



## SYNTHESIS METHODOLOGY OF SUBSTITUTED TETRAPHENYLBORATE SALTS

N. Malek <sup>a\*</sup>, M. Saied <sup>b</sup>, J. D. Wuest <sup>a</sup>

<sup>a</sup> *Département de Chimie, Université de Montréal, Montréal, Québec, H3C 3J7, Canada*

<sup>b</sup> *Département de Chimie, Faculté des Sciences, Campus Universitaire, 2092 El Manar, Tunis, Tunisie*

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**ABSTRACT:** Tetraphenylborate substituted at the meta, para or 3,5 positions with diaminotriazine groups can be used like charged subunits for the construction of anionic hydrogen-bonded networks by the strategy of molecular tectonics. We have developed a synthesis methodology leading to various substituted tetraphenylborates salts **2**, **3** and **4** and to their precursors such as cyanotetraphenylborates **8**, **9** and **10** and iodo or bromotetraphenylborates **5**, **5a**, **6**, **6a** and **7**, **7a** mainly used in gravimetry, which consist in cation separations by selective precipitations.

**Key words:** Gravimetric, synthetic methodology, hydrogen bonding, anionic networks, tetraphenylborates.

**RESUME:** Les sels de tetraphenylborate substitués en méta, para ou en 3,5 avec des groupements diaminotriazine peuvent être utilisés en tectonique moléculaire comme des sous unités chargées pour la construction supramoléculaire de réseaux anioniques par le biais de ponts hydrogène. Nous avons développé une méthodologie de synthèse d'une variété de sels tétraphénylborate substitués **2**, **3**, **4** et leurs précurseurs comme les cyanotétraphénylborates **8**, **9**, **10** ainsi que les iodo ou les bromotétraphénylborates **5**, **5a**, **6**, **6a**, **7**, **7a** qui sont utilisés principalement en gravimétrie.

**Mots clés:** Gravimétrie, méthodologie de synthèse, ponts hydrogène, réseau anionique, tetraphenylborates.

### INTRODUCTION

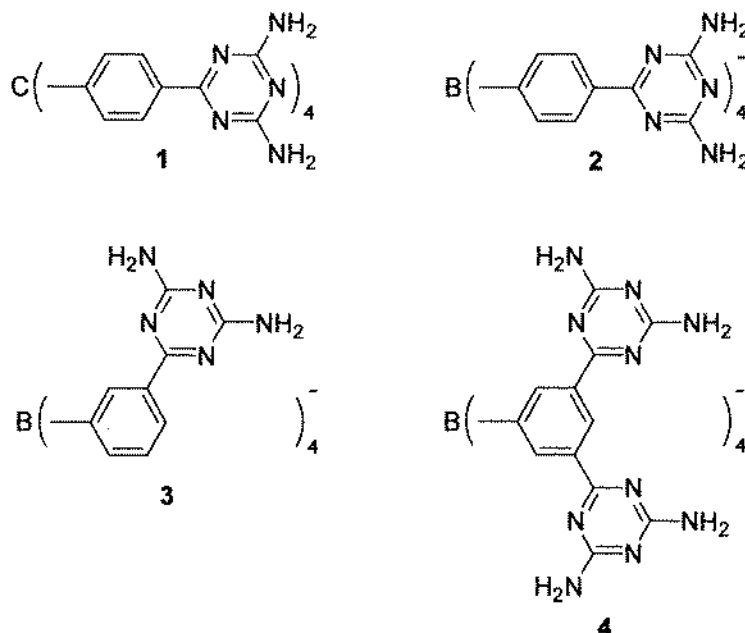
Crystal engineers have tested various approaches to predict exactly the detailed structure of molecular crystals [1]. One of the most effective strategies is the use of molecules with geometrically well-defined cores and multiple peripheral sticky sites that direct intermolecular association according to reliable motifs and thus determine the resulting structures [2]. In this direction, molecular tectonics is a strategy of molecular assemblage using intermolecular association who are directional and reversible between molecules named tectons to built and generate molecular building with ordered, predicted and partially controlled geometries [3]. This recognition between tectons from the Greek word for builder is essentially governed by hydrogen bonds [4]. When joined by strong hydrogen bonds, such networks can have remarkable porosity and structural integrity [5].

