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Bis(pentafluorophenyl)borinic Acid: a Cyclic Trimer in the Solid State and a Monomer, with Hindered Rotation around the B−OH Bond, in Solution

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Summary: The title molecule in the solid state exists as a cyclic trimer, with B−O(H)−B bridges and a cyclohexane-like structure (C_2 twist-boat conformation); dissolution in toluene-d_8 affords the $B(C_6F_5)_2OH$ monomer, in which the low-temperature ^{19}F NMR data reveal restricted rotation of the OH substituent around the Ar_2B-OH bond ($E_a = 39$ kJ mol^{-1}), as a result of the partial double-bond character of this interaction.

The chemistry of bis(pentafluorophenyl)borinic acid, $(C_6F_5)_2B(OH)$ (**1**),[1] has been at present actively investigated, and several applications in catalysis and organic synthesis have been reported.[1−4] This is mainly attributable to some peculiar features of this molecule, where both Lewis and Brønsted acidic sites are simultaneously present, as well as a Lewis basic site (i.e. the nonbonding electrons on the oxygen substituent). A variety of intra- and intermolecular interactions could result from such multiplicity of active sites, and we report here on the cyclotrimerization of **1** in the solid state and its deoligomerization in solution, to give a monomer in which the pπ−pπ boron−oxygen interactions are strong enough to "freeze" the rotation around the B−OH bond.

Single-crystal X-ray analysis[5] revealed that, in the solid state, **1** exists as a cyclic trimer constituted of three $B(C_6F_5)_2OH$ monomers interconnected through B−O(H)−B bridges. The resulting structure resembles that of cyclohexane, but the $[(C_6F_5)_2BO(H)]_3$ hexagon has a C_2 twist-boat conformation (see Figure 1) and not the archetypal chair conformation. Indeed, a chair conformation of idealized C_3 symmetry, having three "axial" perfluorophenyls on the same side of the six-membered ring, would be rather crowded. In the solid-state experimental conformation, the perfluorophenyl substituents, being either equatorial or bisectional, are spread around the ring in a more homogeneous way; in addition, the three hydroxyl hydrogens are involved in bifurcated O−H···F hydrogen bonds with six (one for each perfluorophenyl ligand) ortho fluorine atoms (average O−H, H···F, and O···F distances 0.79, 2.09, and 2.67 Å, respectively).

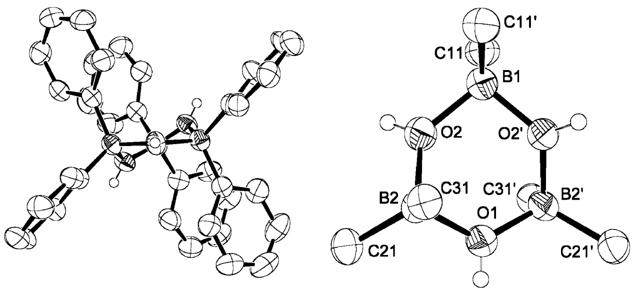

Figure 1. Two views of **1** highlighting the idealized C_2 symmetry (2-fold axis through B1 and O1) and the labeling scheme.

An X-ray powder diffraction spectrum of a sample of $B(C_6F_5)_2OH$ (synthesized according to ref 1c, with a melting point in agreement with literature data[1a]) confirmed that the bulk is made up of the same phase of the examined single crystal.

Several boron−oxygen compounds exhibit cyclic structures, with the boron atoms connected through oxygen bridges;[6] those more closely related to the present derivative are $[B_3(\mu\text{-O})_3(C_6H_5)_4]^-$ [7] and $[B_3(\mu\text{-O})_3$-

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[1] (a) Chambers, R. D.; Chivers, T. *J. Chem. Soc.* **1965**, 3933. (b) Ishihara, K.; Kurihara, H.; Yamamoto, H. *J. Org. Chem.* **1997**, *62*, 5664. (c) Bohnen, H.; Hahn, U. Patent WO0017208, 2000, to Aventis R&T GMBH.

