

## Research Article

# A Facile Route to Melaminophenyl Boronates using 2, 4-Diazido-6-Chloro-1, 3, 5-Triazine as an Electrophilic Reagent

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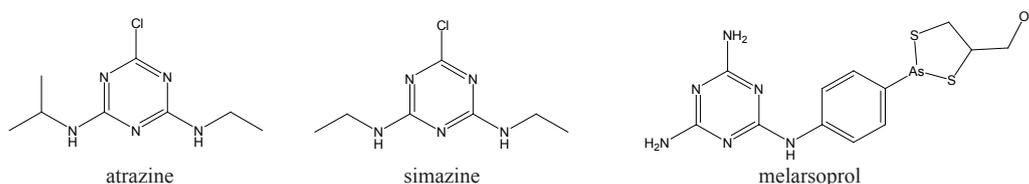
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**Abstract:** We have synthesised a novel class of melaminyl derivative, containing a phenyl boronate or boronate ester group. The synthetic methodology employed was designed to be facile involving the use of 2, 4-diazido-6-chloro-1, 3, 5-triazine as an electrophilic reagent for nucleophilic substitution of chlorine with a weakly reactive amine. The reagent was chosen with a view to improve the organic solubility of the product and aid isolation by allowing the reaction to be followed by fluorescence quenching (Tlc,  $F_{234}$ ) and IR (the presence of two  $N_3$  peaks).

**Keywords:** boronates, melarsoprol, diazidotriazine, BNCT, melaminophenyl boronates

## 1. Introduction

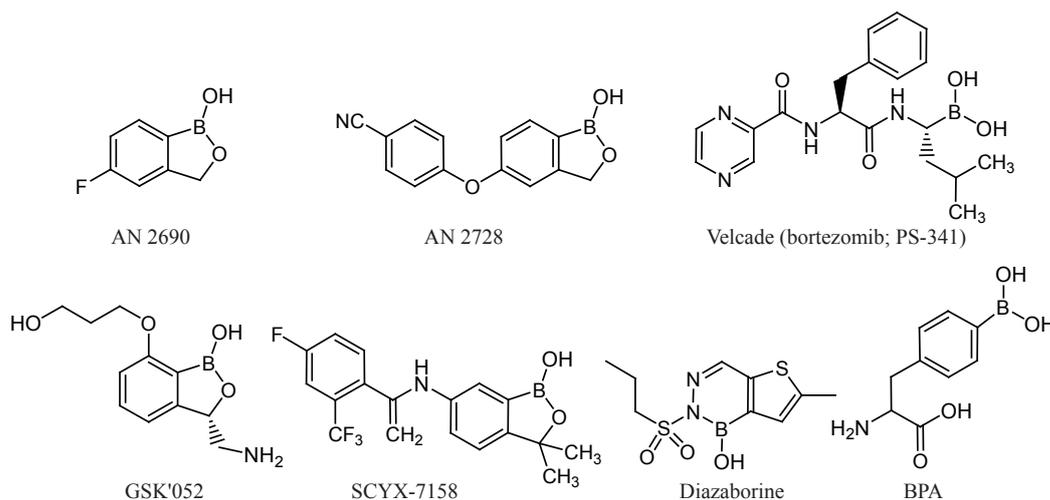
The 1, 3, 5 triazine skeleton and its derivatives are present in herbicides such as simazine, atrazine, the melaminyl dithiaarsane drug, melarsoprol (Figure 1), used for the treatment of late stage East African trypanosomiasis<sup>1,2</sup> and in the treatment of cardiovascular, neuropsychiatric disorders, diabetes, cancer and as a diuretic agent.<sup>3,4</sup> Melarsoprol alone or with all-trans-retinoic acid (ATRA) has shown promise in retarding the growth and anti-proliferative activity of MCF-7 human breast cancer cells, as well as the PC-3 and DU 145 human prostate cancer cells, both in vitro and in vivo.<sup>5</sup>



**Figure 1.** The chemical structures of melaminyl molecules with biological activity

Boronic acid derivatives have been studied extensively as potential therapeutics.<sup>6-9</sup> A number of boronate peptides, heterocyclic benzoxaboroles and diazaborines have been identified with biological activity against a variety of diseases.

