

## Review

# The coordination chemistry of substituted anthraquinones: Developments and applications



Emily E. Langdon-Jones, Simon J.A. Pope\*

School of Chemistry, Main Building, Cardiff University, Park Place, Cardiff CF10 3AT, UK

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## ABSTRACT

Anthraquinone has found diverse use within the sphere of coordination chemistry. The sheer breadth of application in this context has been driven by the remarkable physical and biological properties that are known for a wide variety of anthraquinone derivatives. This review discusses three main areas of research and development: (i) the coordination chemistry of substituted anthraquinones, including self-assembled systems, coordination polymers and metal organic frameworks; (ii) the incorporation of anthraquinone into ligand structures and their resultant chemistry with both *d*- and *f*-block metal ions; and (iii) the application of metal–anthraquinone species to biological and chemosensing disciplines. Key aspects regarding synthetic approaches and physical characteristics are discussed throughout, with particular attention and focus on the electronic and redox properties of the species in question.

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## 1. Introduction

The synthesis and study of anthraquinone (AQ; also often referred to as anthrone) derivatives has been driven by the vast range of realised applications, from their use as dyes and pigments through to biological and medicinal products (Fig. 1). A number of AQ species are known to occur in both plant and insect life (*i.e.* natural products) [1], allowing inspiration to be taken for developing both pigments and pharmacological agents.

The AQ core is polycyclic, comprising two benzene rings fused with carbonyl groups at the 9 and 10 positions (Scheme 1). AQ

is commonly prepared either from the Friedel–Crafts reaction of benzene and phthalic anhydride in the presence of  $\text{AlCl}_3$  [2], or by simply oxidising anthracene (as is most common in industry) [3]. A very large number of AQ derivatives are commercially available (including halo-, amino-, hydroxy-, nitro-, sulfonate- and alkyl-substituted species) and provide myriad opportunities for the synthetic development of more complex AQ-derived species.

A number of commercially available colourants incorporate multiple substitution of the AQ core, and their development and properties have been dealt with in great detail elsewhere [4].

### 1.1. Brief comment on the synthesis of anthraquinones

From a synthetic perspective it is important to note that the carbonyl groups of AQ activate the 1, 4, 5 and 8 positions towards

\* Corresponding author. Tel.: +44 02920 879316.  
E-mail address: [popesj@cardiff.ac.uk](mailto:popesj@cardiff.ac.uk) (S.J.A. Pope).