[2] Ishihara, K.; Kurihara, H.; Yamamoto, H. *Synlett* **1997**, 597.

[3] Yamamoto, H., *Lewis Acids in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 2000.

[4] Recent patents dealing with synthesis or uses of **1**: (a) Ikeno, I.; Mitsui, H.; Iida, T.; Moriguchi, T. Patent WO0248156, 2002, to Nippon Shokubai Co. (b) Ikeno, I.; Mitsui, H.; Iida, T.; Moriguchi, T. Patent WO0244185, 2002, to Nippon Shokubai Co. (c) Schottek, J.; Fritze, C. Patent DE10009714, 2001, to Targor. (d) Kratzer, R. Patent DE10059717, 2001, to Basell Polyolefins. (e) Kratzer, R.; Fritze, C.; Schottek, J. Patent DE19962814, 2001, to Targor. (f) Frances, J. M.; Deforth, T. Patent WO0130903, 2001, to Rhodia Chimie. (g) Schottek, J.; Fritze, C.; Bohnen, H.; Becker, P. Patent DE19845240, 2000, to Targor. (h) Bohnen, H. Patent DE19733017, 1999, to Hoechst AG.

[5] Crystal data: $C_{36}H_3B_3F_{30}O_3$, $M_r = 1085.81$, monoclinic, space group $P2_1/c$ (No. 14), $a = 19.575(3)$ Å, $b = 13.127(2)$ Å, $c = 14.823(2)$ Å, $\beta = 98.14(1)°$, $V = 3771(1)$ Å^3, $Z = 4$, $T = 295$ K, graphite-monochromated Mo Kα radiation, $\lambda = 0.710\,73$ Å, $\rho_{calcd} = 1.913$ Mg m^{-3}, $F(000) = 2112$, white crystal, $0.28 \times 0.28 \times 0.18$ mm, μ(Mo Kα) = 0.220 mm^{-1}, absorption correction with SADABS (Sheldrick, G. M. SADABS, University of Göttingen, Göttingen, Germany, 1996), SMART diffractometer, ω scan, frame width 0.3°, maximum time per frame 30 s, θ range 1.9−23.3°, 23 734 reflections collected, 5426 independent reflections ($R_{int} = 0.0365$), no crystal decay, solution by direct methods (Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna R. SIR97. *J. Appl. Crystallogr.* **1999**, *32*, 115) and subsequent Fourier syntheses, full-matrix least squares on F_o^2 (Sheldrick, G. M. SHELXL-97: Program for Structure Refinement, 1997), anisotropic thermal factors assigned to all atoms but the three hydroxyl hydrogen atoms, which were refined with a common isotropic thermal factor, data/parameters = 3997/659, GOF(F_o^2) = 0.775, R1 = 0.0589 and wR2 = 0.0775 on all data, R1 = 0.0332 and wR2 = 0.0693 for reflections with $I > 2\sigma(I)$, weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 0.3065P]$, where $P = (F_o^2 + 2F_c^2)/3$, largest peak and hole 0.19 and −0.20 e Å^{-3}.

[6] Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 2nd ed.; BH, 1998.

