Universal Set of Dyes for Digital Inkjet Textile Printing

Leader: Hitoshi Ujiie
Philadelphia University, Philadelphia, PA 19144

URL address: http://faculty.philau.edu/ujiieh

Project Goal:

The goal of this project is to develop a universal set of dyes for digital ink jet (DIJ) printers that allows printing on chemically diverse textile materials. An expected outgrowth of this project is the creation of an integrated, professional team of scientists within the Center for Excellence of Digital Inkjet Printing for Textiles at Philadelphia University that is devoted to fundamental research aimed at improving the performance and environmental compatibility of chemicals used for DIJ printing in the US textile industry.

Abstract:

The development of a set of dyes suitable for DIJ printing on diverse textile substrates is critical to the further integration of this technology into the printing segment of the textile industry. Chemical-sensor ligands using a boronic acid functional group as the recognition element, in conjunction with combinatorial chemistry, chemoinformatics, and molecular modeling are being used to develop a collection of dyes specifically designed for DIJ printing applications that eliminates the need to change ink cartridges when printing on chemically diverse materials such as cotton, polyester, and silk.

Background:

The global textile printing industry produces approximately 20 million linear meters annually, but North America currently controls only 10% of the market share. A greater portion of print production can be returned to the US by addressing several key issues: (1) rapid market responsiveness *via* mass customization, (2) cost reduction in mid- to short-runs, and (3) use of unique printing techniques to foster enhanced creativity of designers. A universal set of dyes for DIJ printing will impact all of these factors.

There is clearly a need to develop a universal printing system for textile materials that has the capacity and flexibility to keep pace with current, as well as future, trends in mass customization within the printing segment of the US textile industry. DIJ printing has the potential to provide such capacity and flexibility, but it has been adopted only for mid- to short-runs, due to its relatively slow application speed. Engineering improvements in DIJ hardware are being made, and application speeds will certainly increase as a result. However, DIJ technologies have matured more rapidly than the corresponding ink for textile printing. Unlike the graphics industry from which this technology evolved, textile companies that process chemically different substrates face expensive and time-consuming operations whenever ink/fabric combinations must be changed. Many firms have resorted to utilizing different DIJ printers for each ink/fabric combination to prevent frequent ink cartridge changes.

The availability of a set of dyes for DIJ printing that can function on multiple textile substrates will benefit the textile industry in a variety of ways, *e.g.* by decreasing the need for companies to maintain a complex inventory of colorants and by significantly reducing machine down time. In addition, the economic and environmental costs of unused dye in printing effluents can be minimized.

Over the past decade, there has been significant interest in the US in developing a universal set of dyes [1,2,3]. However, the general approach has been to retrofit existing chemical systems for ink formulations, and pre-and post-treatments of substrates, rather than explore alternative "chemistries" specifically designed for the stringent requirements of DIJ technology.

Approach:

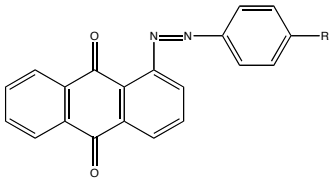
A multi-disciplinary approach using chemical-sensor technology, combinatorial chemistry, chemoinformatics, and molecular modeling is being employed to develop dyes that exhibit chemoselective affinity for a variety of chemically different textile substrates, that display superior technical properties, and that are environmentally safe. This is a formidable task because of the polar or ionic nature of some substrates (*e.g.* cotton and silk) and the hydrophobic nature of others (*e.g.* polyester and nylon). Ordinarily, printing such chemically diverse materials requires significantly different types of dyes and/or pretreatments. The core idea in this project is to graft chemical-sensor subgroups onto anthracene and anthraquinone chromophores that can serve as affinity ligands and effectively distinguish between different substrate functional groups. This type of approach has proved to be extremely beneficial in medicinal chemistry [4], but it has not been explored in the context of textile chemistry or DIJ printing technology. In addition to introducing chemical-sensor technology to the printing industry, other approaches, including immobilization, and derivatization, with a variety of groups present as a linker system, are being actively pursued.