Some have been used clinically or have entered human clinical trials for cancer and as antifungal, anti-inflammatory, antibacterial, antimalarial, antitrypanosomiasis agents as exemplified by PS-341, AN2690, AN2728, AN3365 (GSK'052),<sup>10</sup> diazaborine and AN5568 (SCYX-7158)<sup>11</sup> (Figure 2). Some boron compounds, preferentially accumulate in certain types of cancers such as boronophenylalanine (BPA) (Figure 2) and have found use in boron neutron capture therapy (BNCT), a targeted radiotherapy for cancer cells.<sup>12,13</sup> The therapy is based on the capture by the boron-10 nucleus of neutrons, when irradiated and its subsequent fission to yield an alpha particle (<sup>4</sup>He) and recoiling lithium (<sup>7</sup>Li) nuclei. Boron neutron capture therapy is primarily used for the treatment of difficult-to-treat tumours, particularly brain tumours, where surgery, chemotherapy, and radiotherapy prove ineffective or lead to the incapacity of the patient.



**Figure 2.** The chemical structures of boron-containing molecules with biological activity

Our interest in melaminyl derivatives is in the preparation of a bioisosteric analogue of melarsoprol (Figure 1) in which the arseno group is replaced by a boronate group that is topologically similar and share some of its physicochemical properties. The traditional synthetic route to this type of compound involves the reaction of 2, 4-diamino-6-chloro-1, 3, 5-triazine with an amino substituted phenylboronate. However, the diamino groups on the triazine ring reduces the electrophilic character of the chlorine to nucleophilic substitution, requiring hard conditions (reflux EtOH/H<sub>2</sub>O) to achieve product formation even with reactive amines which creates problems, such as the loss of protecting groups<sup>14</sup> and with sterically hindered amines, like 1-adamantanamine,<sup>15</sup> heating at 285°C in sulfolane. The use of solvent free microwave conditions on silica-gel at 800 W offer a solution, for sterically hindered amines.<sup>16</sup> However, when the amine is poorly nucleophilic, due to an electron withdrawing boronate substituent, have a labile protecting group, then substitution and isolation becomes problematic. This paper describes the use of 2, 4-diazido-6-chloro-1, 3, 5-triazine as a new facile reagent for the preparation of melaminophenyl boronates, that have not been previously prepared, as bioisosteric analogues of melarsoprol (Figure 3).

## 2. Experimental section

All commercially available reagents were purchased from Sigma-Aldrich (UK), or Alfa Aesar (UK) and used without purification. Melting points were determined on an Electrothermal apparatus and are uncorrected unless specified otherwise. Preparative thin-layer chromatography (PTLC) was performed on silica gel 60 F<sub>234</sub> plates purchased from Merck. <sup>1</sup>H and <sup>13</sup>C Nuclear Magnetic Resonance (NMR) spectra were obtained in the designated solvent and frequency on a Japan Electron Optics Laboratory (JEOL) 270 MHz Fourier transform NMR (FTNMR) spectrometer using trimethylsilane as an internal standard. Infrared spectra were recorded with a Thermo Nicolet 370 Fourier Transform Infrared spectrometer (FTIR). Mass spectrometry was undertaken as a service at the Environmental Physical

Research Council (EPSRC) mass spectrometry facility at Swansea (UK). The preparation, storage and reaction of azido compounds was carried out in reaction vessels protected with aluminium foil. Care should be taken in the handling (light and heat sensitivity) and storage of large quantities of 2, 4-diazido-6-chloro-1, 3, 5-triazine (**2**) due to the explosive properties of related compounds reported in the literature.<sup>17,18</sup> We note that dilute solution of **2** left to evaporate in thin glass vials in the dark on many occasions were found shattered.