Crystallization of this type of molecules disadvantage close packing, generate open networks and the volume unfilled by the networks themselves is occupied by included guests or by independent interpenetrating networks [6]. For example, crystallization of tecton **1** is directed by hydrogen bonding of its 2,4-diaminotriazine groups to produce a robust three-dimensional network that has properties of porosity similar to those of zeolites. In particular, the network incorporates parallel channels that are nearly 12 Å in diameter, approximately 45% of the volume of the solid is occupied by exchangeable guest molecules and a significant fraction of guest can even be removed without causing the network to become disordered [7]. Unlike typical open zeolitic frameworks, however, those derived from tecton **1** and similar compounds are uncharged. We have now developed a methodology of synthesis of various salts tetraphenylborates **2**, **3** and **4** which are a charged analogue of tetraphenylmethane **1**, and we have found that para-substituted salts crystallize with different cations and solvents (DMSO/toluene, DMF/toluene, H<sub>2</sub>O) to generate a new family

\* corresponding author.; e-mail: nadia.malek@gmail.com



of porous anionic hydrogen-bonded networks with special properties of porosity. Tetraphenylphosphonium salt and other salts were prepared in quantitative yield from the sodium salt by cation exchange [5].



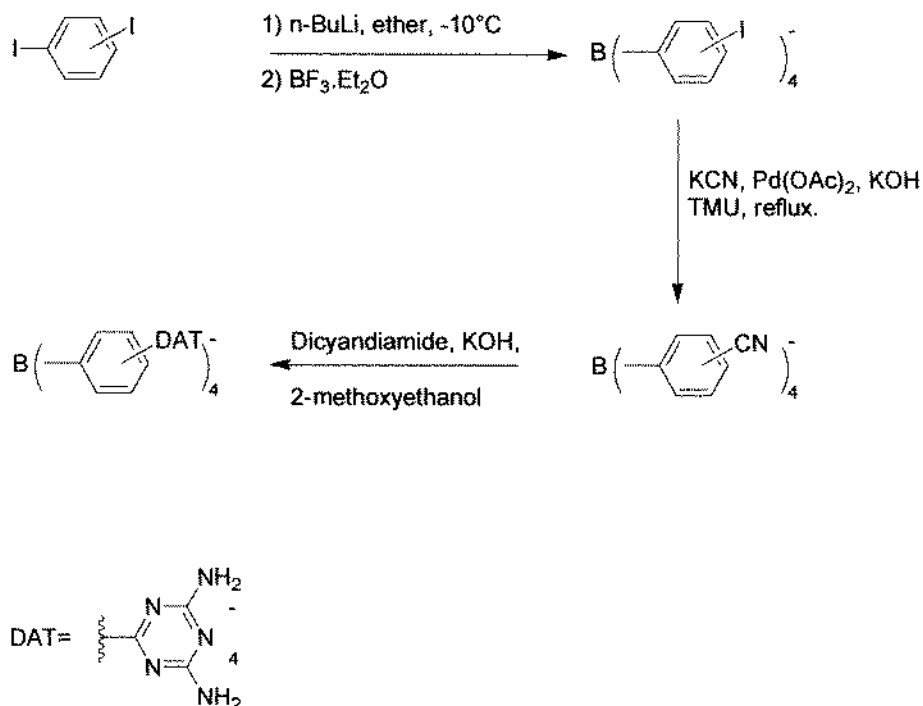
## RESULTS AND DISCUSSION

### Synthesis Methodology of The Tetraphenylborate Salts

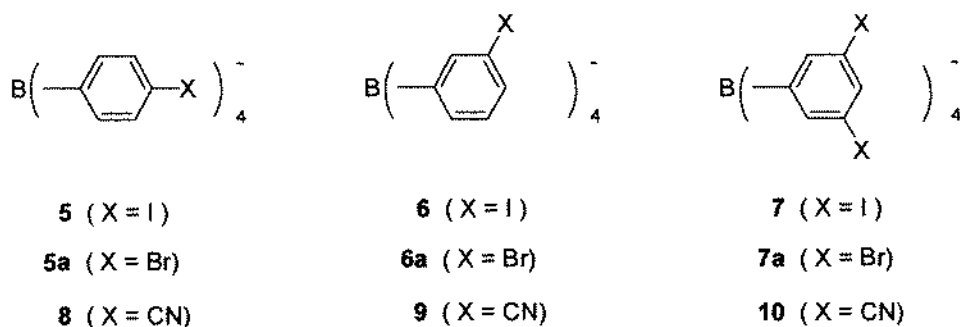
The synthesis of substituted salts of tetraphenylborates is used mainly in the gravimetry, which consists in cation separations by selective precipitations [8]. These salts are rather stable in neutral aqueous solution. In acid medium, salts of tetraphenylborate are very unstable and degraded in triphenylborane and correspondents arenas following ipso protonation [9]. This instability in acid medium limits application of derivatives of tetraphenylborate. To cure that, the