For those unfamiliar with combinatorial chemistry, it is an approach employed in synthetic organic chemistry that entails a grid-based sampling of physical and chemical variables [5]. In less than a decade "combichem" has developed from a curiosity to a technique that has become an integral component of the daily operation in many leading national and international research and development laboratories [6]. The purpose of using combinatorial chemistry in this project is twofold. First, to quickly assemble a collection of compounds for screening, with the objective of finding one or more "lead" structures with the desired colorimetric and chemoselective properties. Second, once a lead compound is found, combinatorial chemistry can focus on synthesis of non-genotoxic analogues with an enhanced range of chromaticities and chemoselectivity toward targeted textile substrates. One of the many challenges in using combinatorial synthesis is to select the necessary building blocks and reaction conditions that are synthetically amenable to automation while leaving benign chemical by-products.

Progress:

In the first year of this project (seed project) a set of building blocks for the construction of a new molecular framework that contains *both* the anthraquinone and azo chromophore was identified and a practical synthetic methodology was established. The methodology developed

was an extension of previous azo dye research conducted in the Center but focused on the targeted anthraquinone chromophore. The chemistry we developed was demonstrated and a variety of new dyes that contain the basic skeleton shown below were synthesized.



In Table 1 the physical data for five representative new dyes are shown; their technical textile properties, *e.g.* lightfastness, washfastness, and substantivity have also been assessed using conventional AATCC procedures and were generally found to be quite good.

Table 1: **Physical Characteristics of Selective Anthraquinone Dyes**

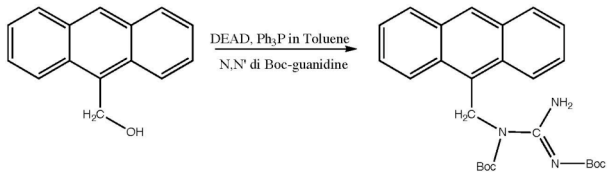
R	**Yield %**	**Melting Point °C**	λ_{max}, nm (methanol)	**Log ε**
$-NH_2$	65	228-229	475	3.45
$-NMe_2$	80	239-240	430	3.84
-OH	78	242-243	410	3.18
-OMe	53	237-238	472	3.18
$-B(OH)_2$	70	230-231	470	3.43

The boronic acid group was specifically chosen because this functionality is known to form esters with vicinal diols such as carbohydrates, and this property has been utilized in the synthesis of several chemical sensors designed for medicinal purposes [4]. Unfortunately the values of λ_{max} and log ε for the new dyes in Table 1 showed only a marginal improvement compared to anthraquinone itself. Density functional theory (DFT) [7,8] and ZINDO semi-empirical calculations on the 3D-structure of azobenzene, N,N-dimethylaminoazobenzene and 4-(phenylazo)benzene boronic acid provide computational support for these experimental data [9]. Calculations also showed that formation of the boron-oxygen-carbon (B-O-C) linkage in the model dehydration reaction

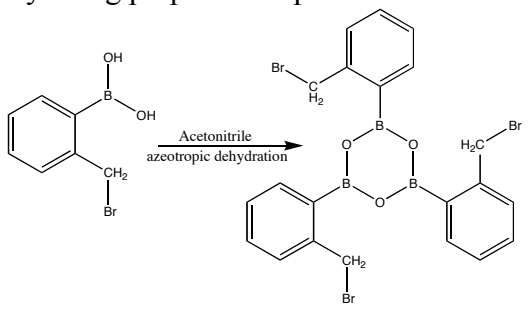
$$H_2B(OH) + H_3C\text{-}OH \longrightarrow H_2B\text{-}O\text{-}CH_3 + H_2O$$

is initiated by a nucleophilic attack of the methanol oxygen atom on the electron deficient boron atom [10]. Reaction barriers for the formation of the bornate ether in this reaction proved to be rather high. Thus, at the beginning of the second year, our experimental efforts were expanded to incorporate two binding sites on the dyes being synthesized: a reactive guanidinium moiety, $-CH_2NHC(NH_2)NH$ was added to the dye framework. We speculated that the cationic nature of the guanidinium group had the potential to enhance both the solubility properties of our boronic acid-based dyes and improve their electrostatic interactions with ionic substrates. In fact, the power of including a guanidinium group for the binding of anionic guest molecules in competitive media was recently demonstrated [11]. We developed a novel methodology to incorporate the guanidinium group onto an anthracene unit, in a single step, using a revised version of the Mitsunobu reaction [12,13]. Since the use of solid supports to facilitate combinatorial synthesis has become a popular way of generating libraries of new compounds

with desired properties; this procedure was also extended to the use of polymer supported reagents.