### 2.1 2, 4-Diazido-6-chloro-1, 3, 5-triazine (**2**)

To an ice cold stirred solution of cyanuric chloride (**1**) (2 g; 0.011 M) suspended in acetone (80 cm<sup>3</sup>) was added a solution of sodium azide (1.55 g; 0.024 M) in water (10 cm<sup>3</sup>). After 1 h, a precipitate was formed, which was filtered, washed with water and dried. The filtrate was then evaporated under vacuum to a small volume, water added and a further quantity of precipitate filtered, washed with water, and suction dried under vacuum over P<sub>2</sub>O<sub>5</sub>. The combined colourless precipitates, totalled 1.2 g; 55.4% and were determined homogenous by TLC and used, without further purification (cyanuric azide and polyazido nitrogen rich molecules<sup>18</sup> can be explosive by nature and structural confirmation of such compounds require the use of crystallography<sup>17</sup> due to thermal decomposition and re-arrangement using mass spectral techniques, so was used as isolated).<sup>19</sup> Infrared Radiation (IR) ( $\nu_{\max}$ ) (nujol mull): 2350, 2159 cm<sup>-1</sup> (N)<sup>20</sup>.

### 2.2 4, 6-Diazido-N-(4-(4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolan-2-yl) phenyl)-1, 3, 5-triazine-2-amine (**4**)

A mixture of 4-aminophenylboronic acid pinacol ester (**3**) (0.3 g; 0.0014 M), 2, 4-diazido-6-chloro-1, 3, 5-triazine (**2**) (0.21 g; 0.0014 M), DMAP (0.008 g; 0.065 mM) was dissolved in a 1:1 mixture of THF & DIPEA (5 cm<sup>3</sup>) and the solution left stirring at room temperature (RT) for 20 h. Chloroform was then added to the reaction mixture and the solution washed with HCl (1 M), water, brine, dried (MgSO<sub>4</sub>) and evaporated under vacuum to give an oil. Titration of the oil (2 ×) with pet-ether (40-60) and decantation caused solidification of the product to give a colourless solid (0.2 g; 38.14%). Mp; 138-140°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.34 (s; 4 × CH<sub>3</sub>), 7.6 (d; 2 × ArH), 7.64 (bs; NH), 7.8 (d; 2 × ArH). C<sup>13</sup> (CDCl<sub>3</sub>)  $\delta$  25.0, 84.0, 119.5, 135.6, 141.5, 154.20. IR ( $\nu_{\max}$ ) (nujol mull): 3318 (NH); 2170, 2135 (N<sub>3</sub>), 1356 (B-O). HRMS: (ESI) m/z Calc for C<sub>15</sub>H<sub>16</sub>O<sub>2</sub>N<sub>10</sub>B [M-H] 379.1556 Found 379.1547.

### 2.3 N<sup>2</sup>-(4-(4, 4, 5, 5-Tetramethyl-1, 3, 2-dioxaborolan-2-yl) phenyl)-1, 3, 5-triazine-2, 4,6-triamine (**5**)

4, 6-Diazido-N-(4-(4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolan-2-yl) phenyl)-1, 3, 5-triazine-2-amine (**4**) (0.19 g; 0.0005M) dissolved in EtOH (5 cm<sup>3</sup>) containing Pd/C (10%) (0.015 g) was hydrogenated for 20 h. The solution was filtered through celite, washed with EtOH and EtOAc and evaporated under vacuum to give an oil which was dissolved in a small amount of acetone and precipitated with hexane as colourless crystals (0.13 g; 78.0%). Mp; 244-248°C (decomp). <sup>1</sup>H NMR (D<sub>6</sub>MSO)  $\delta$  1.31 (s; 4 × CH<sub>3</sub>), 3.87 (bs; H<sub>2</sub>O), 7.68 (d; 2 × ArH), 7.77 (d; 2 × ArH). C<sup>13</sup> (D<sub>6</sub>MSO)  $\delta$  25.3, 84.02, 120.18, 135.33, 142.79, 147.19, 160.31, 162.13. IR ( $\nu_{\max}$ ) (nujol mull); 3329, 3164 (NH); 1361 (B-O); HRMS (ESI) m/z Calc for C<sub>15</sub>H<sub>23</sub>O<sub>2</sub>N<sub>6</sub>B [M+H] 329.1892 Found 329.1896.