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$(C_6F_5)_5]^{2-}$.[8] To the best of our knowledge, however, the title compound is the first trimeric structure based on tetracoordinated boron atoms only. Donor−acceptor bonds involving tetracoordinated boron atoms can easily dissociate, since they afford "stable" closed-shell fragments; accordingly, a few dimeric $(C_6F_5)_2B(\mu\text{-}X)_2B(C_6F_5)_2$ structures are known in the solid state ($X = H$,[9] N_3[10]), which in solution undergo complete[10] or partial[9,11] conversion into the $(C_6F_5)_2BX$ monomer.[12] The same occurs in the present case. The NMR data indicate that the dissolution of **1** in toluene-d_8 at room temperature is accompanied by disruption of the trimeric structure $\mathbf{1_t}$. Indeed, resonances attributable to the intact oligomer $\mathbf{1_t}$ could be detected only when the dissolution of **1** was performed at low temperature.[13] At higher temperatures these signals convert into a novel set of resonances (Figure S1; Supporting Information), attributable to the monomeric species, hereafter called $\mathbf{1_m}$.[14] Indeed, the ^{11}B chemical shift of $\mathbf{1_m}$ (42.2 ppm, invariant with the temperature, Figure S2; Supporting Information) falls in the range typical of three-coordinated boron,[16,17] while the resonance of $\mathbf{1_t}$ and that measured in the solid state (7.2 and 2.4 ppm, respectively) fall in the range diagnostic of tetrahedral neutral boron compounds.[20]

The rate of the $\mathbf{1_t} \rightarrow \mathbf{1_m}$ conversion is strongly dependent upon the amount of water in solution.[25] This can be attributed to nucleophilic attack of water on a boron atom, causing the cleavage of one of the B−O bonds in the B_3O_3 cyclic structure, which in turn results in the fast dissociation of the oligomer.

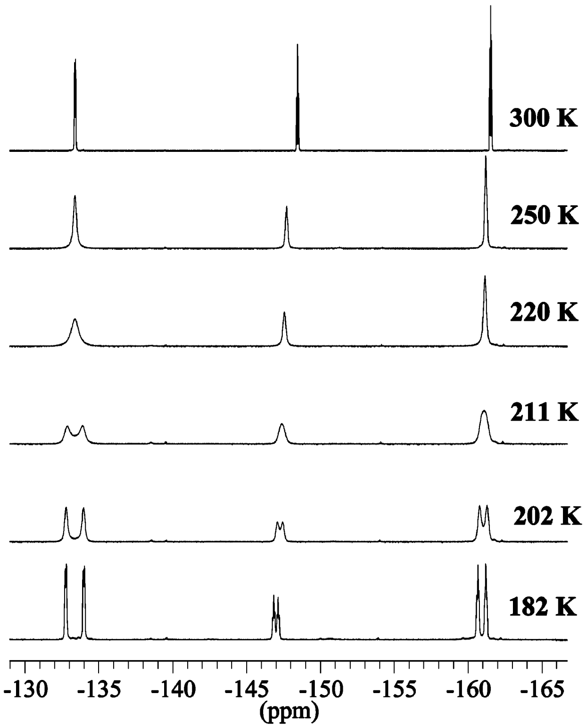

Figure 2. Variable-temperature ^{19}F NMR spectra of $\mathbf{1_m}$ in toluene-d_8.

The ^{19}F signals of $\mathbf{1_t}$ are sharp also at low temperature, down to 188 K. In contrast, when the temperature is lowered, each of the three ^{19}F resonances of $\mathbf{1_m}$ split into two signals of equal intensity (Figure 2). The splitting of the para signal indicates magnetic unequivalence of the two perfluoroaryl rings, confirmed by the separated scalar connectivities (ortho → meta → para) for each of the two sets of three ^{19}F signals (see the 2D ^{19}F COSY at 188 K in Figure S3; Supporting Information). The presence of one averaged signal for the two ortho (and meta) positions of each ring indicates that free rotation around the $B-C_{ipso}$ bond is maintained even at the lowest temperatures.

The nonequivalence of the two phenyl rings can be explained only by assuming freezing of the free rotation of the OH substituent around the Ar_2B-OH bond (see Scheme 1). In agreement with this, (i) a $^1H-^{19}F$ NOE experiment showed that the proton of $\mathbf{1_m}$ at 180 K has a strong correlation with the ortho fluorine atoms of one aryl ring only (Figure S4; Supporting Information) and (ii) the protonic resonance, which at room temperature is a quintet (averaged $J_{H-F} = 1.6$ Hz), at 180 K became a triplet (averaged $J_{H-F} =$ ca. 3 Hz, Figure S5; Supporting Information).

