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Some Observations on the Visible Absorption Spectra and Stability Properties of the Silicon Phthalocyanine System

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ABSTRACT

The synthesis of silicon phthalocyanine dye was carried out. The dye was found to have comparable half-bandwidth with squarylium dyes. This dye, however, has excellent stability properties, both thermally and photochemically. © 1997 Elsevier Science Ltd

Keywords: phthalocyanine, squarylium, bandwidth, molar absorption coefficient, Q-band, wavelength, spectrum.

INTRODUCTION

The silicon phthalocyanines are well known [1–6] and generally have better solubility in organic solvents than metal-free or metal phthalocyanine complexes, particularly if long alkyl or oxyalkyl chains are attached to the central silicon atom. One particular advantage of the silicon system is that the two side chains extend above and below the plane of the phthalocyanine ring and this inhibits stacking of the phthalocyanine molecules in solution, i.e. aggregation is minimised. As aggregation is associated with band broadening and absorption at shorter wavelengths, the silicon phthalocyanines have characteristically bright cyan colours with narrow absorption bands in fluid solutions and in polymer hosts. The narrow bandwidth properties have important applications in areas such as laser-protective plastics with high visible transmission, laser-optical recording media, and good thermal and photochemical stability is an advantage in such areas. Few other dyes have such narrow bandwidths, but perhaps the most widely studied of these are the squarylium dyes, but these generally have poor stability properties [7, 8]. Little data have been reported concerning the general spectroscopic and stability properties of the silicon phthalocyanines. The synthesis of a representative example is now described, and its visible absorption spectrum and stability characteristics (thermal and photochemical) are compared with those of squarylium dyes of similar hue and absorption bandwidth.

EXPERIMENTAL

1,3-Diiminoisoindoline

Ammonia was bubbled at a moderate rate for 40 min into a stirred mixture of ophthalonitrile (100 g), sodium metal (0.63 g), and methanol (130 cm^3). The mixture was then brought to reflux and maintained there for 3.2 h with continuous stirring and periodic addition of ammonia. Upon cooling the product was filtered off as greenish crystals which were washed with ether and dried, (27 g). A second crop (17 g) was obtained after leaving the filtrates to stand for 24 h, giving a total yield of 41%. Recrystallisation of the product from methanol and ether (charcoal) gave colourless crystals, m.p. 195°C (Lit. [9], 195–196°C).

Dichlorosiliconphthalocyanine (1)

A mixture of 1,3-diiminoisoindoline (7.3 g, 0.05 mol), silicon tetrachloride (8.3 cm^3, 0.072 mol) and quinoline (83 cm^3) was brought slowly to reflux with stirring over 30 min, cooled to 184°C and the product filtered off. A purple crystalline product was obtained after washing with quinoline, benzene, methanol and acetone and drying at 110°C; yield 5.5 g (71%).

Dihydroxyl(phthalocyanino)silicon (2)

A mixture of dichlorosiliconphthalocyanine (3.2 g) and sodium metal (8 g) in methanol (20 cm^3) was added to ethanol (200 cm^3) containing water (10 cm^3). The suspension was refluxed for 1 h, cooled and the product filtered off, (2.46 g, 83%), m.p. 356°C.

Bis(1-dodecyloxy)phthalocyaninosilicon (3)

A mixture of dihydroxy(phthalocyanino)silicon (4 g), 1-dodecanol (56 g) and tetrahydronaphthalene (400 cm^3) was refluxed for 1 h. The solution was filtered and the resultant green solution distilled to small volume *in vacuo* and the dye precipitated with ligroin. It was purified by recrystallisation from toluene (5.56 g, 83%), m.p. 178°C.

$C_{56}H_{66}N_8SiO_2$ requires	C, 73.84; H, 7.25; N, 12.30%
Found	C, 74.08; H, 7.10; N, 12.60%

Determination of thermal and photochemical stabilities

The method adopted for the assessment of the thermal and photochemical properties of the silicon phthalocyanine dye was to cast films of cellulose acetate containing the dye in a fully dissolved state. Such films were then subjected to heat, or to photochemical treatments, and the degradation of the dye assessed by visible absorption spectroscopy. For comparative purposes, a reference blue dye (**5**), which has reasonable but not exceptional stability as far as textile applications are concerned, and which was readily soluble is cellulose acetate, was employed.

For photochemical stability evaluation, each film was cut into suitable pieces and mounted in a slide frame. The films, together with the standard film made with dye **5**, were irradiated for 72 h using a Microsal Fadeometer. The optical densities of the films were measured prior to and after irradiation. The difference between the two measurements, expressed as a percentage of the original optical density, corresponds to the amount of dye decomposed during exposure.

In order to assess the thermal stability of the dyes, pieces of the coloured films were sandwiched between Melinex clear films, and heated between the plates of a transfer printing press at 190°C for 1 h. From the optical density of the films before and after heating, the percentage loss of dye was calculated. Measurement of the visible spectra of the Melinex films enabled detection of any loss from the acetate film through sublimation to be made. In the event, none of the samples showed any dye tranfer under the conditions used; thus, the calculated percentage loss of dye in each case represents the thermal degradation of the chromophore only.

