Rubazonic acids: Promising organic dyes for functional materials

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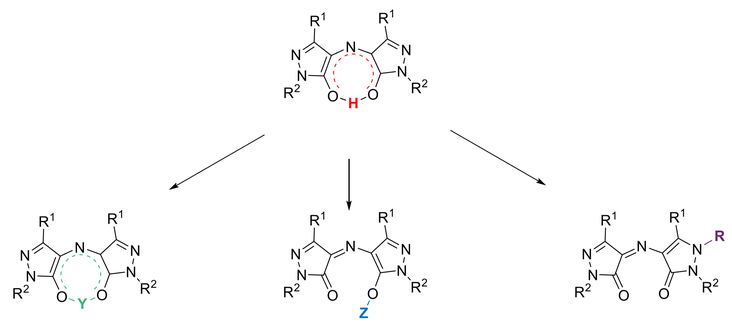
Introduction

Rubazonic acids were first described by *Ludwig Knorr* as early as 1887.[1] These unique organic dyes exhibit a vibrant red color that is pH-dependent, along with pronounced solvatochromism.[2] The presence of a structurally defining, highly intriguing O-H-O hydrogen bonding interaction imparts the c_2-symmetric character of these molecules.[3] This acidic hydrogen position has been acknowledged for its reactivity, notably in facilitating the exchange of metal ions.[3,4] However, despite this reactivity of Rubazonic acids, studies concerning their synthesis, properties, and applications have remained relatively scarce.[5] In 2020, our group developed a highly practical one-pot procedure for Rubazonic acid synthesis using a diazidation and reduction sequence[2] from readily accessible pyrazolones.

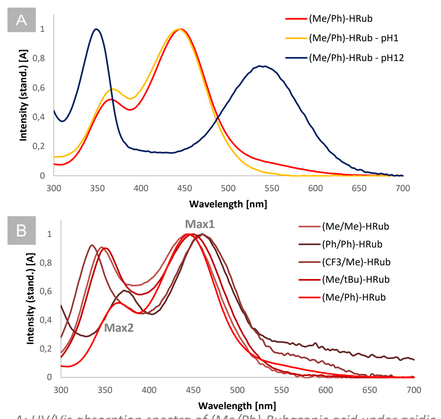
Consequently, we now present the variety of Rubazonic acid derivatives and their downstream products to evaluate potential future applications in functional materials.



Synthesis of Rubazonic acid derivatives

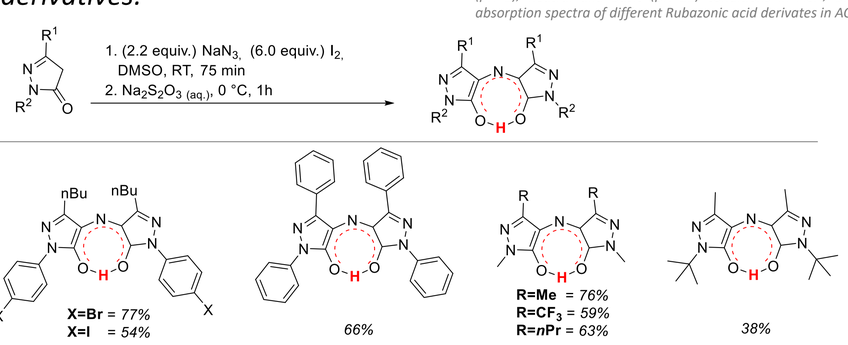
Synthesis[2] of Rubazonic acid derivates

- starting from readily accessible pyrazolones
- moderate to good yields
- intensive orange/ red color
  - pronounced pH dependency (pH=1 - 12)
  - Max1: minor shifts due to variation of R^1 / R^2
  - Max2: major shifts due to variation of R^1 / R^2



A: UV/Vis absorption spectra of (Me/Ph)-Rubazonic acid under acidic (pH=1), neutral and basic (pH=12) conditions in ACN; B: UV/Vis absorption spectra of different Rubazonic acid derivates in ACN.

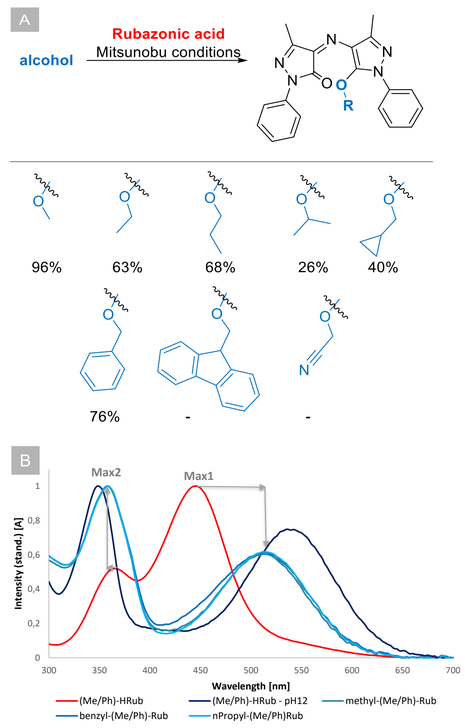
Selected Rubazonic acid derivatives:



