1). Prolonged 308 nm irradiation does not result in complete disappearance of **5**, but the intensity of the signals of the photoproducts can be increased by increasing the amount of matrix isolated **5**, indicative of a photostationary equilibrium.

By comparison of the relative intensities from a number of experiments, one set of signals, with a strong absorption at 1450 cm^{-1}, a group of signals between 1080 and 1120 cm^{-1} with a band at 1080 cm^{-1} the strongest, and a number of weaker bands, is assigned to the major photoproduct. By comparison with B3LYP computations, this photoproduct is identified as iodobenzoborirene **2b**. The parent borirene **4** and the borirene radical, cyclo-$(CH)_2B$, have intensive ring stretching modes at around 1175 cm^{-1},[17] and benzannelation is red-shifting this most intense mode of the system to about 1080 cm^{-1}. An additional band at 2159 cm^{-1} grows at the same rate as absorptions assigned to **2b**, which upon careful annealing to 20–30 K shifts by 27 cm^{-1} to 2186 cm^{-1}. These absorptions are assigned to HI, which is known

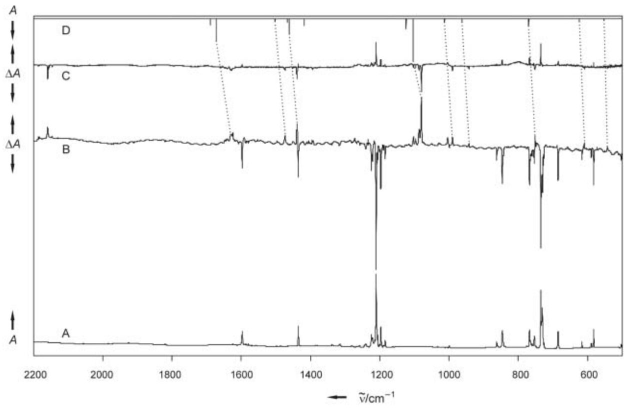


Fig. 1 (A) IR spectrum of diiodophenylborane (**5**) isolated in solid argon at 10 K; (B) difference spectrum obtained after 308-nm-photolysis of **5** (bands pointing downwards decrease, bands pointing upwards appear upon irradiation); (C) difference spectrum obtained after subsequent 254-nm irradiation; (D) IR spectrum computed at the B3LYP/6-311 + G** level of theory for iodobenzoborirene (**2b**) with natural boron composition.

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† Electronic supplementary information (ESI) available: experimental and computational details, computed structures of **2a**, **2b**, and IR spectral data of **2b**. See http://www.rsc.org/suppdata/cc/b4/b419415b/

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to interact with π systems resulting in a pronounced red-shift of the ν(HI) vibration from the 2227 cm^{-1} gas-phase value.[21]

Annealing also changes the relative intensities of the group of absorptions observed in the 1080–1100 cm^{-1} range possibly arising from disturbances due to HI molecules lying nearby. The second most intense signal of **2b**, a C–C stretching vibration involving the three-membered ring, is computed at 1673 cm^{-1}, but only a broad band (centered at 1632 cm^{-1}) can be observed. No reliable integration is possible, because of overlap with the water monomer at 1624 cm^{-1}.

Monochromatic 254-nm-irradiation of the matrix after 308-nm-irradiation completely bleaches the newly formed signals within several minutes and results in formation of **5**. It is well known that HI can be cleaved into the atoms by 254 nm irradiation.[22] We conclude that the observed photochemistry is due to the equilibrium:

Reversible photochemical reactions can also be observed by UV spectroscopy. The UV/vis spectrum of **5** is characterized by three major absorptions at 301, 274, 222 nm in good agreement with computation (304, 287, and 219 nm at B3LYP/cc-pVTZ). These absorptions decrease upon 308-nm-irradiation and subsequently increase in intensity on short wavelength (λ = 254 nm) irradiation. No new absorptions due to **2b** can be detected. According to the DFT computations, the strongest absorption of **2b** (265 nm) overlaps with the 274-nm-band of **5**, but only has about half of its oscillator strength.

The iodo substituent in **2b** is found to destabilize the benzoborirene ring system by 2.3 kcal mol^{-1} [CCSD(T)/cc-pVTZ-(PP) energies, see ESI†] compared to **2a** according to equation (1).[9c] Nonetheless, very similar geometries are obtained for **2a** and **2b**, with the largest deviations being less than 0.01 Å.

$$\mathbf{2b} + BH_3 \rightarrow \mathbf{2a} + BH_2I \qquad (1)$$

Borirene **4a** is highly strained, 69 kcal mol^{-1}, according to the computational analysis of Budzelaar *et al.*, but it enjoys a large resonance energy of 48 kcal mol^{-1}.[9c] Equation (2) measures the strain that results from the fusion of **4a** and benzene to be 14.3 kcal mol^{-1}.

$$\mathbf{2a} + H_2C{=}CH_2 \rightarrow \text{benzene} + \mathbf{4a} \qquad (2)$$

Similar values, 15 (experiment)[23] and 16–18 (theory)[24] kcal mol^{-1}, have been derived for the strain in **1** due to the fusion of benzene and cyclopropane.

In summary, we could show that the benzoborirene system forms upon 308-nm-irradiation of **5** in an argon matrix at 10 K. The strain of **2a** is similar to that of cyclopropabenzene **1**, while the iodo substituent causes some additional destabilization.

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