Such hindered rotation results from the partial double-bond character of the B−OH interaction, arising from π-donation from oxygen to the electron-poor B atom.[26] These $p\pi-p\pi$ interactions are a common feature of

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(11) Parks, D. J.; Spence, R. E. von H.; Piers, W. E. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 809.

(12) At the extreme end, the chloride derivative is monomeric also in the solid state: Piers, W. E.; Spence, R. E. v. H.; MacGillivray, L. R.; Zaworotko, M. J. *Acta Crystallogr.* **1995**, *C51*, 1688.

(13) Toluene-d_8 was added to a sample of **1** in an NMR tube at 193 K, and the tube was shaken for a short time and introduced into the NMR probe, at 253 K. ^{19}F NMR (toluene-d_8, 283 K): δ −139.3 (ortho), −150.0 (para), −159.9 (meta) ppm. ^1H NMR: δ 7.78. ^{11}B NMR: δ 7.2 ppm. Solid-state ^{11}B MAS NMR: δ 2.4 ppm.

(14) NMR data (toluene-d_8, 293 K): ^1H, δ 6.32 ppm (q, $J = 1.6$ Hz), lit.[15] 6.30 ($J = 1.7$ Hz); ^{19}F, −133.5 (ortho), −148.6 (para), −161.7 ppm (meta), lit.[1b] ($CHCl_3$) −132.8, −147.7, −160.9; ^{11}B, δ 42.2 ppm.

(15) Bradley, D. C.; Harding, I. S.; Keefe, A. D.; Montevalli, M.; Zheng, D. H. *J. Chem. Soc., Dalton Trans.* **1996**, 3931.

(16) Kidd, R. G. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic Press: New York, 1983; Vol. 2.

(17) Typical values for the ^{11}B chemical shift in three-coordinated boron derivatives bearing pentafluorophenyl substituents are in the range 32.5−74.9 ppm.[9,10,18,19] Particularly significant is the value of 39.5 ppm observed for the closely related borinate $B(C_6F_5)_2(O^nBu)$.[9]

(18) (a) Vagedes, D.; Fröhlich, R.; Erker, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 3362. (b) Doerrer, L. H.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1999**, 4325. (c) Dagorne, S.; Guzei, I. A.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 274.

(19) Kehr, G.; Fröhlich, R.; Wibbeling, B.; Erker, G. *Chem. Eur. J.* **2000**, *6*, 258.

(20) The resonances for a neutral tetrahedral boron derivative containing pentafluorophenyl substituents are usually in the range −20 to +20 ppm.[9,10,19,21−24]

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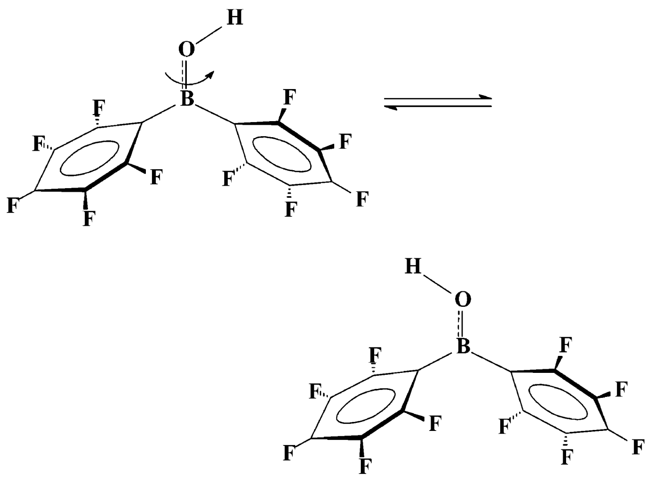
(23) Parks, D. J.; Piers, W. E.; Parvez, M.; Atencio, R.; Zaworotko, M. J. *Organometallics* **1998**, *17*, 1369.

