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Synthesis and Structure of Borabenzene−4-Phenylpyridine, a Heterocyclic Analogue of *p*-Terphenyl

Shuang Qiao, Diego A. Hoic, and Gregory C. Fu*

Department of Chemistry, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139

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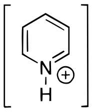
Summary: The synthesis and X-ray crystal structure of borabenzene−4-phenylpyridine is reported. This compound, which incorporates a pyridine, a benzene, and a borabenzene ring, is the first hetero-p-terphenyl analogue to be structurally characterized.

We recently reported the synthesis of 1*H*-boratabenzene,[1] the third member of the isoelectronic series, pyridinium ion (**1**), benzene (**2**), and 1*H*-boratabenzene (**3**).



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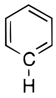

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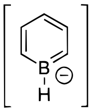

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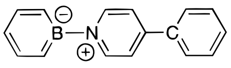


4

As part of our program in the development of borabenzene and boratabenzene chemistry,[1,2] we have undertaken the synthesis of borabenzene−4-phenylpyridine (**4**), an aesthetically pleasing, para-linked triaromatic compound which incorporates one unit of each of the first-row (hetero)cycles **1**−**3**. We anticipate that **4**, a zwitterionic analogue of *p*-terphenyl,[3,4] may possess interesting properties for materials science.[5] In this report, we describe a facile synthesis, as well as the crystal structure, of borabenzene−4-phenylpyridine. To the best of our knowledge, this is the first hetero-*p*-terphenyl analogue to be structurally characterized.[6,7]

Treatment of boracycle **5**[2a] with 4-phenylpyridine in CH_2Cl_2 at room temperature affords borabenzene−4-phenylpyridine (**4**) in 76% yield (eq 1). Whereas **4** is air-stable up to 150 °C as a crystalline orange solid, it is unstable to air in solution. The UV/vis spectrum of **4** reveals absorptions at 280 nm ($\epsilon = 2.0 \times 10^4$ M^{-1} cm^{-1}) and 484 nm ($\epsilon = 6.7 \times 10^3$ M^{-1} cm^{-1}), compared with 170−175 and 190 nm for *p*-terphenyl.[8]

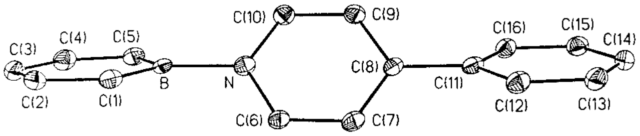
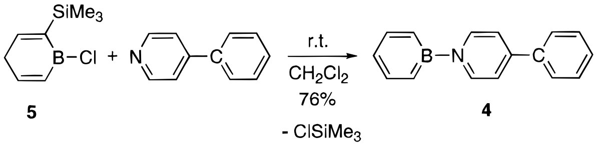


Figure 1. ORTEP illustration, with thermal ellipsoids drawn at the 35% probability level, of **4**. Bond distances: B−N 1.551(3) Å; C(8)−C(11) 1.480(3) Å; Torsion angles: borabenzene−pyridine 48.7°; pyridine−phenyl 42.7°.



(1)

A crystal suitable for X-ray diffraction was grown by diffusion of hexane into a CH_2Cl_2 solution of **4** at room temperature. The borabenzene ring and the phenyl ring are nearly coplanar (dihedral angle of 6°), with the central pyridine ring twisted by about 45° relative to each of the other rings (Figure 1; Table 1). In the case of *p*-terphenyl, crystallographic studies reveal a similar coplanar relationship between the remote rings, with the central ring twisted by about 15°.[4] The 49° dihedral angle between the borabenzene and pyridine rings of **4** compares with a 43° angle for borabenzene−pyridine, a hetero-biphenyl analogue.[7b] For compound **4**, the B−N and C8−C11 bond lengths are 1.551(3) and 1.480(3) Å, respectively, compared with a C−C(inter-ring) bond distance of 1.50 Å for *p*-terphenyl[4] and a B−N bond distance of 1.56 Å for borabenzene−pyridine.[7b]

Thus, we have synthesized and structurally characterized borabenzene−4-phenylpyridine, an analogue of *p*-terphenyl that incorporates three different first-row, six-membered aromatic rings: borabenzene, pyridine, and benzene. Future studies will focus on the properties of this compound and its derivatives.

Experimental Section

4-Phenylpyridine (Aldrich) was used as received. Dichloromethane was distilled from calcium hydride.

^1H and ^{13}C nuclear magnetic resonance spectra were recorded on a Varian XL-300 NMR spectrometer at ambient temperature. Infrared spectra were obtained on a Perkin-Elmer Series 1600 FT-IR spectrophotometer. High-resolution mass spectra were recorded on a Finnegan MAT System 8200

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[1] Hoic, D. A.; Davis, W. M.; Fu, G. C. *J. Am. Chem. Soc.* **1995**, *117*, 8480−8481.

