Chem. Soc. **2001**, *123*, 5268; f) W. Li, X. Zhang, *J. Org. Chem.* **2000**, *65*, 5871; g) Y.-Y. Yan, T. V. Rajanbabu, *Org. Lett.* **2000**, *2*, 4137.

[6] a) F. Guillen, J.-C. Fiaud, *Tetrahedron Lett.* **1999**, *40*, 2939; b) C. Claver, E. Fernandez, A. Gillon, K. Heslop, D. J. Hyett, A. Martorell, A. G. Orpen, P. G. Pringle, *Chem. Commun.* **2000**, 961; c) M. T. Reetz, G. Mehler, *Angew. Chem.* **2000**, *112*, 4047; *Angew. Chem. Int. Ed.* **2000**, *39*, 3889; d) M. van den Berg, A. J. Minnaard, E. P. Schudde, J. van Esch, A. H. M. de Vries, J. G. de Vries, B. L. Feringa, *J. Am. Chem. Soc.* **2000**, *122*, 11539; e) I. V. Komarov, A. Börner, *Angew. Chem.* **2001**, *113*, 1237; *Angew. Chem. Int. Ed.* **2001**, *40*, 1197.

[7] V. B. Birman, A. L. Rheingold, K.-C. Lam, *Tetrahedron: Asymmetry* **1999**, *10*, 125.

[8] D. J. Cram, R. C. Helgeson, S. C. Peacock, L. J. Kaplan, L. A. Domeier, P. Moreau, K. Koga, J. M. Mayer, Y. Chao, M. G. Siegel, D. H. Hoffman, G. D. Y. Sogah, *J. Org. Chem.* **1978**, *43*, 1930.

[9] Orpen and Pringle et al. have reported the X-ray structure of a Pt complex of a monodentate biarylphosphonite (see ref. [6b]).

[10] Crystal data for [Rh(cod){(*S*)-**1a**}$_2$](OH)·CH_2Cl_2: $C_{47}H_{55}N_2Cl_2O_5P_2Rh$, $M_r = 963.68$, $T = 293$ K, tetragonal, space group $P4_12_12$, $a = 10.495(2)$, $b = 10.495(2)$, $c = 42.528(12)$ Å, V4684.1(19) Å^3, $Z = 4$, 4099 unique reflections, $R1 = 0.0519$. CCDC 179716 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[11] The salt of the Rh^I complex obtained as a single crystal was [Rh(cod){(*S*)-**1a**}$_2$](OH), instead of expected [Rh(cod){(*S*)-**1a**}$_2$]BF_4. This might be because the [Rh(cod)$_2$]BF_4 used in the preparation of catalyst contained water of crystallization [Aldrich 33498-7 (2000–2001)]. The single crystal of [Rh(cod){(*S*)-**1a**}$_2$](OH) was also tested in the catalytic hydrogenation of **4a**, and 97.6% *ee* (at 10°C) was obtained.

[12] a) B. D. Vineyard, W. S. Knowles, M. J. Sabacky, G. L. Bachman, D. J. Weinkauff, *J. Am. Chem. Soc.* **1977**, *99*, 5946; b) A. S. C. Chan, J. J. Pluth, J. Halpern, *Inorg. Chim. Acta*, **1979**, *37*, L477; c) A. S. C. Chan, J. J. Pluth, J. Halpern, *J. Am. Chem. Soc.* **1980**, *102*, 5952.

Gas-Phase Detection of the Elusive Benzoborirene Molecule**

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The cyclic delocalization of π electrons, responsible for the important concepts of aromaticity and antiaromaticity,[1] has been fascinating ever since the discovery of benzene by Michael Faraday almost 200 years ago.[2] The π system of benzene can be ported to the five- and seven-membered rings by removing or introducing a CH$^+$ unit to result in the cyclopentadienyl anion ($C_5H_5^-$) and tropylium cation ($C_7H_7^+$ (**1a**),[3] Scheme 1), respectively. Volpin et al. suggested that it is possible to generate heteroaromatic homologues of aromatic hydrocarbons by substitution of a CH$^+$ unit by an isoelectronic BH group.[4] Borirene **2b**[5] and 1*H*-borepin **1b**,[6] first synthesized in a low-temperature argon matrix and in solution, thus resemble the 2π-electron cyclopropenylium **2a**[7] and the 6π-electron tropylium cation **1a**, respectively (Scheme 1). Extension of the 6π-electron system onto a second ring results in benzocyclopropenylium **3a** and benzoborirene **3b** as the simplest systems (Scheme 1). Although studied theoretically,[8] **3a** and **3b** have not yet been observed experimentally.

benzene
1a: X = CH$^+$
1b: X = BH
2a: X = CH$^+$
2b: X = BH
3a: X = CH$^+$
3b: X = BH

Scheme 1. Structures of (potentially) π aromatic compounds.

