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CNDO/II Study on the Fading of Anthraquinone Dyes

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ABSTRACT

The light fastness of different amino/hydroxy anthraquinone dyes has been investigated employing the CNDO/II, an all-valence electron MO method. The results of the calculations indicate that the fading of these dyes is related to the ease of electrophilic attack on the nitrogen and oxygen atoms.

INTRODUCTION

Photodegradation of the dye and physical deterioration of the substrate are the two main changes observed when a dyed fibre is exposed to sunlight. Generally, fading of dye colour is observed before the physical degradation of the fibre is noticeable.

The action of light on dyes, however, is a complex phenomenon and has been widely investigated.[1–6] Bancroft initially proposed an oxidation/reduction of dyes when faded in sunlight. The chemical structure of the dye and the substrate,[6,7] the physical nature of the substrate, and the distribution and concentrations[8] of the dye in the substrate all contribute

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to the photosensitivity of the dye on a substrate. Relations have also been proposed between moisture content,[9–11] temperature[9–12] and the fading of dyes.

Anthraquinones are useful dyes for a variety of natural and synthetic fibres and several investigations have been carried out to evaluate light fastness–dye structure–substrate interaction.[13–15] A correlation between the ionisation potentials and light fastness of 1-amino-4-substituted anthraquinone dyes on polyester has been established.[15] The light fastness of 1-amino-substituted anthraquinones on polyesters has been correlated[16] with the pK_a of the amine salt. The orientation of the amino/hydroxy substituents has a marked effect on the light fastness of the dyes.[16–19]

Few data are available on the correlation of the light fastness of anthraquinone dyes with the electron density distribution/energy of the molecular orbitals as obtained from all-valence MO calculations, and we report here the results of CNDO/II calculations[20] on a series of anthraquinone dyes having low, medium and high light fastness.

RESULTS AND DISCUSSION

All-valence MO calculations

The MO method used for these studies was the CNDO/II method, which is known to reproduce adequately both the geometry of organic molecules and the stability of any hydrogen bonds which they may form.[21] A series of anthraquinone dyes having a wide range of light fastness properties on polyester resin was taken as model compounds.

The geometrical parameters were taken from comparable molecules. Since no optimization was done, constant values were used for the length of similar bonds and for the magnitude of comparable angles, so that orbital energies were mainly influenced by changes of the electronic environment.

Light fastness values[14–16,22–26] and the results of MO calculations are shown in Table 1. With respect to their light fastness values on polyester, the dyes can be classified into three categories: low fastness (values 1–2), moderate fastness (values 3–5) and high fastness (values 6–8). Since the substrate was the same for all dyes, the effect of substrate structure on the light fastness will be more or less the same for all the dyes.

On exposure to light, the electrons from the occupied molecular orbitals, particularly from the HOMO, will be excited and it is this excited level that determines the light stability. Anthraquinone itself is stable, and thus the chemical or physical reactivity is likely to be governed

TABLE 1

Light Fastness Values of Anthraquinone Dyes on Polyester, Energy of LUMO and LUMO Frontier Electron Density

Substituent	*Light fastness*	*LUMO frontier electron density*[a]	*LUMO (eV)*
2-amino	1	0·0140 (N)	1·202
2-*N*-methylamino	1	0·0140 (N)	1·137
3-amino-3-carboxy	1	0·0237 (N)	0·880
2-amino-3-chloro	1	0·01479 (N)	0·964
2-hydroxy	1	0·00696 (O)	0·892
2-methoxy	1	0·0074 (O)	0·989
1-amino	4–5	0·004 (N)	1·036
1-amino-3-chloro	5	0·0032 (N)	0·932
1-amino-2-hydroxy	4–5	0·006 (N)	0·937
2-amino-3-hydroxy	4	0·0054 (N)	1·066
1,4-diamino	4	0·007 (N)	0·921
1-amino-2-chloro	5	0·0046 (N)	0·845
1-amino-4-hydroxy	6	0·0056 (N) 0·0038 (O)	0·745
1-amino-3-carboxy	8	0·0065 (N)	0·563
1-hydroxy	8	0·0023 (O)	0·615
1,4-dihydroxy	8	0·0028 (O)	0·557
1,2-dihydroxy	8	0·0078 (O) 0·0037 (O)	0·589

[a] N represents the nitrogen of NH_2 and O the oxygen of OH/OCH_3.

principally by substituent groups present in the nucleus. Consequently, a relation between light fastness and the LUMO frontier electron density on the N-atom of different amino-substituted anthraquinone dyes would be expected.

The LUMO frontier electron density on the N-atom is highest for the dyes having lowest fastness, i.e. when exposed to light, the N-atom in such dyes becomes a comparatively electron-rich centre relative to that in the other dyes. However, for dyes having moderate and high light fastness values, the LUMO electron densities on the N-atoms were not significantly different from each other.

The fastness can therefore be related to the ease of electrophilic attack at the N-atom of amino-substituted anthraquinone dyes in the excited state. The greater the propensity for electrophilic attack, the lower the light fastness. While this conclusion appears to break down for moderate and high light fastness dyes, it must be noted that the energy of the LUMOs of dyes having high light fastness is lower than in dyes having moderate light fastness. This makes the excited level of the high fastness dyes more stable compared with those of moderate fastness dyes. Consequently, the N-atom is more susceptible to electrophilic attack in the latter case.

It is also of interest to compare the LUMO frontier electron densities on the oxygen atoms of hydroxy anthraquinone dyes. The low fastness dyes have higher LUMO frontier electron densities on the oxygen atoms of OH or OCH_3 substituents, compared with high fastness dyes.

The LUMO frontier electron density on the oxygen of one of the OH groups in 1,2-dihydroxy anthraquinone (high fastness) is comparable with that in 2-hydroxy/methoxy anthraquinones (low fastness). However, in the former the LUMO energy is lower (Table 1), thus making this excited level comparatively more stable than those in the latter compounds. It is also notable that the energies of the LUMO in anthraquinone dyes having high light fastness are the lowest in the series of dyes studied.

It may be concluded, therefore, that the fading of anthraquinone dyes on exposure to light is directly related to the attack of electrophiles on the nitrogen and/or oxygen atoms of substituted groups.

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