(24) See: Beringhelli, T.; Maggioni, D.; D'Alfonso, G. *Organometallics* **2001**, *20*, 4927 and references therein.

(25) When **1** was dissolved (at low temperature) in toluene-d_8, "dried" with standard methods (i.e. upon standing for more than 1 day over activated 4A molecular sieves), a ^{19}F spectrum acquired at 253 K within 5 min from dissolution showed that $\mathbf{1_m}$ was already the dominant species (>70%). In contrast, the amount of $\mathbf{1_m}$ was almost negligible (Figure S1a; Supporting Information) when **1** was dissolved in toluene "dried" as above *and* containing a small amount (0.15 equiv) of $B(C_6F_5)_3$, which is able to remove any adventitious water, owing to the quantitative formation of the $[(C_6F_5)_3B(OH_2)]$ adduct.[24] Under these more anhydrous conditions the rate of the $\mathbf{1_t} \rightarrow \mathbf{1_m}$ conversion was significantly reduced ($t_{1/2} = 29$ min at 283 K, Figure S1b−d).

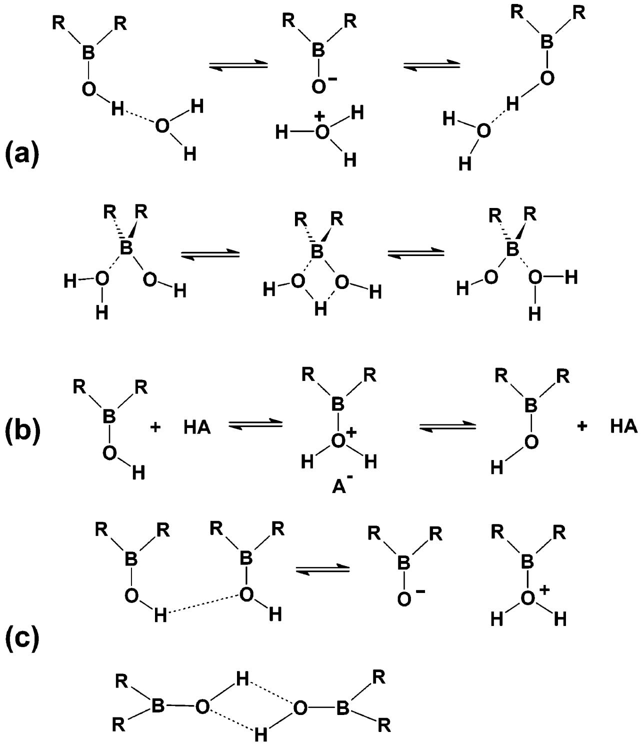
Scheme 1



trigonal boron compounds bearing substituents with nonbonding electron pairs.[6,10] For BF_2OH the planar configuration was found to be more stable than the orthogonal one,[27] and theoretical computations concerning boron−oxygen compounds have found considerable π-electron O→B delocalization, even more marked than in the corresponding halogeno compounds.[28]

The equalization of the phenyl rings at higher temperatures could result not only from the fast rotation of the OH group around the B−O bond but also from several intermolecular processes, such as those depicted in Scheme 2. However, direct proton exchange between different molecules of **1** (paths c) and protonation equilibria caused by the presence of adventitious acids (path b) have been ruled out, because we verified that the exchange rate did not increase on increasing the concentration of **1**[29] or of a strong Brønsted acid, such as the $[(C_6F_5)_3B{\cdot}OH_2]$ adduct.[30] In contrast, we observed a marked decrease of the exchange rate upon addition of a small amount of $B(C_6F_5)_3$ as water scavenger:[29] this indicated a significant role of adventitious water as proton shuttle, according to paths a. This contribution can be removed by removing water. Definitive evidence of the absence of intermolecular proton transfer under strictly anhydrous conditions was provided by ^1H EXSY experiments, which showed no exchange cross-peak between the (sharp) signals of **1** and $[(C_6F_5)_3BOH_2]$, at temperatures (193−212 K) where the exchange rate of the phenyl rings is already >10 s^{-1}.[31] Therefore, the rate