How could the elusive benzoborirene **3b** be "made" in the laboratory? Ground-state boron and carbon atoms are known to react with a variety of unsaturated systems in crossed-beam experiments by an atom addition–hydrogen elimination mechanism.[9, 10] This protocol was used very recently to produce **2b** from atomic boron and ethene in the gas phase through reaction (1).[9a] Here we extend this novel concept and report on the formation of the hitherto unknown benzoborirene **3b**, the isoelectronic boron analogue of the elusive **3a**, through the atom–molecule reaction (2).

$$ {}^{11}B + C_2H_4 \rightarrow \underset{(\mathbf{2b})}{{}^{11}BC_2H_3} + H \qquad (1)$$

$$ {}^{11}B + C_6D_6 \rightarrow \underset{([D5]\text{-}\mathbf{3b})}{{}^{11}BC_6D_5} + D \qquad (2)$$

This reaction was studied in the gas phase at the molecular level by employing a crossed molecular beam setup.[11] We prepared a pulsed boron beam by laser ablation of a boron rod and by entraining the ablated atoms in helium gas; this beam perpendicularly crossed a beam of benzene seeded in argon in a scattering chamber at a collision energy of (23.1 ± 0.8) kJ mol^{-1}. The reaction products were detected with a rotatable quadrupole mass spectrometer after electron ionization (EI); the ionizer was suited in an ultra-high-vacuum chamber. Velocity distributions of the product were collected with the time-of-flight (TOF) technique, that is, recording the arrival time of a distinct mass-to-charge ratio (*m*/*z*) of the ionized product, at different scattering angles (Figure 1).[11] Integrating these TOF spectra leads to the laboratory angular distribution.

TOF spectra were recorded at *m*/*z* 93 ($^{11}BC_6D_5^+$) and 91 ($^{11}BC_6D_4^+$). At both mass-to-charge ratios, superimposable spectra were obtained suggesting that the signal at *m*/*z* 91 originates from cracking of the parent molecule (*m*/*z* 93) in

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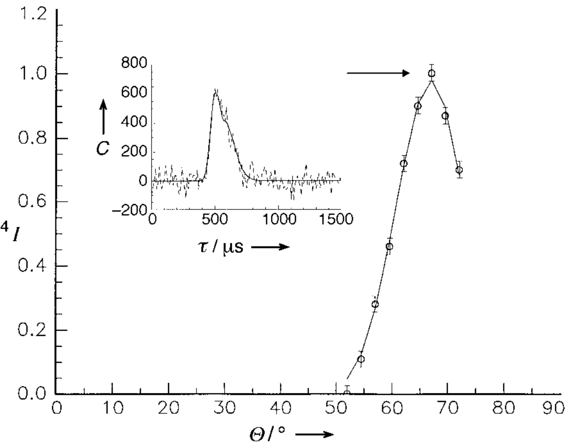


Figure 1. The laboratory angular distribution I at m/z 93 of the $^{11}BC_6D_5$ product from the reaction of atomic boron with [D$_6$]benzene; the direction of the boron beam is defined as 0°, that of the benzene beam as 90°. The solid line represents the angular distribution obtained from the best-fit center-of-mass angular and translational energy distributions, the open circles the experimental data (I: integrated counts; Φ: laboratory angle; τ: time of flight; C: counts). The time-of-flight spectrum recorded at the center-of-mass angle is shown as an inset (dashed line: experimental data; solid line: best fit from the center-of-mass functions).

