

Organic Boron-Nitrogen Dyes

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ABSTRACT The combination of a boron group and an amino group connected *via* aromatic or conjugated olefinic π -systems leads to the formation of the following novel, structurally different types of organic boron-nitrogen dyes: *B,N*-arylmethane dyes, *B,N*-cross-conjugated indigo systems and annaromatic *B,N*-pentalenes have been synthesized and characterized for the first time after their spectroscopic properties had been calculated. All of these dyes having the *B,N* chromophoric system show very interesting spectroscopic properties. Potential optoelectronic applications are discussed.

ORGANIC BORON-NITROGEN DYES

Polarized π -electron systems are important because they act as chromophores in organic dyes and, furthermore, are of increasing importance as materials with non-linear optical properties used in optoelectronic techniques. Usually, both electron donating and electron withdrawing groups are connected *via* aromatic or conjugated olefinic π -systems, resulting in an internal charge-transfer band in the UV-VIS area.

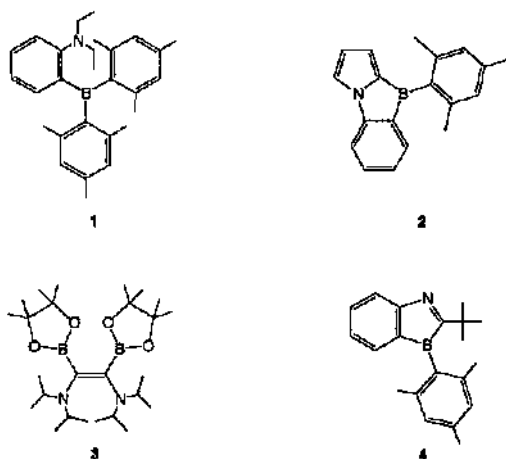
Based on calculations of their spectroscopic properties we have synthesized the following three types of organic dyes with different *B,N* chromophoric systems for the first time.

In the frequently used arylmethane dyes, conjugation is transferred over the central carbenium ion. Formally, such a carbenium ion is isoelectronic with an sp^2 -hybridised boron atom and replacement of the former by the latter leads to the novel class of organic dyes 1. We have developed a general and simple approach to arylmethane dyes as well as pyrrole- and indole-arylboranes, starting with commercially available starting materials. The stepwise

procedure allows the introduction of three different aryl substituents. The stability of the products towards air and water could be increased distinctly by the introduction of two sterically demanding *o*-disubstituted arènes at the boron atom. Solid state parameters were derived from X-ray structure analyses.

With the exception of boroles, only little is known about ann-aromatic boron heterocycles. Therefore, we became interested in the synthesis and properties of derivatives of the anti-aromatic π -electron, bicyclic pentalene and *ab initio* calculations for the parent compound. Combination of nitrogen and boron within the benzopentalene skeleton led to the first air and heat sensitive 8-borafluorazene derivative 2.

Indigo is the best known, classical example of a cross-conjugated chromophoric system. Formal substitution of the carbonyl groups by boron leads to the first example of the parent m -chromophore 3. A potential type of precursor molecule to a diboraindigo dye is represented by the benzoazaborole 4. Their syntheses are discussed in detail.



In order to study the optical properties of the dyes in detail, we have measured their UV and fluorescence spectra. Especially, the organic *B,N* dyes of type 1 show a strong fluorescence with very high quantum yields. The polar excited states are especially stabilized by polar solvents. We have observed a strong shift of the emission maxima going from cyclohexane to DMSO without any significant change in the excitation spectra. Potential applications of these novel organic boron-nitrogen dyes in the field of optoelectronic effects and sensor systems are discussed.

CONCLUSION

The combination of boron and nitrogen as pull and push substituents represents a novel type of chromophoric systems which can be inserted into different structural types of organic dyes. Due to a very efficient interaction of boron and nitrogen these systems show a very strong fluorescence in combination with a strong solvatochromy. Resulting potential applications in the fields of optoelectronic and sensor technologies are now under discussion.

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