chemists substituted the aromatic nucleus tetraphenylborate in para position and (or) meta by various electron withdrawing groups in order to return the B-C bond more stable and susceptible to an electrophilic attack. The synthesis of the halogens tetraphenylborate was always done by addition of  $\text{NaBF}_4$  on a phenylmagnesium [10]. We changed this concept by an addition of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  on phenyllithium. The purification is made by simple dilution followed by filtration, yield is rather good. For the synthesis of salts of cyanophenylborate, we studied two different ways. The first way uses  $\text{CuCN}$  in hot DMF but we observe a degradation of the starting product [11]. The second way which gives the expected product with acceptable yields uses  $\text{Pd}(\text{OOCCH}_3)_2$  as catalyst,  $\text{KCN}$  as agent of cyanation and  $\text{KOH}$  like co-catalyst in refluxed TMU [12]. The purification of the product is made by distillation of solvent at reduced pressure, followed by several successive washings of the solid with saturated  $\text{KCl}$  solution, deionized  $\text{H}_2\text{O}$  and  $\text{CH}_2\text{Cl}_2$  to eliminate traces of starting product. The synthesis of the diaminotriazines is done, by heating at high temperature, a mixture of nitrile, dicyandiamide and  $\text{KOH}$  in 2-methoxyethanol. Meijer and coll [13] synthesized different 2,4-diaminotriazines by using this way of synthesis. We prepared the tetrakis[4-[2-(4,6-diamino-1,3,5-triazinyl)]phenyl]methane **1** by the same procedure of cyclization [14]. In the case of the borate salts, we use the same conditions of reaction except that the purification of the product is done by distilling the solvent under reduced pressure followed by dissolving the product in deionized boiled water. We add thereafter with this aqueous solution a saturated solution of  $\text{NaCl}$  to generated

precipitation of sodium salt borate. Salt is thereafter filtered, washed with deionized water and is dried to provide the product in a good yield (Scheme 1).

