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Supporting Information

Two-Dimensional Hydrogen-Bonded Networks in Crystals of Diboronic Acids

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4,4'-Diphenylacetylenediboronic acid (4)

A solution of bis(4-bromophenyl)acetylene (1.02 g, 3.04 mmol)[1] was dissolved in dry THF (60 mL) and cooled to -78 °C under N_2. *n*-Butyllithium (4.3 mL, 1.5 M, 6.4 mmol) was then added dropwise, and the mixture was stirred under N_2 with continued cooling for 1 h. Triisopropyl borate (1.6 mL, 1.3 g, 6.9 mmol) was then added slowly. The resulting mixture was stirred at -78 °C for 1 hour and was then allowed to warm to 25 °C. After 1 h, the mixture was quenched with 1 M aqueous HCl and extracted with ether. The combined ether extracts were then extracted with 4 M aqueous NaOH. The aqueous extracts were acidified with 6 M aqueous HCl, and the resulting precipitate was collected by filtration and dried to give 4,4'-diphenylacetylenediboronic acid (**2**; 0.677 g, 2.55 mmol, 84%). The product was further purified by recrystallization from THF/hexane to give compound **4** as a colorless solid: m.p. > 250 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.52 (d, 4H, ^3J = 8.2 Hz), 7.83 (d, 4H, ^3J = 8.2 Hz), 8.18 (s, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 91.2, 124.5, 131.2, 135.2; HRMS (APCI) calcd for $C_{14}H_{12}B_2O_4$ + H *m/e* 267.09945, found 267.10026.

X-ray crystallographic studies

X-ray diffraction data were collected with Cu Kα radiation using a Bruker SMART 2000 CCD diffractometer. The structures were solved by direct methods using SHELXS-97 and refined with SHELXL-97.[2] All non-hydrogen atoms were refined anisotropically, except for disordered solvent molecules. Hydrogen atoms were placed in ideal positions and refined as riding atoms.

References

1 H. J. Barber and R. Slack, *J. Chem. Soc. Abstracts*, 1944, 612.

2 G. M. Sheldrick, in *SHELXS-97, Program for the Solution of Crystal Structures* and *SHELXL-97, Program for the Refinement of Crystal Structures*, Gottingen, 1997.