the ionizer. Therefore, in accord with Equation (2), a molecule with the gross formula $^{11}BC_6D_5$ is formed.[12] However, our ultimate goal is not only to assign the chemical formula of the reaction product, but to also elucidate the chemical structure of this organoboron species. Therefore it is necessary to extract information on the chemical dynamics and to unravel the underlying reaction mechanism from the experimental data. We achieved this by fitting the TOF spectra and the laboratory angular distribution of the $^{11}BC_6D_5$ product at m/z 93. This procedure yields two "best-fit" functions: the center-of-mass translational energy flux distribution $P(E)$ and the angular flux distribution $T(\theta)$ of the products, which are both displayed in Figure 2.[13]

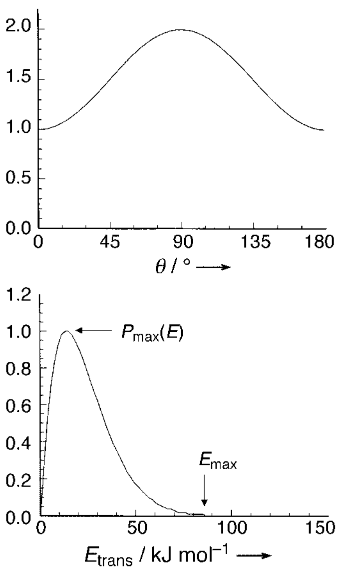
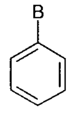


Figure 2. Best fit center-of-mass angular (T, left) and translational energy (P, right) flux distributions of the reaction of atomic boron with [D$_6$]benzene to form benzoborirene plus atomic deuterium. θ: center-of-mass angle; E_{trans}: translational energy.

The maximum translational energy ($E_{max} = 80-90\ kJ\,mol^{-1}$) can be used to identify the nature of the products. Here, E_{max} is simply the sum of the reaction exoergicity plus the collision energy. Therefore, if we subtract the latter from E_{max}, the exoergicity of reaction (1) is calculated to be (62 ± 5) kJ mol^{-1}. The assignment of the $^{11}BC_6D_5$ product is possible by comparing the experimentally determined reaction exoergicity with theoretical data obtained from electronic structure computations for the conceivable reaction products [D$_5$]-**3b**, [D$_5$]-**4**, and [D$_5$]-**5**. Geometries were fully optimized with Gaussian 98[14a] utilizing Becke's[14b,c] three-parameter hybrid functional in conjunction with the correlation functional of Lee et al.[14d] and the 6-311 + G(d,p) basis set [B3LYP/6-311 + G(d,p)]. Second derivatives were obtained analytically and used to compute unscaled harmonic vibrational frequencies and zero-point vibrational energies for the deuterated species. Energies were refined by single-point coupled-cluster computations involving single and double excitations, as well as a perturbative estimate of triple excitations[14e] in conjunction with Dunning's[14f] correlation-consistent triple-ζ basis set [CCSD(T)/cc-pVTZ] using the MOLPRO program.[14g–i]



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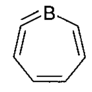

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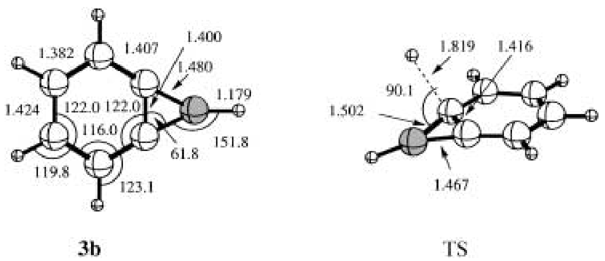
We found [D$_5$]-**3b** to be the most stable isomer at the CCSD(T)/cc-pVTZ//B3LYP/6-311 + G(d,p) level of theory, while [D$_5$]-**4** and [D$_5$]-**5** are less stable by 131 and 176 kJ mol^{-1}, respectively. Good agreement between the experimental [(62 ± 5) kJ mol^{-1}] and theoretical (69.7 kJ mol^{-1}) reaction energies is reached only for the formation of [D$_5$]-**3b**, while the reactions yielding [D$_5$]-**4** and [D$_5$]-**5** are strongly endoergic by 61.5 and 106.3 kJ mol^{-1}, respectively. Therefore, taking into account the collision energy of 23.1 kJ mol^{-1}, formation of [D$_5$]-**4** and [D$_5$]-**5** is not feasible under our experimental conditions. Thus, we conclude that benzoborirene [D$_5$]-**3b** is the sole reaction product at m/z 93. This is the very first time that a boron-bearing aromatic, bicyclic molecule has been synthesized in which the six π electrons can be delocalized over seven atoms. The geometry of [D$_5$]-**3b** (Figure 3) is very similar to those obtained in previous lower-level calculations.[8d–f] The nucleus-independent chemical shifts (NICS)[15a] were computed 1 Å above the ring centers,[15b–d] and indicate that the aromatic character (based on magnetic criteria) of the six- and three-membered rings [NICS(1.0) values are −9.5 and −15.3 ppm, respectively] is slightly attenuated and intensified, respectively, compared to that of benzene [NICS(1.0) = −10.2] and borirene [NICS(1.0) = −14.4].