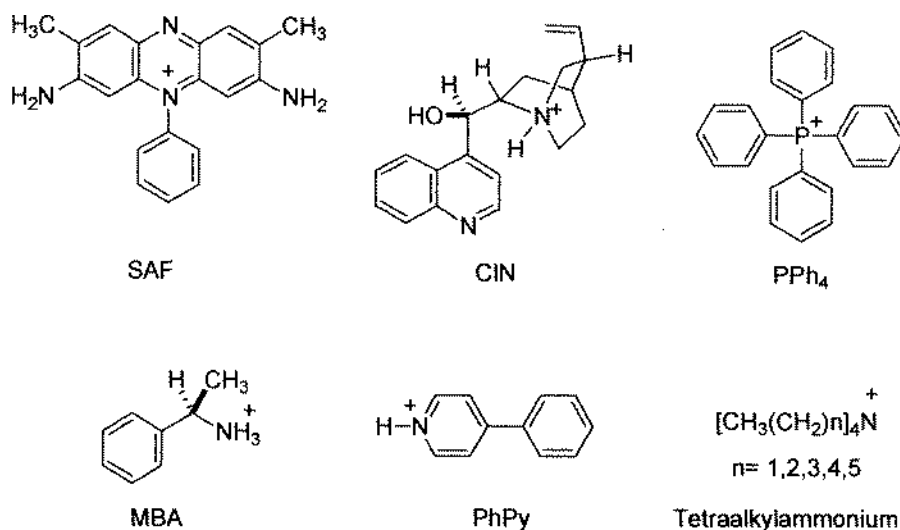
**Scheme 1:**



Anionic tecton salts **2**, **3**, **4** were prepared as it follows. Monolithiation of 4-diiodobenzene, 3-diiodobenzene or 1,3,5-triiodobenzene (BuLi, 1 eq,  $-10^\circ\text{C}$ ), followed by the addition of  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  (0.2 eq,  $25^\circ\text{C}$ ), provided lithium tetrakis(4-iodophenyl)borate **5**, lithium tetrakis(3-iodophenyl)borate **6**, lithium tetrakis(3,5-diiodophenyl)borate **7**, in respectively 85%, 70%, and 72% yields. Subsequent Pd-catalyzed cyanation ( $\text{KCN}$ ,  $\text{Pd}(\text{OOCCH}_3)_2$ ) gave 85%, 54%, and 47% in respectively yields potassium tetrakis(4-cyanophenyl)borate **8**, potassium tetrakis(3-cyanophenyl)borate **9** and potassium tetrakis(3,5-cyanophenyl)borate **10**. Intermediates **8**, **9** and **10** were then converted in respectively 87%, 80%, and 77% yields into the sodium salt of anionic tecton **2**, **3**, **4** by reaction with dicyandiamide under standard conditions.



All the other salts were prepared in quantitative yields from the sodium salt of tectons **2**, **3**, **4** and also from the products **5**, **5a**, **6**, **6a**, **7**, **7a**, **8**, **9**, **10** by cation exchange using a saturated solution of the chloride or bromide salt of a new cation.



CIN= cinchonidinium, MBA= methylbenzylammonium, PhPy= 4-phenylpyridinium, PPh<sub>4</sub>= tetraphenylphosphonium, Saf= safranin o =3,7-diamino-1,8-dimethyl-5-phenylphenazin-5-ium .

### Crystallization and Structure of the Tetraphenylborate Salt: 2•PPh<sub>4</sub><sup>+</sup>

As already published, the anionic network produced by crystallization from DMSO/toluene of tecton 2•PPh<sub>4</sub><sup>+</sup> is exceptionally porous [5]. Only 26% of the volume of the crystals is occupied by the ordered tectons themselves, and the remaining 74% are available for including disordered cations and guests. The observed porosity is greater than that of all the other networks built from small molecules. Similar crystallization of tecton 2 with other salts listed in (Table 1) produced a similar ionic network. We could make a multitude of exchange of ions in single crystals with retention of the starting architecture as well as selective cation exchange with different tetraalkylammonium bromide bearing alkyl radical of different length. In all the crystallographic studies using CAD-4 or the CCD the included cations and guests are disordered.

**Table 1:**

	a (Å)	b (Å)	c (Å)	β°	Vol. (Å <sup>3</sup> )	Z
2•CIN	12.30(2)	18.24(2)	23,73(3)	96.43(13)	5289(12)	2
2•MBA	12.387(9)	18.114(13)	23,624(16)	94.16(5)	5287(6)	2
2•PhPy	12.355(7)	18.215(10)	23.711(10)	95.84(4)	5308(5)	2
2•PPh <sub>4</sub>	13.045(6)	17.151(8)	24,023(8)	92.21(3)	5371(4)	2
2•Saf	12.845(8)	17.134(10)	23,896(16)	92.11(5)	5255(6)	2

### Experimental Section

Ether was dried by distillation from the sodium and benzophenone. All other reagents were commercial products that were used without further purification.