Selective alkylation of Rubazonic acids

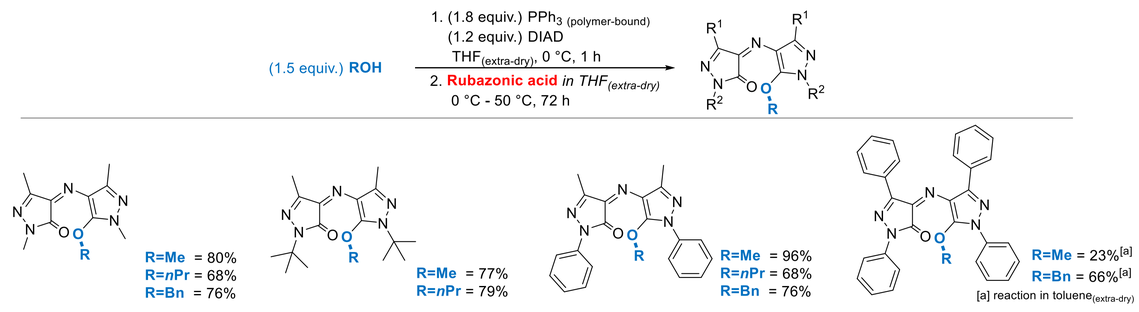
A Selective O-alkylation of Rubazonic acids

- broad variety of alcohols used
- up to 96% yield
- challenging isolation from both DIAD and O=PPh_3 was successfully overcome
- color change to pink/violet
  - Max1: bathochromic & hypochromic shift
  - Max2: hypsochromic & hyperchromic shift
  - resemblance with basic/deprotonated form (pH=12)
  - no significant dependency on the type of alcohol
  - no significant pH dependency
- unsymmetrical molecules
- optimized conditions
  - simplified workup by using polymer-bound PPh_3
  - initially activating the alcohol prior to its treatment with Rubazonic acids



A: Synthesis of O-alkylated (Me/Ph)-Rubazonic acids using various alcohols; B: UV/Vis absorption spectra of selected O-alkylated (Me/Ph)-Rubazonic acids in comparison to (Me/Ph)-Rubazonic acid under neutral and its deprotonated form under basic (pH=12) conditions in ACN.

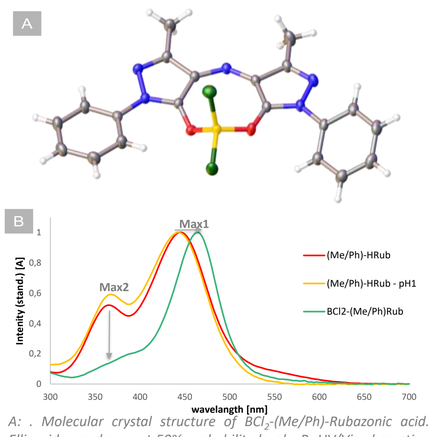
Expanded scope of O-alkylated Rubazonic acid derivatives :



New class of Rubazonic acid based dioxaborinanes

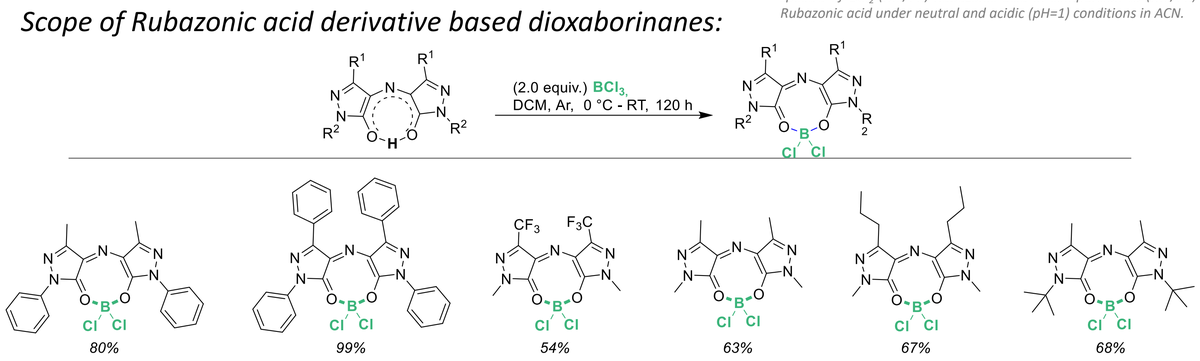
Rubazonic acid based dioxaborinanes

- mild reaction conditions
- symmetrical molecules: so far unknown tetravalent BCl_2-moiety bridging oxygens confirmed by X-Ray analysis
- color change to yellow/light orange
  - Max1: minor bathochromic shift
  - Max2: hypochromic shift (~ disappears)
  - no resemblance with neutral or acidic form (pH=1)