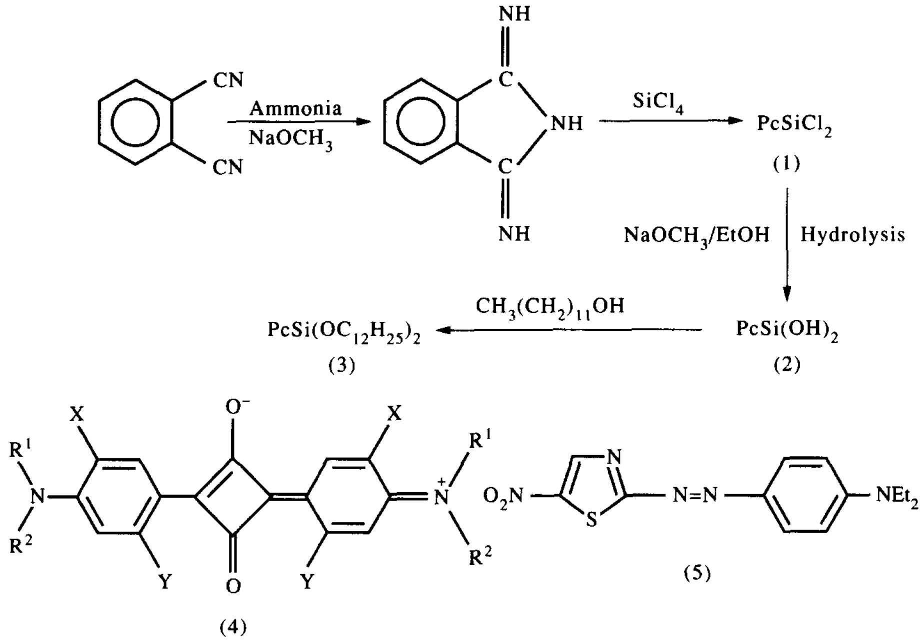
General procedure for preparing cellulose acetate film

Cellulose acetate (2.5 g) was added to a mixture of dichloromethane/methanol (25 cm^3, 9:1) containing the calculated amount of dye in a beaker covered with a watch glass. The mixture was thoroughly stirred for 1.5–2 h at room temperature until a uniform solution was obtained. The film was cast on a glass sheet using a TLC spreader adjusted to a thickness of 50 μm. After casting, a similarly sized glass sheet was immediately placed over the wet film a few millimetres from its surface to prevent 'clouding' caused by moisture condensation on the surface of film due to rapid evaporation of solvent. When the film was dry, it was carefully peeled off from the glass, and kept in a vacuum desiccator for at least 3 days. The film was cut into suitable pieces and mounted in a slide frame. The films were then subjected to heat or photochemical treatments and the degradation of the dye assessed by visible absorption spectroscopy.

RESULTS AND DISCUSSION

The synthesis of the silicon phthalocyanine dye (**3**) was carried out as shown in Scheme 1, and for comparison purposes dyes (**4**) were prepared following the literature method [7, 8].

Absorption spectra of dye (**3**) and the squarylium dyes (**4**) were recorded in dichloromethane and the results are summarised in Table 1. Dye (**3**) has maximum absorption wavelength at 680 nm in dichloromethane, with molar



a; $R^1 = R^2 = Et, X = Y = H$

b; $R^1 = R^2 = Et, X = H, Y = OH$

c; $R^1 = R^2 = Et, X = H, Y = NHAC$

d; $R = R = Bu^n, X = Y = H$

Scheme 1

TABLE 1
Spectroscopic and Relative Stabilities of the Dyes

Dye no.	λ_{max} *(CH$_2$Cl$_2$) (nm)*	*a*$\Delta\lambda^{1/2}$ *(nm)*	$_{max}$*(CH$_2$Cl$_2$) (l mol^{-1} cm^{-1})*	*Thermal stability (%)*	*Photochemical stability (%)*
3	630	34	259 00	2.3	5.3
4a	640	32	326 00	66.9	45.5
4b	648	30	350 00	2.1	25.0
4c	682	30	350 00	10.9	15.3
4d	649	40	340 00	49.0	54.0
Std **5**	—	—	—	10.0	5.3

a = Bandwidth at half peak height.

absorption coefficient of 259,000 lmol^{-1}cm^{-1} and the absorption band was very sharp with a half-bandwidth of 34 nm, which was comparable to, but not better than, those of the squarylium dyes [8]. Dye (**3**) also exhibits two weak bands at shorter wavelengths than the main 680 nm band at about 605 and 645 nm (Fig. 1) and these are due to vibrational fine structure. The long wavelength band of the phthalocyanine system is referred to as the Q band. The spectrum of the phthalocyanine dye (**3**) is given in Fig. 1, and of particular note is the narrower absorption by this dye over the visible region of the spectrum, and the dye could thus be of value in laser protective filters, optical data recording, imaging, and security printing.