**Lithium tetrakis(4-iodophenyl)borate 5.** A solution of 1,4-diiodobenzene (10.0 g, 30.3 mmol) in ether (300 mL) was stirred at  $-10\text{ }^{\circ}\text{C}$  under  $\text{N}_2$  and treated dropwise with a solution of butyllithium (12.1 mL, 2.5 M in hexane, 30 mmol). The resulting mixture was kept at  $-10\text{ }^{\circ}\text{C}$  for 10 min, and  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  (0.796 g, 5.61 mmol) was then added. The temperature was allowed to rise to  $25\text{ }^{\circ}\text{C}$ , and after 18 h the mixture was filtered to remove a solid. The solid was washed with ether (200 mL), and the desired product was extracted with acetone (20 mL). Acetone was removed from the filtered extracts by evaporation under reduced pressure, leaving a residue of lithium tetrakis(4-iodophenyl)borate **5** as a colorless solid (3.95 g, 4.76 mmol, 85%). An analytically pure sample was prepared by recrystallization from  $\text{CH}_2\text{Cl}_2$ : mp  $289\text{--}290\text{ }^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  6.87 (m, 8H), 7.29 (d, 8H,  $^3J = 8.0\text{ Hz}$ );  $^{11}\text{B}$  NMR (96.0 MHz, DMSO- $d_6$ )  $\delta$   $-6.35$ ;  $^{13}\text{C}$  NMR (100.6 MHz, DMSO- $d_6$ )  $\delta$  88.5, 134.5, 137.9, 161.1 (q,  $^1J_{\text{C-B}} = 49\text{ Hz}$ ). HRMS (FAB, 3-nitrobenzyl alcohol) calcd for  $\text{C}_{24}\text{H}_{16}^{11}\text{B}_4$  *m/e* 822.7524, found 822.7503. Anal. Calcd for  $\text{C}_{24}\text{H}_{16}\text{B}_4\text{Li}$ : C, 34.74; H, 1.94. Found: C, 34.80; H, 1.76.

**Lithium tetrakis(3-iodophenyl)borate 6.** An analytically pure sample was prepared by recrystallization from  $\text{CH}_2\text{Cl}_2$ : 70% yield; mp  $280\text{ }^{\circ}\text{C}$ ; IR (KBr): 3436, 1960, 1883, 1805, 1611, 1561, 1534, 1453, 1379, 1299, 1248, 1171, 1145, 1123, 1085, 1056, 989, 915, 858, 782;  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  7.38 (m, 4H); 7.24 (d, 4H,  $^3J = 7.6\text{ Hz}$ ); 7.12 (m, 4H); 6.86 (t, 4H,  $^3J = 7.5\text{ Hz}$ ).  $^{13}\text{C}$  NMR (75.4 MHz, DMSO- $d_6$ ):  $\delta$  95.3, 128.7, 131.2, 134.4, 143.2, 164.9. HRMS (FAB, 3-nitrobenzyl alcohol) calcd for  $\text{C}_{24}\text{H}_{16}^{11}\text{B}_4$  *m/e* 822.7503, found 822.

**Lithium tetrakis(3,5-diiodophenyl)borate 7.** An analytically pure sample was prepared by recrystallization from  $\text{CH}_2\text{Cl}_2$ : 72% yield; mp  $> 300\text{ }^{\circ}\text{C}$ ; IR (KBr): 3623, 2558, 3069, 2973, 2880, 1604, 1541, 1514, 1445, 1378, 1283, 1241, 1153, 1133, 1100, 1089, 1063, 988, 913, 841, 777;  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ) RMN  $^1\text{H}$  (300 MHz, DMSO):  $\delta$  7.65 (ls, 4H); 7.26 (lm, 8H);  $^{13}\text{C}$  NMR (100.6 MHz, DMSO- $d_6$ )  $\delta$  96.1, 138.9, 142.4, 166.2 (q,  $^1J_{\text{C-B}} = 47\text{ Hz}$ ).