[2] (a) Hoic, D. A.; Wolf, J. R.; Davis, W. M.; Fu, G. C. *Organometallics* **1996**, *15*, 1315−1318. (b) Qiao, S.; Hoic, D. A.; Fu, G. C. *J. Am. Chem. Soc.* **1996**, *118*, 6329−6330. (c) Hoic, D. A.; Davis, W. M.; Fu, G. C. *J. Am. Chem. Soc.* **1996**, *118*, 8176−8177.

[3] Thompson, Q. E. In *Kirk-Othmer Encyclopedia of Chemical Technology*; 4th Ed.; Wiley: New York, 1992; Vol. 4, pp 223−237.

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[5] For example, see: Abe, J.; Shirai, Y. *J. Am. Chem. Soc.* **1996**, *118*, 4705−4706.

[6] Based on a search of the Cambridge Crystallographic Data Base with the following constraints: three para-linked six-membered aromatic rings with hydrogens at the 14 non-biaryl positions; all ring atoms unspecified.

[7] For crystallographic studies of hetero-*bi*phenyl analogues, see the following. (a) Bipyridinium: Wang, B.-C.; Cordes, A. W. *Inorg. Chem.* **1970**, *9*, 1643−1650. (b) Borabenzene−pyridine: Boese, R.; Finke, N.; Henkelmann, J.; Maier, G.; Paetzold, P.; Reisenauer, H. P.; Schmid, G. *Chem. Ber.* **1985**, *118*, 1644−1654. (c) 1-(4-pyridyl)-pyridinium: Brencic, J. V.; Ceh, B.; Leban, I. *Z. Anorg. Allg. Chem.* **1988**, *565*, 163−170.

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Table 1. Crystallographic Data for Borabenzene−4-Phenylpyridine (4)

empirical formula	$C_{16}H_{14}BN$
fw	231.09
cryst color, habit	orange plate
cryst dimens (mm^3)	0.78 × 0.24 × 0.08
cryst system	monoclinic
space group	$P2_1/c$
a (Å)	7.04920(10)
b (Å)	16.4895(6)
c (Å)	10.4136(4)
β (deg)	95.672(2)
V (Å^3)	1204.53(7)
Z	4
ρ_{calc} (Mg/m^3)	1.274
radiation, monochromator	Mo Kα ($\lambda = 0.710\,69$ Å), graphite
temp (K)	153(2)
μ(Mo Kα) (cm^{-1})	0.073
diffractometer	Siemens SMART/CCD (3-circle, χ fixed at 54.78°)
scan type; limiting indices	ω; $-7 \leq h \leq 4$, $-18 \leq k \leq 17$, $-9 \leq l \leq 11$
θ range for collcn (deg)	2.32−23.30
tot. reflcns	4727
unique reflcns	1731 ($R_{int} = 0.0749$)
corrs	Lorentz−polarization; no abs
struct solution, refinement	direct methods, full-matrix least-squares on F^2
data/restraints/params	1730/0/220
R_1; wR_2	0.0544; 0.1323
goodness of fit	1.153
extinction coeff; largest peak, hole (e Å^{-3})	0.009(3); 0.204, −0.271
programs used	Siemens software package: SMART, SAINT, XPREP, SHELXTL 5.0

spectrometer. UV/vis spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer.

Borabenzene−4-Phenylpyridine (4). A solution of 4-phenylpyridine (0.51 g, 3.3 mmol) in 6 mL of CH_2Cl_2 was added slowly to boracycle **5**[2a] (0.67 g, 3.6 mmol) in 2 mL of CH_2Cl_2, resulting in the formation of a red precipitate. The reaction mixture was stirred at room temperature for 12 h. Evaporation of the solvent provided a red solid, which was washed with CH_2Cl_2, affording orange-red borabenzene−4-phenylpyridine (0.58 g, 76%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 9.03 (d, 2H, J = 6.6), 7.93 (d, 2H, J = 6.9), 7.80 (m, 2H), 7.59 (m, 3H), 7.41 (t, 2H, J = 8.4), 6.68 (d, 2H, J = 9.9), 6.53 (t, 1H, J = 7.2). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 152.9, 144.8, 135.8, 135.6, 131.7, 130.3, 127.9, 124.3, 119.6, 116.8. ^{11}B NMR (96 MHz, CD_2Cl_2): δ 32.8. IR (KBr): 2990, 1624, 1530, 1479, 1411, 1292, 1137, 846, 773, 723, 698 cm^{-1}. HRMS: Calcd for $C_{16}H_{14}NB$, m/e 231.1219, m/e found: 231.1218.

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Supporting Information Available: Crystal structure data, including tables of X-ray data, positional and thermal parameters, and bond distances and angles and ORTEP diagrams (12 pages). Ordering information is given on any current masthead page.

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