### 2.4 4-(4, 6-Diamino-1, 3, 5-triazin-2-ylamino) phenylboronic acid (**6**)

N<sup>2</sup>-(4-(4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolan-2-yl) phenyl)-1, 3, 5-triazine-2, 4,6-triamine (**5**) (0.050 g ; 0.00015 M) was dissolved in MeOH (3 cm<sup>3</sup>) and TEA.3HF (0.12 g; 0.00074 M) added drop wise to the stirred solution. After 24 h at room temperature, water was added to the solution and it was evaporated to dryness. The residue was suspended in water and extracted with EtOAc and the aqueous suspension evaporated to dryness. The residue was suspended in a small amount of water and filtered to give the product (0.019 g; 51.5%) as colourless crystals on drying over P<sub>2</sub>O<sub>5</sub>. Mp; 178-182°C. <sup>1</sup>H NMR (D<sub>6</sub>MSO)  $\delta$  7.3 (d; 2 × NH<sub>2</sub>), 7.7 (m; 4 × ArH), 9.73 (s, NH), 11.2 (bs, BOH). C<sup>13</sup> (D<sub>6</sub>MSO)  $\delta$  118.25, 121.44, 131.60, 150.87, 158.89, 176.24. IR (KBr), 3620, 3439 (B-OH), 3368, 3272, 3183 (N-H); 1326 (B-O). HRMS: (ESI) m/z Calc for C<sub>9</sub>H<sub>12</sub>N<sub>6</sub>O<sub>2</sub>B [M + H] 247.1109 Found 247.1113. HRMS (ESI) m/z Calc for C<sub>9</sub>H<sub>12</sub>N<sub>6</sub>B O<sub>2</sub> [M + Na] 269.0940 Found 269.0932.

### 2.5 3-(4, 6-Diazido-1, 3, 5-triazin-2-ylamino) phenylboronic acid (8)

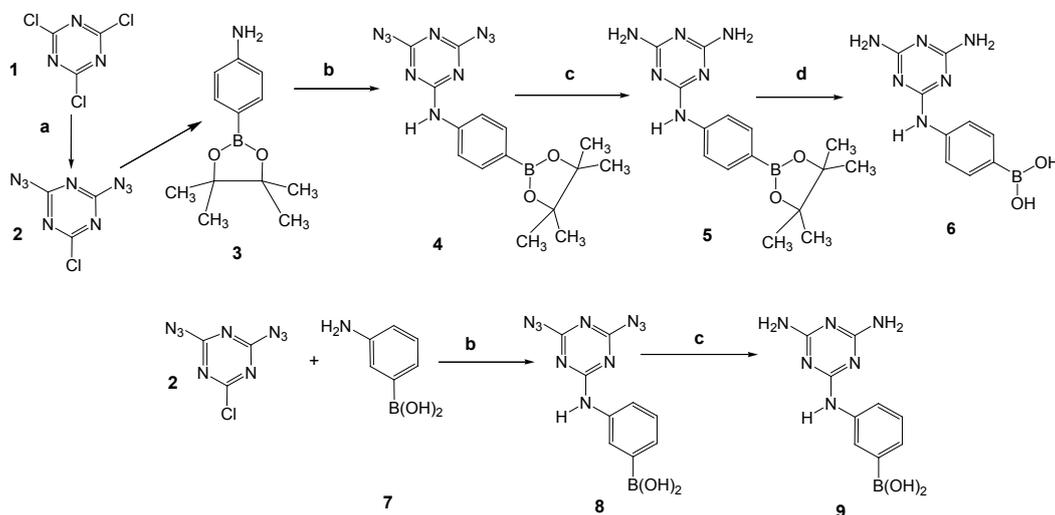
A mixture of 3-aminophenylboronic acid (7) (1.0 g; 0.0073 M), 2, 4-diazido-6-chloro-1, 3, 5-triazine (2) (1.0 g; 0.0064 M), DMAP (0.01 g; 0.082 mM) was dissolved in a 1:1 mixture of THF & DIPEA (20 cm<sup>3</sup>) and the solution left stirring at RT for 20 h. The solution was partially evaporated to remove THF and extracted with pet ether (60-80°), then acidified with HCl (1 M) and extracted with EtOAc with a small amount of MeOH to solubilise undissolved material. Then washed with water, brine, dried (MgSO<sub>4</sub>) and evaporated under vacuum to give a colourless solid (0.54 g; 28.1%). Mp; > 360°C (decomp). <sup>1</sup>H NMR (D<sub>6</sub>MSO) δ 3.8 (s, B(OH)<sub>2</sub>, NH, 2 × NH<sub>2</sub>, H<sub>2</sub>O), 7.31 (t, Ar-H), 7.55 (d, Ar-H), 7.66 (t, t, Ar-H), 7.99 (s, Ar-H). C<sup>13</sup> 123.85, 127.83, 128.13, 130.50, 137.51, 165.41, 170.06, 170.92. IR (ν<sub>max</sub>) (KBr) 2174, 2135 (N<sub>3</sub>), 1341 (B-O). HRMS (ESI) Calc for C<sub>9</sub>H<sub>7</sub>N<sub>10</sub>O<sub>2</sub>B [M + H] 299.0924 Found 299.0924.