**Potassium tetrakis(4-cyanophenyl)borate 8.** A mixture of lithium tetrakis(4-iodophenyl)borate (**5**; 4.50 g, 5.42 mmol), KCN (3.90 g, 59.9 mmol), KOH (0.054 g, 0.96 mmol), and  $\text{Pd}(\text{OOCCH}_3)_2$  (0.018 g, 0.080 mmol) in tetramethylurea (9 mL) was heated at reflux under  $\text{N}_2$ . After 18 h, volatiles were removed by evaporation under reduced pressure, the residual solid was washed with  $\text{H}_2\text{O}$ , saturated aqueous KCl, and  $\text{CH}_2\text{Cl}_2$ , and the product was then dried *in vacuo*. This provided potassium tetrakis(4-cyanophenyl)borate **8** as a beige solid (2.03 g, 4.43 mmol, 82%). An analytically pure sample was prepared by recrystallization from  $\text{CH}_3\text{CN}$ : mp  $> 300\text{ }^{\circ}\text{C}$ ; IR (KBr)  $2222\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  7.23 (m, 8H), 7.44 (d, 8H,  $^3J = 7.8\text{ Hz}$ );  $^{11}\text{B}$  NMR (96.0 MHz, DMSO- $d_6$ )  $\delta$   $-5.92$ ;  $^{13}\text{C}$  NMR (100.6 MHz, DMSO- $d_6$ )  $\delta$  105.6, 120.2, 129.7, 135.6, 167.6 (q,  $^1J_{\text{C-B}} = 49\text{ Hz}$ ). HRMS (FAB, 3-nitrobenzyl alcohol) calcd for  $\text{C}_{28}\text{H}_{16}^{11}\text{BN}_4$  *m/e* 419.1468, found 419.1454.

**Potassium tetrakis(3-cyanophenyl)borate 9.** An analytically pure sample was prepared by recrystallization from  $\text{CH}_3\text{CN}$ : 54% yield; mp  $> 300\text{ }^{\circ}\text{C}$ ; IR (KBr)  $2222\text{ cm}^{-1}$ : 3459, 3072, 2381, 2226, 1636, 1470, 1385, 1315, 1267, 1126, 882, 745  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  7.41 (m, 8H); 7.31 (m, 8H); HRMS (FAB, 3-nitrobenzyl alcohol) calcd for  $\text{C}_{28}\text{H}_{16}^{11}\text{BN}_4$  *m/e* 419.14540, found 419.14779.

**Potassium tetrakis(3,5-cyanophenyl)borate 10.** 47% yield; mp  $> 300\text{ }^{\circ}\text{C}$ ; IR (KBr)  $2222\text{ cm}^{-1}$  3448, 2924, 2360, 2345, 2230, 1637, 1465, 1382, 1261, 1168, 1126, 921, 882, 745;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.12 (ls, 4H); 7.63 (lm, 8H).

**Sodium Salt of tetrakis[4-(2-(4,6-diamino-1,3,5-triazinyl))phenyl]borate 2.** A mixture of potassium tetrakis(4-cyanophenyl)borate (**8**; 1.50 g, 3.27 mmol), dicyandiamide (1.36 g, 16.2 mmol), and KOH (0.441 g, 7.86 mmol) in 2-methoxyethanol (9 mL) was heated at reflux under  $\text{N}_2$ . After 18 h, volatiles were removed by evaporation under reduced pressure, and the residual solid was washed with  $\text{CH}_3\text{OH}$  and dried. The solid was dissolved in boiling deionized  $\text{H}_2\text{O}$  (20 mL), and saturated aqueous NaCl was added. The resulting suspension was filtered, and the solid was washed with deionized  $\text{H}_2\text{O}$  and dried *in vacuo*. This provided the sodium salt of tetrakis[4-[2-(4,6-diamino-



1,3,5-triazinyl)]phenyl]borate **2** as a colorless solid (2.21 g, 2.84 mmol, 87%). A purified sample was prepared by recrystallization from H<sub>2</sub>O: mp >300 °C; <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>) δ 6.56 (bs, 16H), 7.28 (m, 8H), 7.90 (d, 8H, <sup>3</sup>J = 7.7 Hz); <sup>11</sup>B NMR (96.0 MHz, DMSO-d<sub>6</sub>) δ -5.98; <sup>13</sup>C NMR (75.5 MHz, DMSO-d<sub>6</sub>) δ 125.4, 130.8, 135.1, 167.3 (2C), 171.4 HRMS (FAB, 3-nitrobenzyl alcohol) calcd for C<sub>36</sub>H<sub>32</sub>BN<sub>20</sub> *m/e* 755.58300, found 755.58320. HRMS (FAB+ 3-nitrobenzyl alcohol) calcd for Na *m/e* 23.0 found 23.0.