3b TS

Figure 3. Selected bond lengths [Å] and bond angles [°] for **3b** and the transition state TS as computed at the B3LYP/6-311 + G(d,p) level of theory.

Finally, we would like to discuss the reaction mechanism and investigate the angular flux distribution $T(\theta)$ closer. The latter shows a symmetric profile around 90° (see Figure 2); this indicates that the intensity of the flux distribution is the same at a center-of-mass angle θ and at the angle $180^\circ - \theta$. This symmetric shape is characteristic for a bimolecular gas-phase reaction which goes through a reactive intermediate having a lifetime larger than its rotation period.[11] This intermediate is a $^{11}BC_6D_6$ isomer. It is known from reaction (1) that an initial boron addition to the π system is followed by a deuterium migration before the accumulated reaction energy is used for hydrogen ejection.[9] A feasible reaction path also exists on the C_6D_6B potential energy surface which involves, according to CCSD(T)/cc-pVTZ//B3LYP/6-311 + G(d,p) investigations, addition of a boron atom to benzene to yield C_6D_6–B ($-34.6\ \mathrm{kJ\,mol^{-1}}$, 2A) and subsequent [1,2]-D shift to C_6D_5–BD ($-253.6\ \mathrm{kJ\,mol^{-1}}$, 2A′) with a barrier ($-0.6\ \mathrm{kJ\,mol^{-1}}$ with respect to the reactants) well below the available collision energy of $+23\ \mathrm{kJ\,mol^{-1}}$. The actual shape of the function $T(\theta)$ reflects the direction in which the hydrogen atom leaves the fragmenting intermediate to form the $^{11}BC_6D_5$ product: the peak at 90° is indicative of emission of a deuterium atom perpendicular to the molecular plane of the $^{11}BC_6D_5$ moiety.[11] The translational energy flux distribution $P(E)$ (see Figure 2) provides two additional sets of information on the ejection of the deuterium atom. First, the distribution maximum $P_{\max}(E)$ of $10-20\ \mathrm{kJ\,mol^{-1}}$ can give the order of magnitude of the barrier height in the exit channel.[11] This data suggests a significant geometry and electron density change from the decomposing $^{11}BC_6D_6$ intermediate to the products. In other words, the reversed reaction—the addition of a deuterium atom to the $^{11}BC_6D_5$ molecule—has an entrance barrier of this order of magnitude. These experimental conclusions are confirmed by electronic structure computations. We find that the barrier for the addition of a deuterium atom to one of the bridgehead carbon atoms of [D_5]-**3b** via the transition state TS has a barrier of $27.4\ \mathrm{kJ\,mol^{-1}}$. The attacking D atom is oriented roughly perpendicularly to the molecular plane of [D_5]-**3b** in this transition state (Figure 3).

In summary, our study identified for the first time the benzoborirene molecule in the gas phase by a combination of crossed-beam experiments and high-level electronic structure computations. It seems reasonable to assume that the versatile boron–hydrogen exchange reaction can be employed to synthesize even more complex heteroaromatic polycyclic boron-bearing molecules. For instance, the reaction of boron atoms with naphthalene should likely yield a tricyclic heteroaromatic molecule with ten π electrons via the boron versus hydrogen exchange channel.

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[1] a) P. von R. Schleyer, *Chem. Rev.* **2001**, *101*, 1115; b) for a recent compilation of reviews on aromaticity, see: *Chem. Rev.* **2001**, *101* (5).

[2] M. Faraday, *Philos. Trans. R. Soc. London* **1825**, 440.