### 2.6 3-(4, 6-Diamino-1, 3, 5-triazin-2-ylamino) phenylboronic acid (9)

3-(4, 6-Diazido-1, 3, 5-triazin-2-ylamino) phenylboronic acid (8) (0.3 g; 0.001 M) dissolved in EtOH (5 cm<sup>3</sup>) containing Pd/C (10%) (0.04 g) was hydrogenated for 20 h. The solution was diluted with hot ethanol and filtered through celite, washed with EtOH and evaporated under vacuum to give an oil which solidified to give cream coloured crystals. The crystals were titrated in diethyl ether, filtered and obtained as cream coloured crystals (0.19 g; 76.2%). Mp; 220°C (decomp). <sup>1</sup>H NMR (D<sub>6</sub>MSO); δ 3.7 (bs, B(OH)<sub>2</sub>, NH, 2 × NH<sub>2</sub>, H<sub>2</sub>O); 7.3 (t, Ar-H), 7.56 (d, Ar-H), 7.72 (t, Ar-H). C<sup>13</sup> (D<sub>6</sub>MSO); δ 125.07, 128.40, 128.59, 130.86, 137.20, 141.73, 167.0. IR (ν<sub>max</sub>) (nujol mull); 3343 (B-OH), 3188 (NH); 1338 (B-O); HRMS (ESI) Calc for C<sub>9</sub>H<sub>11</sub>N<sub>6</sub>O<sub>2</sub>B [M + H] 247.1109 Found 247.1112.

## 3. Results and discussion

As shown in Figure 3, commercially available 4-aminophenylboronic acid pinacol ester 3 was used as the starting material as well as 3-aminophenylboronic acid, 7. 3-Aminophenyl boronic acid was investigated to ascertain if the technique could be used without boronate group protection, in regard to product isolation and purification.



**Figure 3.** Reagents and conditions: (a) Sodium azide, (CH<sub>3</sub>)<sub>2</sub>CO/H<sub>2</sub>O, 0°C, 1 h; (b) THF/DIPEA, DMAP, RT, 20 h; (c) Pd/C/EtOH, 20 h, RT; (d) TEA.3HF/MeOH, 24 h, RT

Our synthetic strategy was to identify a triazine reagent with enhanced electrophilic character, where the diamino groups were masked, as in, 2, 4-diazido-6-chloro-1, 3, 5-triazine, 2. The role of the diazo groups was to improve the electrophilic characteristics of the chlorine on the triazine ring, to nucleophilic substitution whilst enhancing the