**Tetrabutylammonium salt of tetrakis[3-(2-(4,6-diamino-1,3,5-triazinyl))phenyl] borate 3.** A mixture of potassium tetrakis(3-cyanophenyl)borate (**9**; 0.539 g, 1.18 mmol), dicyandiamide (0.488 g, 5.76 mmol), and KOH (159 mg, 2.35 mmol) in 2-methoxyethanol (3 mL) was heated at reflux under N<sub>2</sub>. After 18 h, volatiles were removed by evaporation under reduced pressure, and the residual solid was washed with CH<sub>3</sub>OH and dried. The solid was dissolved in boiling deionized H<sub>2</sub>O (20 mL), and saturated aqueous tetrabutylammonium chloride was added. The resulting suspension was filtered, and the solid was washed with deionized H<sub>2</sub>O and dried *in vacuo*. This provided the tetrabutylammonium salt of tetrakis[3-[2-(4,6-diamino-1,3,5-triazinyl)]phenyl]borate **3** as a colorless solid (0.94 g, 0.94 mmol, 80%). mp >300 °C; IR (KBr) 2222 cm<sup>-1</sup>: 3402, 3354, 3201, 3185, 2961, 1638, 1537, 1439, 1403, 1376, 1268, 1165, 1069, 1023, 882, 829, 801, 736, 708 <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>) δ 8.27 (m, 4H); 7.77 (d, 4H, <sup>3</sup>J = 7.7 Hz); 7.38 (m, 4H); 7.0 (t, 4H, <sup>3</sup>J = 7.6 Hz); 6.47 (m, 16H), 3.13 (m, 8H); 1.55 (m, 8H); 1.28 (m, 8H); 0.90 (t, 12H, <sup>3</sup>J = 7.7 Hz) HRMS (FAB, 3-nitrobenzyl alcohol) calcd for C<sub>36</sub>H<sub>32</sub>BN<sub>20</sub> *m/e* 755.58300, found 755.58410.

**Sodium Salt of tetrakis[3,5-(2-(4,6-diamino-1,3,5-triazinyl))phenyl]borate 4.** Considering the low solubility of the tecton **4** its characterisation was made by NMR spectra not highly reliable. 77% yield; mp >300 °C.

**Other salts obtained from the tetraphenylborate 2, 3, 4, 5, 6, 7.** The sodium or lithium salt of Tetraphenylborate **2, 3, 4, 5, 6, 7** were dissolved in boiling deionized H<sub>2</sub>O, and the resulting solution was treated with a concentrated aqueous solution containing a large excess of the chloride or bromide salt of the desired cation. The product was filtered from the resulting suspension, washed with cold deionized H<sub>2</sub>O, and dried *in vacuo*.

