The investigation of the H-chromophore dyes and their application

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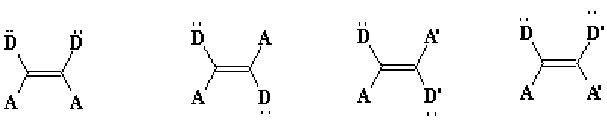
1. ABSTRACT

H-Chromophores have technically useful oxidation-reduction properties, which have been exploited for thousands of years in textile dyeing by the "*vatting*" process. Thus indigoid-type dyes can be reduced in a two-stage process to the so-called "*leuco dianions*", which unlike the original dyes are readily soluble in water and have a high affinity for cellulosic fibers. In recent years this redox behavior has also found use in the area of functional dyes, particularly where the color change associated with reduction/oxidation can be employed in sensors and indicators, *e.g.* in enzyme assay and diagnostic systems.

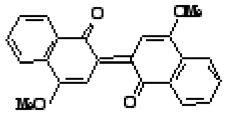
2. INTRODUCTION

H-Chromophores are a special type of donor-acceptor system, and can be regarded as made up of two cross-conjugated donor-acceptor systems sharing a common conjugating bridge. 1 (a) and (b) represent symmetrical cis and trans H-chromophores respectively, and (c) and (d) represent corresponding unsymmetrical H-chromophores (Figure 1).

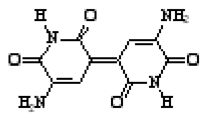


(a) (b) (c) (d)

Figure 1. Schematic representation of H-Chromophores (D represents an electron donor group, A an electron acceptor group). Other types of heterocyclic and carbocyclic H-chromophores are known, for example (1) and (2).



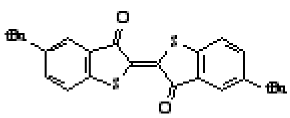
(1)

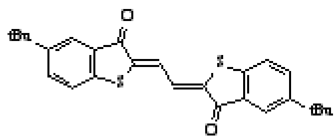


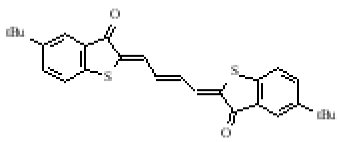
(2)

λ_{max}(benzene) = 633 nm λ_{max} (DMSO) = 612 nm

The true H-Chromophores are exceptional in that they do not obey the usual rules for the effect of extended conjugation on the absorption wavelength. For example, the thioindigo vinylogues (3)-(5) show a progressive trend towards shorter wavelengths as the length of the conjugating bridge increases.[1)]





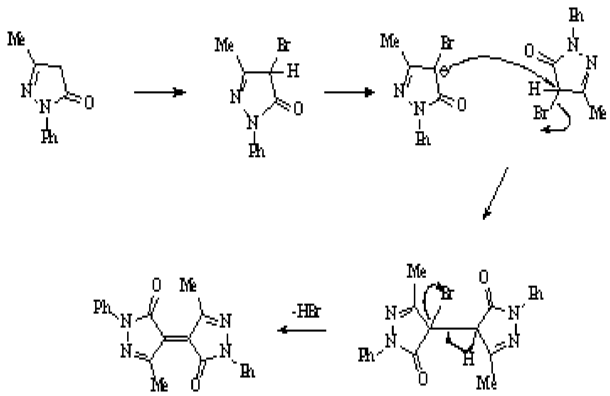


(3) (4) (5)

λ_{max} (benzene) = 554 nm (3) λ_{max} (benzene) = 534 nm (4) λ_{max} (benzene) = 532 nm (5)

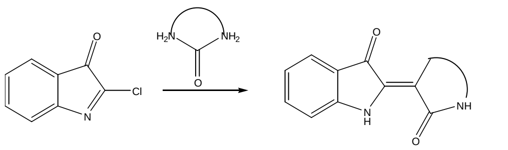
3. EXPERIMENT and DISCUSSION

The pyrazolone system was next considered, as the derivative can be converted to "*Pyrazole Blue*", the latter being known for many years, although it has no technical value as a colorant.[2)] This blue compound can be synthesized by a dimerization/elimination process using 4-bromo-3-methyl-1-phenyl-5-pyrazolone (Scheme 1),[3)] or direct oxidative dimerization. We found that the former method, carried out in the presence of ferric chloride gave best results.



Scheme 1. Synthesis of the pyrazolone blue

The reaction scheme 2 and the series of blue dyes is summarized in figure 2.



Scheme 2. The Knoevenagel reaction mechanism

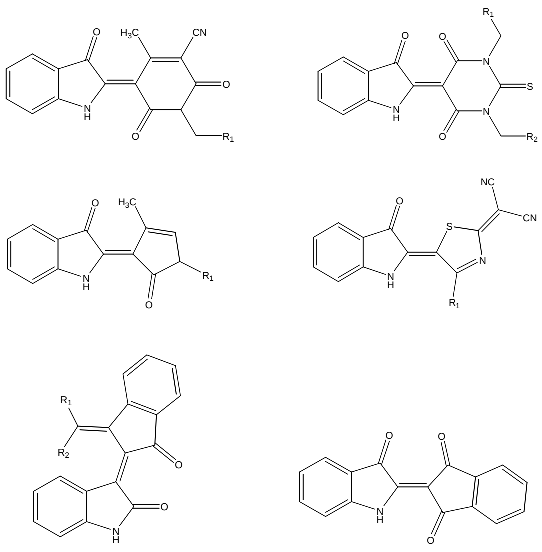


Figure 2. The blue chromophores

3. CONCLUSION

Several new H-chromophore systems were synthesized with a view to examining there color properties, pH sensitivity and redox behavior. Thus the parent symmetrical dyes (Pyrazoline Blue and indigo respectively) are both blue, and yet the hybrid system is red. This work was extended by examining new chromophores systems containing the same terminal groups used for the H-chromophores combined with various electron acceptor residues.

4. REFERENCES

[1] J. Fabian and H. Hartmann, “Light Absorption of Organic Colorants”, Springer Verlag, Berlin, 124, (1980).
[2] J. Formanek, Z. Angew, Chem., 41, 1133 (1928).
[3] L. Knorr, Justus Liebigs Ann. Chem., 238, 137 (1987).