The squarylium dyes (**4**) have half-band widths of *ca* 30–40 nm, as summarised in Table 1, with correspondingly high molar absorption coefficients (*ca* 350 000 lmol^{-1}cm^{-1}), and are thus similar to dye **3**. However, the two weak bands at shorter wavelengths present in dye **3** are not evident in the aryl squaryliums (**4**) as can be seen in Fig. 2 for representative dye. An

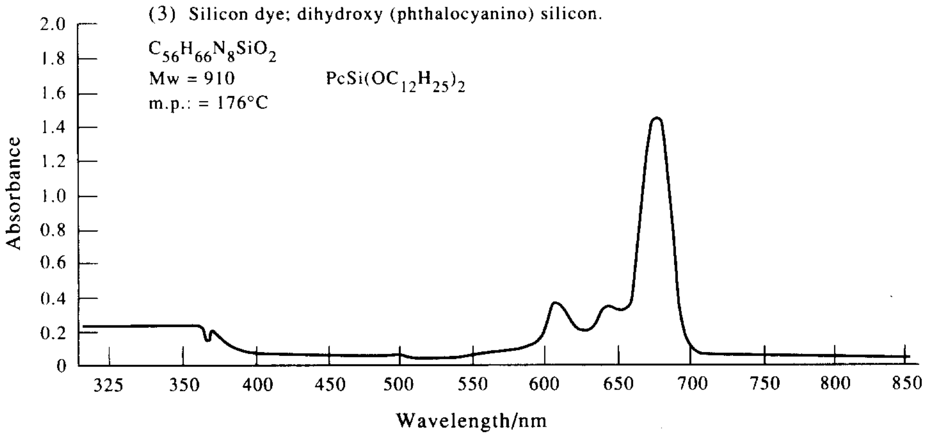
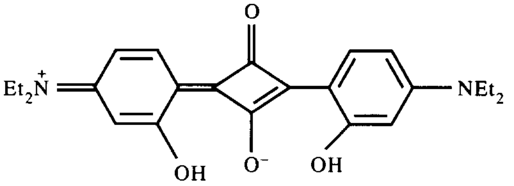


Fig. 1. Visible absorption spectrum of dye (**3**) in dichloromethane.

(4b) Squarylium dye; 2,4-bis(4-diethylamino-2-hydroxyphenyl)-

$C_{24}H_{28}N_2O_4$
Mw = 408
m.p.: = 268°C



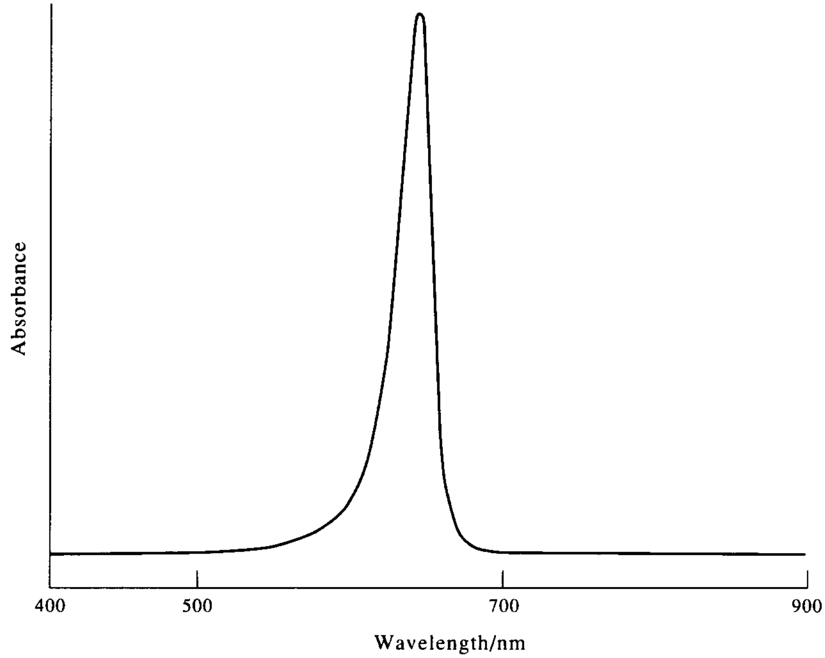


Fig. 2. Visible absorption spectrum of dye (**4b**) in dichloromethane.

interesting feature of the squarylium dyes is their minimum absorption in the rest of the visible and near UV spectrum (Fig. 2).

The photochemical and thermal stabilities of the silicon phthalocyanine (**3**) were assessed on cellulose acetate film and the results compared with those of squarylium dyes (**4**); the results are shown in Table 1.

In general, the thermal stability of dye **3** was very good and equitable with that of the hydroxy substituted dye **4b**. The lightfastness was also good, and proved to be better than that of the reference standard **5**. The results also show that the silicon phthalocyanine dye (**3**) is superior to all the squarylium dyes, and is very stable both thermally and photochemically.

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