We also developed an efficient, one-step synthesis of a boronic acid anhydride, 2,4,6-tris [o-(bromomethyl) phenyl]boroxine ("boroxin"), a key intermediate in the synthesis of many saccharide, photo-induced electron-transfer sensors. A manuscript describing the details of this novel methodology is currently being prepared for publication.



The need to develop dyes with minimal adverse genotoxic behavior was addressed computationally during the second year using semi-empirical quantum chemical methodology. Quantitative structure-activity relationships (QSARs) for the mutagenicity of a variety of azo dyes were developed. This was accomplished within the context of the largest database of amino compounds (for which the mutagenicity has been measured) that has ever been collected - over 180 derivatives are currently in the database. We showed that multilinear regression techniques can account for approximately 66% of the observed mutagenic behavior and that artificial neural network (ANN) approaches, in conjunction with fuzzy logic, [14,15] can account for more than 90% of the variation. These QSARs provide us with a preliminary screening device for new dyes.

We have also studied computationally the formation of a representative 5-membered *cyclic* boronate ester, HB(-O-CH_2-CH_2-O-), from the dehydration of $HB(OH)_2$ and HO-CH_2-CH_2-OH [16]. Our calculations support the view that this reaction occurs *via* a stepwise, rather than concerted, mechanism: the monoester HB(OH)-O-CH_2-CH_2-OH is formed in an initial bimolecular dehydration step, which subsequently undergoes unimolecular elimination to form the cyclical ester. In the absence of any catalyst, the activation enthalpy for the bimolecular dehydration step, +21.7 kcal/mol, and for the unimolecular elimination, +29.9 kcal/mol, are both rather high and formation of HB(-O-CH_2-CH_2-O-) would proceed slowly. It should be noted that in the reaction field of the aprotic solvent acetonitrile, the activation enthalpy of the bimolecular dehydration *increases* while that of unimolecular elimination *decreases*, leading to activation barriers for the two steps that are within ~1 kcal/mol of each other. Nevertheless, the overall process would be quite slow in acetonitrile.

Our molecular modeling in the second year also focused on understanding the thermodynamics and kinetics of the reaction in which the amino group acts as an internal Lewis base to catalyze the reaction. These studies showed that a primary amine located proximal to a monohydroxy

borane moiety can significantly lower the activation energy for the formation of a B-O-C linkage in the reaction [17]

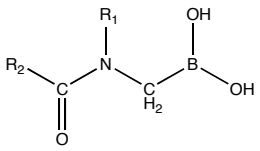
$$H_2N\text{-}CH_2\text{-}CH{=}CH\text{-}BH(OH) + H_3C\text{-}OH \longrightarrow H_2N\text{-}CH_2\text{-}CH{=}CH\text{-}BH(OCH_3) + H_2O.$$

During the first two years of this project it became increasingly evident from both an experimental and theoretical perspective that an internal Lewis base, positioned proximal to the boronic acid moiety, would be required to catalyze ester formation with a cellulosic substrate. Thus, in the third year of this project we concentrated on fundamental scientific issues related to the role of a Lewis base on boronate ether and ester formation. Significant questions have been raised recently in the literature about the strength and utility of intermolecular B-N dative bonds. It had previously been hypothesized that, upon binding of a saccharide to the boronic acid group, the increased acidity of the boron atom promoted the formation of a B-N dative bond *via* a 5-membered ring. Recent data suggest that such B-N dative bonds may *not* be present in the boronate esters formed between boronic acids and saccharide molecules *in aqueous media* due to a competing solvolysis process leading to formation of Zwitterionic structures [18].
These concerns have been addressed during the first half of the third year of this project by the following:

- The differential affinity of boron toward the oxygen and nitrogen lone pairs of electrons in 2-aminocarbonylphenyl boronic acid and its corresponding ester was established for the first time *in vacuo* and in a variety of solvents. Conformers with a (:O=C-C⋯C-B) 5-membered ring motif are consistently found to be more stable than those with the analogous (:N=C-C⋯C-B) motif [19]. This finding has altered our short-term synthetic strategy. It should be mentioned that our publications in boronic acid chemistry [3-5,8,13] funded by the NTC, have attracted the attention of two of the three main experimental groups developing boronic acids for chemical sensors and medicinal purposes; W.W. Bachovchin and Jack H. Lai at Tufts University, and T.D. James in the UK. We plan to initiate contact with the Wang group at NCSU soon. Several joint manuscripts involving these groups are currently in preparation.