compounds solubility in organic solvents. The conjugation of the diazo groups with the triazine ring, also enhanced the UV fluorescence quenching properties of the reagent, allowing the reaction to be followed by Tlc,  $F_{254}$  and its incorporation into the product by IR, two  $N_3$  peaks ( $2364$  &  $2132\text{ cm}^{-1}$  for HTPB-DT).<sup>19</sup> Compound **2** was prepared as described in the literature<sup>19</sup> by reaction of cyanuric chloride, **1** with  $\text{NaN}_3$  (2 mols) at  $0^\circ\text{C}$  in aqueous acetone and isolated in good yield. The presence of two diazido group in **2** at  $2350$  &  $2159\text{ cm}^{-1}$ , by IR<sup>20</sup> confirmed the substitution of the two chlorines in **1**. Reaction of the triazine derivative **2** with **3**, under mild conditions in THF/DIPEA at room temperature gave the desired protected product, compound **4** without the need for extreme conditions confirming the facile nature of the reaction. IR confirmed the incorporation of the triazine group into the product the NH group at  $3318\text{ cm}^{-1}$ , the two  $N_3$  peaks, at  $2170$  &  $2135\text{ cm}^{-1}$ <sup>20</sup> and a peak for the boronate group<sup>21-24</sup> at  $1356$  (B-O). The structure of the compound was confirmed by  $^1\text{H}$  NMR, the pinacol ester at  $\delta$  1.31 and the aromatic peaks at  $\delta$  7.68-7.77, the  $\text{C}^{13}$  NMR and HRMS were in agreement with the molecular formula. Deprotection of **4** to **6** was undertaken via a two-step process that involved first the reduction of the diazido group to the diamino group using hydrogenation, with Pd/C (10%) to give **5** in good yield. The loss of the two  $N_3$  peaks in the IR at  $2170$  &  $2135\text{ cm}^{-1}$  and the appearance of two NH peaks at  $3329$  and  $3164\text{ cm}^{-1}$  in **5** confirmed the reduction of  $N_3$  to  $\text{NH}_2$ , and a peak a  $1361$  (B-O) for the boronate group. The  $^1\text{H}$  NMR confirmed the presence of the pinacol ester at  $\delta$  1.31 and aromatic group at  $\delta$  7.68-7.7. The  $\text{C}^{13}$  NMR and HRMS were in agreement with the molecular formula. Finally, the removal of the boronate ester group **5** was achieved by transesterification, using TEA.3HF in MeOH<sup>25</sup> to give the desired product **6**, in 51.5% yield. Removal of the pinacol ester group, resulted in the appearance of two new peaks in the IR, due to the B-OH group at  $3620$  and  $3439\text{ cm}^{-1}$ . The loss of the peak at  $\delta$  1.31 in the  $^1\text{H}$  NMR, confirmed removal of the pinacol ester and  $\delta$  7.7 the presence of the aromatic group. The  $\text{C}^{13}$  NMR, and HRMS were in agreement with the molecular formula.

Given the encouraging results in the preparation of compound **4** the reaction of reagent **2** was repeated with 3-aminophenylboronic acid, **7**, to test the generality of the reaction. Compound **8** was isolated in moderate yield and the presence of the diazo groups was confirmed in the product, by two  $N_3$  peaks in the IR at  $2135$  and  $2174\text{ cm}^{-1}$ .<sup>20</sup> The compound structure was consistent with the  $^1\text{H}$  and  $\text{C}^{13}$  NMR, and HRMS were in agreement with the molecular formula. Conversion of the diazido groups of **8** to the diamino **9** was undertaken as in **5** by hydrogenation with Pd/C (10%) to give the product in good yield. The IR confirmed the loss of the azido group and the compound structure was consistent with the  $^1\text{H}$  and  $\text{C}^{13}$  NMR, and HRMS were in agreement with the molecular formula.

## 4. Conclusion

In summary, we have synthesised a novel class of triazine compound containing a boronate group. The design concept involved an isosteric replacement of the arsenical group of melarsoprol by a topologically similar boronate group that is capable of adduct formation with oxygen and thiol ligands. The availability of a facile method, to introduce the melaminophenyl group has importance to developing new triazine molecules with labile functional groups under mild conditions (RT).

## Declaration of conflicting interests

The author declares no potential conflicts of interest with respect to the research, authorship and/or publication of this article.

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