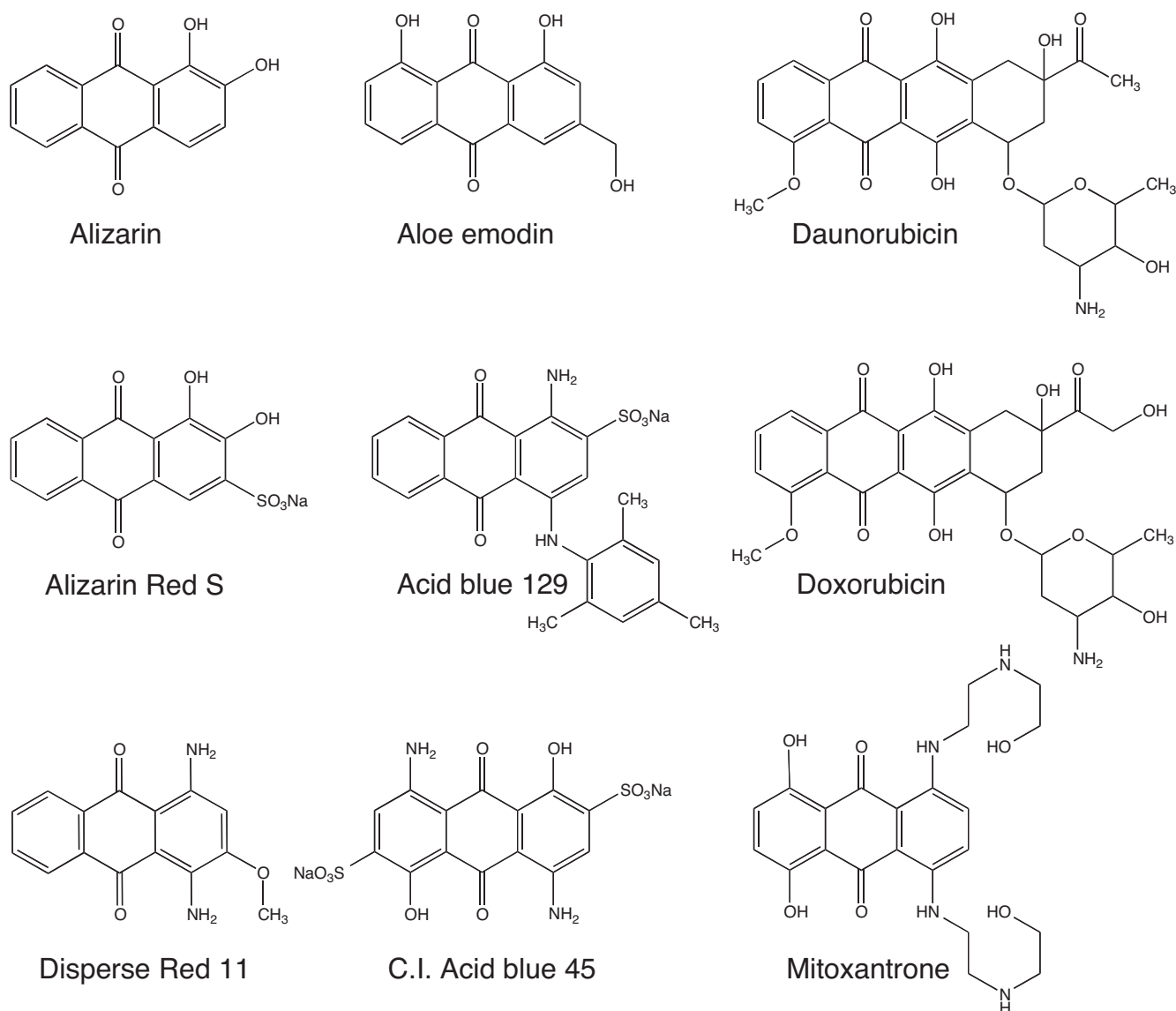
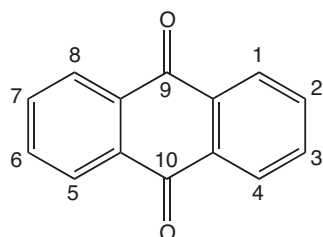


Fig. 1. Examples of commercially available AQ compounds.

nucleophilic substitution. Thus, treatment of 1-chloro-AQ (Fig. 2) with a primary amine will directly yield the 1-amino-substituted product; alkoxy AQs can also be efficiently synthesised from the corresponding fluoro-AQs [5]. In contrast, for amino- and hydroxy-substituted AQ compounds (Fig. 2) the electron withdrawing capacity of the quinone unit can reduce the nucleophilicity of the amine and hydroxy groups.

Despite these limitations recent reports have highlighted the feasibility of synthesising 1-iodo-AQ from the corresponding

1-amino-AQ (Scheme 2) using the diazotisation-Sandmeyer methodology [6]. An example of the utility of 1-iodo-AQ is that it can be reacted with trimethylsilylacetylene using a Sonogashira coupling to give alkynyl-substituted AQs [7]. A wide variety of coupling reactions have also been described with 2,6-diiodo-derived AQs [8]. 1-Amino-AQ and 1-hydroxy-AQ derivatives are key species for the development of pigments and natural products, respectively (Fig. 1). Conveniently 2-acetyl-1,4-naphthoquinones will react with functionalised pyrrolidine or morpholine enamines to give 1-amino and 1-hydroxy-AQ derivatives bearing alkyl substituents at the 3- and 4-positions [9].



Scheme 1. Structure of anthraquinone (AQ).

## 1.2. Electronic properties of anthraquinones

The application of AQ derivatives as dyes, colourants and pigments has driven a detailed understanding of the electronic properties of numerous compounds of this type. Many experimental and theoretical studies have been conducted over several decades, describing the absorption and, where appropriate, the emission spectra of AQ species [10].

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