## BIBLIOGRAPHIE

- [1] J. D. Dunitz, *Chem. Commun.*, **2003**, 545. G. R. Desiraju, *Nature. Materials.*, **2002**, 1,77. A. Gavezzotti, *Acc. Chem. Res.*, **1994**, 27, 309. J. Maddox, *Nature.*, **1988**, 335, 201. D. Braga, *Chem. Commun.*, **2003**, 2751. K. Biradha, *Cryst. Eng. Commun.*, **2003**, 5, 374. M. D. Hollingsworth., *Science*. **2002**, 295, 2410. D. Braga, F. Grepioni, A. G. Orpen, *Crystal Engineering From Molecules and Crystals to Materials*, Eds., Kluwer Dordrecht, Netherlands, **1999**. G. R. Desiraju, *Crystal Engineering The Design of Organic Solids*, Elsevier, Amsterdam, **1989**.
- [2] A. Gavezzotti, *Acc. Chem. Res.*, **1994**, 27, 309.
- [3] a- M. Simard, D. Su, J. D. Wuest, *J. Am. Chem. Soc.*, **1991**, 113, 4696. b- S. Mann, *Nature.*, **1993**, 365, 499.
- [4] a- O. Saied, T. Maris, X. Wang, M. Simard, J. D. Wuest, *J. Am. Chem. Soc.*, **2005**, 127, 10008. b- O. Saied, T. Maris, J. D. Wuest, *J. Am. Chem. Soc.*, **2003**, 125, 14956. c- N. Malek, T. Maris, M. E. Peron, J. D. Wuest, *Angew. Chem. Int. Ed.*, **2005**, 44, 4021.
- [5] N. Malek, T. Maris, M. Simard, J. D. Wuest, *J. Am. Chem. Soc.*, **2005**, 127, 5910.
- [6] a- B. Q. Ma, H.L. Sun, S. Gao, *Chem. Commun.*, **2003**, 2164. b- P. A. Gale, K. Navakhun, S. Camiolo, M. E. Light, M. B. Hursthouse., *J. Am. Chem. Soc.*, **2002**, 124, 11228. c- D. Braga, L. Maini, F. Grepioni, C. Elschenbroich, F. Paganelli, O. Schiemann, *Organometallics.*, **2001**, 20, 1875. d- S. R. Batten, *Cryst. Eng. Commun.*, **2001**, 18, 1. e- S. R. Batten, R. Robson, *Angew. Chem. Int. Ed.*, **1998**, 37, 1460.



- [7] P. Brunet, M. Simard, J. D. Wuest, *J. Am. Chem. Soc.*, **1997**, *119*, 2737.
- [8] a- G. Wittig, G. Keicher, A. Ruckert, P. Raff, *Liebigs. Ann.*, **1949**, 563, 110. b- G. Wittig, P. Raff, *Liebigs. Ann.*, **1951**, 573, 195. c- C. E. Moore, J. J. McLafferty, F. P. Cassaretto, *Anal. Chem. Acta.*, **1965**, *32*, 376. d- C. E. Moore, J. J. McLafferty, F. P. Cassaretto, H. Posvic, *Anal. Chem. Acta.*, **1966**, *35*, 1. e- C. E. Moore, F. P. Cassaretto, H. Posvic, J. T. Vandenberg, *Anal. Chem. Acta.*, **1969**, *44*, 175.
- [9] a- G. Wittig, *Rev. Chem. Soc.*, **1966**, *20*, 191. b- C. E. Moore, F. P. Cassaretto, H. Posvic, J. T. Vandenberg, M. Meisters, *Anal. Chem. Acta.*, **1970**, *49*, 481.
- [10] C. E. Moore, F. P. Cassaretto, M. Meisters, *Anal. Chem. Acta.*, **1969**, *44*, 287.
- [11] H. Shechter, L. Friedman, *J. Org. Chem.*, **1961**, *26*, 2522.
- [12] a- K. Takagi, T. Okamoto, Y. Sakaakibara, A. Ohno, S. Oka, N. Hayama, *Bull. Chem. Soc. Jpn.*, **1976**, *49*, 3177. b- K. Takagi, T. Okamoto, Y. Sakaakibara, A. Ohno, S. Oka, N. Hayama, *Chem. Lett.*, **1973**, 471.
- [13] E. W. Meijer, J. A. J. M. Vekemans, R. P. Sijbesma, F. H. Beijer, H. Kooijman, A. L. Spek, *J. Org. Chem.*, **1996**, *61*, 6371.
- [14] a- B. Kriste, M. Grimm, H. Kurreck, *J. Am. Chem. Soc.*, **1989**, *111*, 108. b- P. Brunet, M. Simard, J. D. Wuest, *J. Am. Chem. Soc.*, **1997**, *119*, 2737.