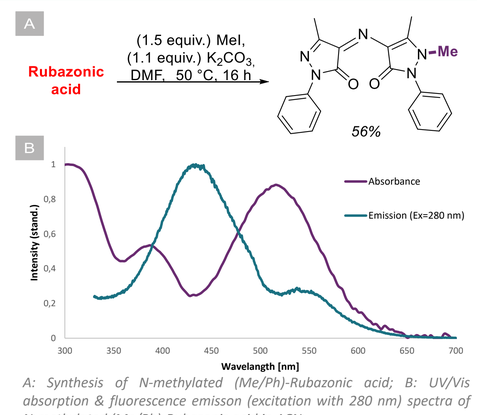
A: . Molecular crystal structure of BCl_2-(Me/Ph)-Rubazonic acid. Ellipsoids are drawn at 50% probability levels; B: UV/Vis absorption spectra of BCl_2-(Me/Ph)-Rubazonic acid in comparison to (Me/Ph)-Rubazonic acid under neutral and acidic (pH=1) conditions in ACN.

Scope of Rubazonic acid derivative based dioxaborinanes:



B Selective N-alkylation of Rubazonic acids

- color change to pink/violet
  - UV/Vis absorption spectra differing from basic/ deprotonated (pH=12) and O-alkylated form
- unsymmetric molecules
- structure confirmed via 2D-NMR
- significant fluorescein properties

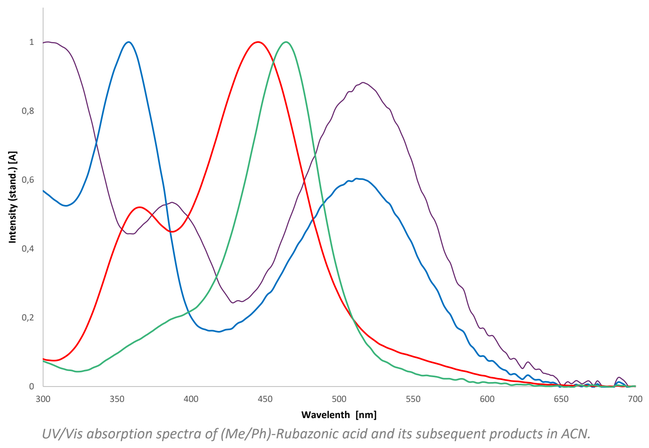


A: Synthesis of N-methylated (Me/Ph)-Rubazonic acid; B: UV/Vis absorption & fluorescence emisson (excitation with 280 nm) spectra of N-methylated (Me/Ph)-Rubazonic acid in ACN.

Summary & Outlook

Starting with easily accessible pyrazolones, we have successfully documented the synthesis of derivatives of Rubazonic acid and its subsequent compounds. We have effectively demonstrated the selective alkylation targeting both the oxygen and nitrogen atoms, resulting in pink/violet products, each exhibiting distinct UV/Vis spectra. Furthermore, we have showcased the synthesis of a novel category of Rubazonic acid-derived dioxaborinanes.

Our investigation encompassed a variety of Rubazonic acid derivatives, allowing us to thoroughly characterize their noteworthy optical and electronical properties.



UV/Vis absorption spectra of (Me/Ph)-Rubazonic acid and its subsequent products in ACN.

Our ongoing research in the field of materials science is focusing on the advancement of polymers incorporating Rubazonic acid both as an organic dye and as a functional unit.

Additionally, we are investigating the applicability of Rubazonic acid and its derivatives in functional materials, leveraging the UV/Vis shifts to create optical sensors for both physical and chemical detection.

[1] L. Knorr, *Liebigs Ann. Chem.* **1887**, 238, 137– 219; [2] M. L. Tong, L. T. Leusch, K. Holzschneider, S. F. Kirsch, *J. Org. Chem.* **2020**, *85*, 6008; [3] a) W. Hänsel, *Liebigs Ann. Chem.* **1976**, 1380; b) G. Cerchiaro, A. M. Da Costa Ferreira, A. B. Teixeira, H. M. Magalhães, A. C. Cunha, V. F. Ferreira, L. S. Santos, M. N. Eberlin, J. M.S. Skakle, S. M.S.V. Wardell, *Polyhedron* **2006**, *25*, 2055; [4] O. V. Kovalchukova, S. B. Strashnova, A. B. Ilyukhin, V. S. Sergienko, B. E. Zaitsev, O. V. Volyanskii, O. V. Korolev, T. Y. Dutova, *Russ. J. Coord. Chem.* **2010**, *36*, 751; [5] S. Bratan-Mayer, F. Strohbusch, W. Hänsel, *Z. Naturforsch.* **1976**, *31*, 1106.