Scheme 2



constants obtained from ^{19}F NMR spectra acquired in the presence of $B(C_6F_5)_3$ as water scavenger can confidently be ascribed to the intramolecular rotation of the OH group. The activation barrier estimated from these constants, $E_a = 39(1)$ kJ mol^{-1}, is comparable to values previously experimentally determined or theoretically evaluated for the barriers to rotation about C−OR bonds in R′C(=O)OR species (R, R′ = H, CH_3),[33] which were attributed to the contribution of a resonance form implying double-bond character of the C−OR bond. To the best of our knowledge, this is the first time that a restricted rotation around a B−OH bond has been observed and measured.

Acknowledgment. We thank Dr. R. Kratzer (Basell Polyolefins) for a sample of $(C_6F_5)_2B(OH)$, Dr. G. Althoff (Bruker Biospin Gmbh), for the solid-state ^{11}B MAS spectrum, and Basell for partial funding of this work. We also thank the anonymous reviewers who suggested useful experiments to provide a firmer basis to our thesis.

Supporting Information Available: Figures S1−S7 (^{19}F NMR monitoring of the $\mathbf{1_t} \rightarrow \mathbf{1_m}$ conversion, variable-temperature ^{11}B spectra, 2D ^{19}F COSY45 spectra, $^{19}F-^1H$ NOE spectra, variable-temperature ^1H spectra, ^{19}F spectra at different concentrations of **1**, Arrhenius plot) and tables giving the pertinent X-ray structural information. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) In fact, OH···F interactions involving the ortho F atoms of the phenyl rings are not the key factor responsible for the observed restricted rotation, since the aromatic rings freely rotate around the B−C_{ipso} bond.

(27) Spoliti, M.; Ramondo, F.; Bencivenni, L. *Folia Chim. Theor. Lat.* **1992**, *20*, 201.

(28) (a) Armstrong, D. R.; Perkins, P. G. *J. Chem. Soc. A* **1967**, 123. (b) Armstrong, D. R.; Perkins, P. G. *J. Chem. Soc. A* **1967**, 790. (c) *Theor. Chim. Acta* **1966**, *5*, 222.

(29) Three samples were prepared by dissolving different amounts of **1** in the same amount of toluene-d_8 “dried” over molecular sieves, and ^{19}F NMR spectra were acquired at 205 K (Figure S6; Supporting Information). The samples containing the lowest and the highest concentrations of **1** were then treated with the same amount of $B(C_6F_5)_3$, causing the exchange rate to become slower and equal in the two samples. The more concentrated sample was then added with the amount of water necessary to double the concentration of the $[(C_6F_5)_3BOH_2]$ adduct: this did not cause any variation of the exchange rate.

(30) It has been reported that $[(C_6F_5)_3BOH_2]$ in acetonitrile must be regarded as a strong acid, comparable to HCl: Bergquist, C.; Bridgwater, B. M.; Harlan, C. J.; Norton, J. R.; Friesner, R. A.; Parkin, G. *J. Am. Chem. Soc.* **2000**, *122*, 10581−19590.

(31) The kinetic constants for the exchange process were obtained by band-shape analysis on ^{19}F NMR spectra using Bruker WIN-DYNAMICS software. *k*, s^{-1} (*T*, K): 40 (193), 170 (205), 330 (212), 580 (216), 1100 (224), 2000 (230), 6000 (242). The temperatures were calibrated with a standard CH_3OH/CD_3OD solution.[32] The Arrhenius plot is reported in Figure S7 (Supporting Information).

(32) Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679.

(33) Computed barriers (MP3/6-311+G**) in the range 36.07−53.63 kJ mol^{-1}: Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1987**, *109*, 5935.