[3] a) W. von E. Doering, L. H. Knox, *J. Am. Chem. Soc.* **1954**, *76*, 3203; b) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, D. L. Pearson, *J. Am. Chem. Soc.* **1957**, *79*, 4557; c) K. M. Harmon in *Carbonium Ions, Vol. 4* (Eds.: G. A. Olah, P. von R. Schleyer), Wiley, New York, **1973**, pp. 1579–1641.

[4] M. E. Volpin, Y. D. Koreshkov, V. G. Dulova, D. N. Kursanov, *Tetrahedron* **1962**, *18*, 107.

[5] L. Andrews, D. V. Lanzisera, P. Hassanzadeh, Y. Hannachi, *J. Phys. Chem. A* **1998**, *102*, 3259.

[6] A. J. Ashe, J. W. Kampf, Y. Nakadaira, J. M. Pace, *Angew. Chem.* **1992**, *104*, 1267; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1255.

[7] R. Breslow, J. T. Groves, G. Ryan, *J. Am. Chem. Soc.* **1967**, *89*, 5048.

[8] a) B. Halton, M. P. Halton, *Tetrahedron* **1973**, *29*, 1717; b) O. Sinanoglu, *Tetrahedron Lett.* **1988**, *29*, 889; c) R. Benassi, S. Ianelli, M. Nardelli, F. Taddei, *J. Chem. Soc. Perkin Trans. 2* **1991**, 1381; d) Z. B. Maksic, M. Eckert-Maksic, K.-H. Pfeifer, *J. Mol. Struct.* **1993**, *300*, 445; e) M. Eckert-Maksic, Z. Glasovac, Z. B. Maksic, I. Zrinski, *Theochem* **1996**, *366*, 173; f) A. Stanger, *J. Am. Chem. Soc.* **1998**, *120*, 12034.

[9] a) N. Balucani, O. Asvany, Y. T. Lee, R. I. Kaiser, N. Galland, Y. Hannachi, *J. Am. Chem. Soc.* **2000**, *122*, 11234; b) N. Balucani, O. Asvany, Y. T. Lee, R. I. Kaiser, N. Galland, M. T. Rayez, Y. Hannachi, *J. Comput. Chem.* **2001**, *22*, 1359.

[10] a) R. I. Kaiser, C. Ochsenfeld, M. Head-Gordon, Y. T. Lee, A. G. Suits, *Science* **1996**, *274*, 1508; b) R. I. Kaiser, I. Hahndorf, L. C. L. Huang, Y. T. Lee, H. F. Bettinger, P. von R. Schleyer, P. R. Schreiner, H. F. Schaefer III, *J. Chem. Phys.* **1999**, *110*, 6091.

[11] R. I. Kaiser, N. Balucani, *Acc. Chem. Res.* **2001**, *34*, 699.

[12] The following data of the integrated TOF spectra at distinct m/z ratios were derived at an electron energy of 200 eV: m/z 95: <0.01; m/z 94: 0.07–0.08; m/z 93: 1.0; m/z 92: 0.18–0.23; m/z 91: 1.3–1.4.

[13] R. I. Kaiser, C. Ochsenfeld, D. Stranges, M. Head-Gordon, Y. T. Lee, *Faraday Discuss.* **1998**, *109*, 183.

[14] a) Gaussian 98 (Revision A.7): M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; c) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623; d) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785; e) K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479; f) T. H. Dunning, *J. Chem. Phys.* **1989**, *90*, 1007; g) C. Hampel, K. Peterson, H.-J. Werner, *Chem. Phys. Lett.* **1992**, *190*, 1; h) P. J. Knowles, C. Hampel, H.-J. Werner, *J. Chem. Phys.* **1993**, *99*, 5129; i) MOLPRO is a package of ab initio programs written by H.-J. Werner and P. J. Knowles; Version 2000.1 was used.

[15] a) P. von R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317; b) P. von R. Schleyer, H. Jiao, N. J. R. van Eikema Hommes, V. G. Malkin, O. L. Malkina, *J. Am. Chem. Soc.* **1997**, *119*, 12669; c) P. von R. Schleyer, M. Manoharan, Z.-X. Wang, B. Kiron, H. Jiao, R. Puchta, N. J. R. van Eikema Hommes, *Org. Lett.* **2001**, *3*, 2465; d) using the GIAO method (K. Wolinski, J. F. Hinton, P. Pulay, *J. Am. Chem. Soc.* **1990**, *112*, 8251) at the B3LYP/6-311 + G(d,p) level of theory.