- In conjunction with Dr. Doug Markham at the Fox Chase Cancer Center, Philadelphia, Pa., the role of a 7-membered hydrogen-bonded ring conformer and a 5-membered dative-bonded ring conformer of the model aminoboronic acid $H_2N\text{-}CH_2\text{-}CH{=}CH\text{-}B(OH)_2$ have been established. Furthermore, the mechanism for the formation of a B-O-C linkage has been investigated for the reaction of $H_2N\text{-}CH_2\text{-}CH{=}CH\text{-}B(OH)_2$ and a simple aliphatic alcohol, $H_3C\text{-}OH$, to give the boronate ether $H_2N\text{-}CH_2\text{-}CH{=}CH\text{-}B(OH)(OCH_3)$ and H_2O [20]. Interestingly, the catalytic role of the primary amine in this compound is not a consequence of intramolecular B-N dative bond formation as we originally thought. Rather, the catalytic effect is a result of the ability of the amine to act as a proton acceptor during a 1,3-proton shift in the process in an intermolecular B-O dative bonded adduct. This is an important result since, as noted above, it appears that it will be necessary to catalyze the formation of a B-O-C linkage in cellulosic materials. A manuscript reporting the results of this work is nearly complete and will be submitted for publication soon.

- In conjunction with Dr. Jack Lai at Tufts University, six new N-acyl-boroGly derivatives, along with their N-acyl-boroSar analogs, have been synthesized by modification of conventional procedures.

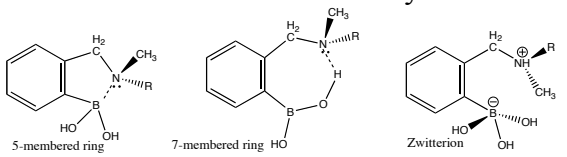


1a: R_1=H, R_2=H
1b: R_1=H, R_2=Me
1c: R_1=H, R_2=Et
1d: R_1=H, R_2=t-Bu
1e: R_1=H, R_2=CF_3
1f: R_1=H, R_2=C_6H_5

2a: R_1=Me, R_2=H
2b: R_1=Me, R_2=Me
2c: R_1=Me, R_2=Et
2d: R_1=Me, R_2=t-Bu
2e: R_1=Me, R_2=CF_3
2f: R_1=Me, R_2=C_6H_5

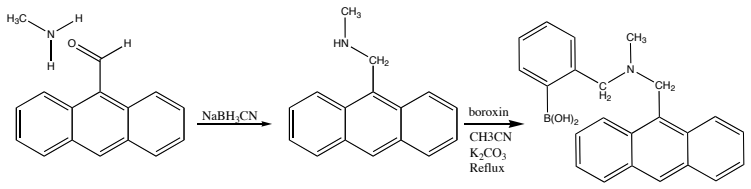
Structural characterization of these α-boronic acids was accomplished by extensive use of ^{11}B, ^{13}C, and ^{1}H NMR spectroscopy. These compounds were prepared to determine the extent of intramolecular B-O dative bond formation within the context of a 5-membered (:O=C-N-C-B) ring motif. It has been shown that the formation of such dative bonds depends on the nature of the substituent at both the acyl carbon (R_2) and nitrogen (R_1) atoms. Computational evidence from second-order Møller-Plesset pertubation theory (MP2) support these findings. A manuscript reporting these results has been submitted [21].

- During the third year, we suspended synthesis of molecular structures containing the aromatic guanidinium functional group in lieu of non-aromatic nitrogenous structures with the capacity to form intramolecular 5-membered ring, 7-membered ring or Zwitterions when proximal to a boronic acid moiety.

