Available online at www.sciencedirect.com
SCIENCE DIRECT®

ELSEVIER

Dyes and Pigments 71 (2006) 103–108

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Novel dyes derived from hydrazones: Part 3. Synthesis and characterizations of 2-[4-(1-phenylethylidene)hydrazino]phenylethylene-1, 1,2-tricarbonitrile

Abdullah Mohamed Asiri*, Abood A. Bahajaj, Iqbal M.I. Ismail, N.A. Fatani

Chemistry Department, Faculty of Science, King Abdul Aziz University, Jeddah 21413, P.O. Box 80203, Saudi Arabia

Received 12 January 2005; received in revised form 11 March 2005; accepted 9 June 2005
Available online 19 August 2005

Abstract

Novel tricyanovinyl dyes derived from hydrazones have been prepared by the reaction of tetracyanoethylene and phenylethylidene hydrazone, and these dyes showed absorption in the region of 500 nm. The dyes showed pronounced solvatochromic effects as the solvent's polarity increased. Some of the new dyes were studied to show their aggregation properties in solution as the concentration changed. Most of the dyes studied showed change in the absorption spectrum and hence the position of the maximum absorption bands.

The thermal stability of some of the prepared dyes was studied in poly(methyl methacrylate) film at 80 °C; the substitution on the aromatic group showed less thermal stability of the dyes.

Keywords: Tricyanovinyl; Hydrazones; Donor-acceptor; NLO chromophores; Solvatochromism

1. Introduction

The electronic and structural properties of donor–acceptor substituted π-conjugated organic compounds are of considerable interest because of their applicability to electro-optic devices and data storage [1,2]. A wide variety of structural modifications on the donor–acceptor and π-conjugated moieties have been carried out [3,4]. Major research efforts have focused on developing NLO chromophores possessing large molecular nonlinearity and good thermal stability as well as improved solubility and process ability. It is well known that the second order molecular nonlinear optical hyperpolarizability (β) increases with increasing donor and acceptor strengths and with increasing length of conjugation [5]. Many donor–acceptor conjugated organic molecules reported in the literature fall into the following categories: substituted benzene, biphenyls, stilbenes, azobenzenes ferrocenyl and Schiff bases [6–8]. In all these classes, benzene rings with or without the π-bridges have been employed as the conjugated moieties to connect donor and acceptor functional groups such as compounds **1–6**. Although, optical studies on compounds containing more than two benzenoid rings has been reported, however, these systems are usually insoluble in most common organic solvents. We have recently [9], reported the synthesis of new NLO chromophores based on pyrazoles as the donor groups for example compound **7**. We have also reported the

---

* Corresponding author. Tel.: +966 2 6952293; fax: +966 2 6952292.
E-mail address: aasiri2@kaau.edu.sa (A.M. Asiri).

0143-7208/$ - see front matter © 2005 Published by Elsevier Ltd.
doi:10.1016/j.dyepig.2005.06.007

synthesis of new tricyanovinyl based on hydrazones such as dyes **8** [10] and **9** [11]. In this paper, we report on the synthesis and spectroscopic investigations of novel push–pull system based on hydrazones as donor groups.

2. Results and discussion

2.1. Synthesis of dyes

The new chromospheres ***11*** were prepared by direct tricyanovinylation of hydrazones and this was achieved by mixing together the appropriate hydrazones ***10*** and tetracyanoethylene (TCNE), as shown in Scheme 1. All the prepared chromospheres were obtained as dark violet solids. The IR spectra of these new dyes exhibited three important absorption bands; the first band centered near 3200 cm^{-1} for the νNH absorption. The second band is a sharp absorption band in the region of 2220 cm^{-1} which was attributed to the cyano group absorption. The third is an absorption band in the region of 1610 cm^{-1} ascribed to the C=N absorption. The tricyanovinylation undoubtedly took place at *para* to the hydrazine group as was evidenced from the ^{1}H NMR signals for the doublet two hydrogen.

2.2. Electronic absorption properties

The electronic absorption spectra of the new chromospheres are characterized by an intense, low-energy band that is dependent on the nature and the position of the substituent on the aromatic rings (Table 2). Dye ***11a***, which contains no substitution on the phenyl ring, showed absorption band at 523 nm in chloroform. A substitution by a methoxy group *para* to the aromatic ring e.g. dyes ***11b*** generally showed a bathochromic shift of 15 nm compared with the unsubstituted dye ***11a***. In addition, substitution on *para* position of the aromatic ring with amino group caused a bathochromic shift e.g. dye ***11d*** (533 nm), however, a hypsochromic shift was observed when the substitution was on *ortho* position of the aromatic ring e.g. dye ***11e***, which also showed a decrease in the intensity of the absorption band compared to dye ***11d*** (Table 1).

2.3. Solvatochromism

The dyes were measured in various solvents having different polarity. Generally increasing the solvent polarity gave a bathochromic shift of the maximum absorption bands of dyes ***11a–d***. In non-polar solvents, for instance in ether dye ***11a*** showed the maximum solvatochromic shift with absorption maxima at 490 nm while in the DMF the maxima is at 549 nm (Table 1). The solvatochromic effect can be estimated from the difference between the absorption maxima in polar and non-polar solvents e.g. $\Delta\lambda$ (Table 1). Figs. 1–5, showed the visible absorption spectra of tricyanovinyl hydrazone dyes ***11a–d*** and **12** in various solvents. The solvent's effects can be rationalized on the basis of the dipole formed by charge migration from the nitrogen to the acceptor tricyanovinyl (Scheme 2).

2.4. Thermal stability

The dyes were tested for their stability against the exposure to heat in poly(methyl methacrylates) matrix at 80 °C. A thin film of poly(methyl methacrylate) (PMMA) doped with dyes **11a–b** and **12** was prepared from a solution of the polymer and the dyes in chloroform (dye contents around 3%), and then the film was casted on a glass substrate. After drying at room temperature, the film was further dried under vacuum. The films were peeled from the glass and the absorption spectra were measured before heating, then the films were heated in an oven set at 80 °C, for intervals for which the absorption spectra were measured. The total heating period was 200 min.

Fig. 6 showed the effects of heating for different time intervals on the degradation of some of the dyes prepared. Also the extents of the degradation (calculated from $(A^0 - A_t) \times 100/A^0$) of the dyes **11a–b** and **12** are shown in Table 2. It is noteworthy to say that the parent dye **11a** is the most stable dye on heating at 80 °C since 3.6% of the dye content was decomposed. On the other hand, dye **11b** is the less stable dye relative to the studied dyes. It is of great importance to notice that the extent of the decomposition is measured after 200 min.

2.5. Aggregation properties

The ability of certain dyes to form associates (aggregates) is called aggregation [12,13]. Until recently, the association of identical molecules of dyes (formation of homogeneous aggregates) was usually investigated using the absorption spectroscopy. The change in the position and the shape of the absorption maxima as the concentration of the dyes are usually appreciable. Table 3, showed the aggregation effects on the absorption properties as the concentration of the dye ***11b*** change in DMF as representative example. From the data presented in Table 3, it can be seen that increasing the concentration of the dyes showed a bathochromic shift and hence the formation of new absorption band, due to the formation of dimers of the dye in solution.

3. Experimental

3.1. General

Melting points were recorded on a Thomas-Hoover capillary melting apparatus without correction.