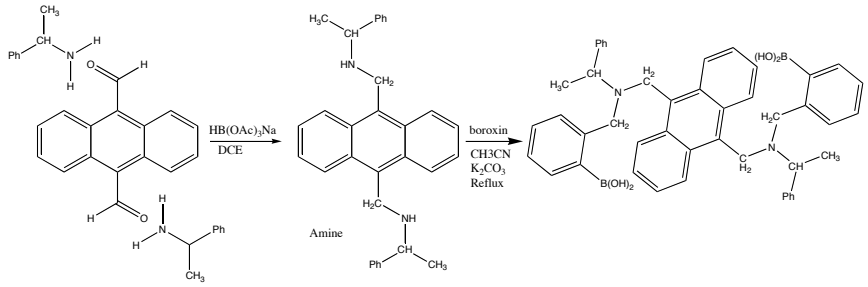


Our initial combinatorial efforts focused on synthesizing binding sites at the 9,10 positions of an anthracene chromophore that would facilitate Lewis acid-base intramolecular interaction between nitrogen and boron. The first synthetic route utilized a two-step reduction [22] of the di-functional aldehyde, 9,10 anthracene dicarboxaldehyde, followed by reaction of the resultant imine with a primary amine, α-methylbenzylamine, using sodium borohydride ($NaBH_4$) to produce a reactive iminium ion. The subsequent reaction with 2,4,6-tris[o-(bromomethyl)phenyl]boroxine ("boroxin") produced the di-functional boronic acid moieties. Isolation, purification, and characterization of the intermediates and product have proven to be very difficult.

- A one-step synthesis of similar compounds was explored using the cyanohydridoborate anion (BH_3CN^-), which selectively reduces aldehyde and imines functional groups [23]. Careful adjustment of pH and temperature provides a means of controlling undesirable, competing side reactions. The di-functional aldehyde, 9,10 anthracene dicarboxaldehyde, and a mono-functional aldehyde, 9-anthraldehyde, in combination with methylamine, have been reacted under similar conditions. Although the one-pot process is attractive for use in combinatorial syntheses, excessive reaction time [72-96 hours] and production of toxic hydrogen cyanide gas as a by-product made this synthetic route undesirable.



- A one-step reductive amination reaction conducted using triacetoxyborohydride provided a safer alternative [24]. The reducing agent converted stoichiometric amounts of the dicarboxaldehyde and 1° amine (methyl amine or α-methylbenzylamine) to the corresponding 2° amines in high yields, requiring a much shorter reaction time [20 min.-2 hr.] while producing only small amounts of benign by-products. Due to the high reactivity of the free amines, an oxygen-free environment was required throughout the reduction reaction. Stable ammonium chloride salts have been isolated, and purification and characterization are currently being carried out. It is anticipated that, by maintaining an oxygen-free environment, the reaction with 2,4,6-tris[o-(bromomethyl)phenyl]boroxine can be conducted immediately following the reductive amination without the HCl salt formation.



Future Work:

Experimental work during the remaining months of this project will focus on developing the combinatorial synthetic route for colored chromophores that contain the boronic acid group to act as a molecular switch in the presence of cellulosic materials. We now have a relatively rapid and safe route to use for the syntheses of anthracene-based molecules using our combichem approach. In addition, the proximity of nitrogen in the structure will facilitate boronate ester formation between boronic acid and cellulose. Intramolecular B-N dative bonds and/or Zwitterion formation will create a reactive environment at near neutral conditions. During the remainder of this year we will also couple the boronic acid functional group with existing, commercially available anthraquinone colorants to compare their technical behavior with the performance of unmodified dye molecules

We are also beginning to focus on ink formulations from the dyes developed in this project. Preparation of inks with the proper rheology, homogeneity, and fixations properties is a complex issue but extremely critical. It is complicated by the presence of the boronic acid moiety on the dye that has the potential of reacting with many of the glycolic agents commonly in such inks used to increase viscosity. A fine balance must be maintained between developing inks that optimize drop formation and those that create sharp, dense, and permanent images. Ink formulations combining some, or all, of the following components will be initiated: demineralized water, hygroscopic thickener, dye, surfactant, biocide, buffer. Performance of all

new inks with respect to jettability, jet sustainability, flow rate, decap, colorfastness, etc. will be evaluated on Epson DX-3 piezo electric ink jet printing systems, which is widely used in current digital textile printing and is available in Philadelphia University's Center for Excellence of DIJ Printing for Textiles. The quality of the image will be quantified using line (blurriness and raggedness) and area (grain, mottle, and density) analyses using the Image Analysis System (IAS) based on ISO 13660.

Current modeling studies are focused on adapting the fundamental results we have established for boronic acids, ethers, and esters to the azo and anthraquinone dyes for DIJ printing. In particular we are now modeling a boronate-cellulose system initially using semi-empirical methodology.

Contacts with Industry:

This project has been conducted in conjunction with the Center for Excellence of Digital Ink jet Printing for Textiles at Philadelphia University. The following industrial partners of the Center agreed to collaborate with The Center: Ciba Specialty Chemicals Corporation USA, Mutoh America, Inc., MacDermid Colorspan, DuPont, Wasatch Computer Technology, Mimaki USA, and Rohm and Haas.

Acknowledgements:

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