Available online at www.sciencedirect.com

SCIENCE DIRECT®

Dyes and Pigments 72 (2007) 109–112

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

The synthesis of some azo dyes formed by *s*-hydrindacene-1,3,5,7-tetrone with some aromatic amines and the investigation of the effects of concentration, acid, base and substituents upon their UV–visible spectra☆

Hasan Esener*, Tahsin Uyar

Department of Chemistry, Gazi University, Teknikokullar 06500, Ankara, Turkey

Received 17 January 2005; received in revised form 13 June 2005; accepted 12 August 2005
Available online 7 November 2005

Abstract

In this study *s*-hydrindacene-1,3,5,7-tetrone (BID: bisindandione) was synthesized from dianhydride of pyromellitic acid, then a new series of azo dyes [2,6-bis(*o*-, *m*-, *p*-substituted phenylazo)-*s*-hydrindacene-1,3,5,7-tetrones] were obtained by the coupling reaction of BID with some *o*-, *m*-, *p*-substituted (hydroxy, etoxy, nitro, carboxy and methyl) benzendiazonium salts. The effects of subtituents, concentration, acid and base upon the UV–visible spectra of these disperse dyes were investigated.

Keywords: BID; AzoBIDdyes; Substituent effect; Acid and base effect; Concentration effect

1. Introduction

Although there are numerous studies upon 1,3-indandione, a β-diketone, and its various derivatives were synthesized and investigated [1,2], the studies on *s*-hydrindacene-1,3,5,7-tetrone (**1**) an analog of 1,3-indandione are highly limited. Especially there is very little information on the structure of the two symmetrical β-diketones attached to the aromatic ring on the physical and chemical properties of the compound in Scheme 1.

The synthesis of aromatic compounds with conjugated π-bands is getting increasingly popular due to their good electrical conductivities.

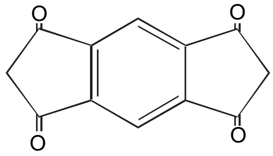
The disodium salt of diethyl *s*-hydrindacene-1,3,5,7-tetrone-2,6-dicarboxylate was first synthesized by Ephraim in 1901 but he could not take his studies further due to the lack of pyromellitic acid and its highly cumbersome synthesis [3]. He named this compound as hydrindacene. This product was later synthesized by various workers and it was acidified with H_2SO_4 in cold to obtain diethyl *s*-hydrindacene-1,3,5,7-tetrone-2,6-dicarboxylate. It was attempted to hydrolyze this dicarboxylate by heating with mineral acids but it yielded black colored polymeric condensation products. It was observed that *s*-hydrindacene-1,3,5,7-tetrone precipitated when heating this dicarboxylate in acetic acid [4]. It was also reported that tetraketone was easily brominated in acetic acid yielding 2,2,6,6-tetrabromo derivative [4]. Also the 2,6-dinitrozo and 2,6-dihydroxyimino

---

☆ This study was supported by TUBİTAK with project no TBAG 1463.

* Corresponding author. Tel.: +90 312 212 60 30/2717; fax: +90 312 212 22 79.
E-mail address: hesener@gazi.edu.tr (H. Esener).

0143-7208/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2005.08.006



Scheme 1.

of *s*-hydrindacene were synthesized and were observed to have semiconduction properties [5–8].

2. Experimental

2.1. General

The chemicals used in the synthesis of all dyes were obtained from Aldrich Chemical Company or Sigma Chemical Company and were used without further purification. The solvents used were of spectroscopic grade.

IR spectra were recorded on a Mattson 1000 FT-IR spectrophotometer in KBr. ^{1}H NMR spectra were taken on a Bruker-Spectrospin Avance DTX 400 Ultra-Shield in DMSO with TMS as internal reference. Absorption spectra were obtained on an ATI-Unicam UV-100 spectrophotometer in various solvents. All melting points were uncorrected.

2.2. Synthesis of *s*-hydrindacene-1,3,5,7-tetrone

Benzenetetracarboxylic acid tetramethyl ester was obtained by Fisher esterification by the reaction of benzenetetracarboxylic acid dianhydride with methanol in H_2SO_4 medium. The dried product was dissolved in chloroform and filtered off. The filtrate was passed through a 10-cm long column filled with silicagel using chloroform as a solvent. The solvent was evaporated giving the pure product. M.p 146–147 °C (lit. 143–143.5 °C), yield: 94%.

Freshly prepared sodium sand was taken in a 250 mL single necked flask. Twenty-four grams of (0.0774 mol) tetramethyl pyromellitate is added to it. The flask was fixed to reflux condenser and heated on an electrical heater for 30 min. The flask was then cooled down at room temperature and 100 mL of ethyl acetate and 1 mL of methanol were added to it. The solution immediately took a red color. The solution was then heated in a oil bath at 80–90 °C under reflux for 24 h. A red precipitate formed as the reaction advanced. The flask was taken off the heater and cooled at room temperature. The product was taken in a beaker after adding ether. The unreacted ethyl acetate was passed into the ether phase and was removed by vacuum filtration. The solid part was grounded in a mortar, 100 mL ether was added to it, was mixed for a while, vacuum filtered again and dried in open air. The precipitate was boiled with distilled water for 10 min and vacuum filtered when hot. Yield: 62%.

Resulting product (1.5 g) was dissolved in 800 mL water by heating. The solution was cooled down, acidified in 10% (v/v) HCl and the resulting product was filtered by vacuum. The solid part was taken in a beaker and 20 mL glacial acetic acid was added to it. It was dispersed in solution and heated by constant stirring. The solution was boiled for 2–3 min, rapidly cooled down in salt/ice mixture and immediately filtered off. The resulting product was highly pure. The product was recrystallized from excess acetic acid when necessary (l L for 1 g). M.p: 290 °C (dec.), yield 60%.

2.3. The synthesis of azo dyes

Diazonium salts are prepared from aniline and its derivatives and *o*-, *m*- and *p*-hydroxyaniline, nitroaniline, toluidine, fenatidine and aminobenzoic acid and coupled with *s*-hydrindacene-1,3,5,7-tetrone.

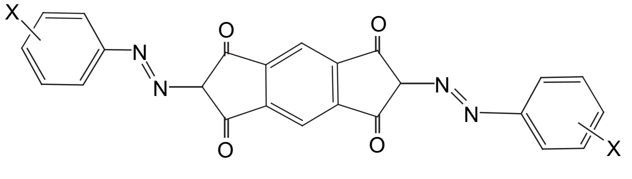
In order to prepare diazonium salt solutions 2.8×10^{-3} mol of aniline derivate was taken and dissolved in 1 mL of 36% (v/v) HCl and 5 mL water. The solution was cooled down in salt/ice bath and cold solution of 0.2 g (2.8×10^{-3} mol) $NaNO_2$ in 5 mL water was added to it in a dropwise manner by constant stirring. The resulting diazonium salt was cooled in salt/ice mixture.

s-Hydrindacene-1,3,5,7-tetrone, 0.3 g (1.40×10^{-3} mol), was dissolved in dilute KOH solution and cooled in salt/ice bath. Cold diazonium solution was added to this cooled solution by stirring in a dropwise manner. The solution was stirred at room temperature for 1 h for the completion of the coupling reaction. It was then acidified with HCl/water solution (3:1) and filtered off in vacuum.

The solid product was taken in a beaker and 25 mL pure water was added to it in order to remove the inorganic salts, was heated for 5 min and filtered off when it was hot. The remaining solid product was dried, boiled with different organic solvents such as acetone, chloroform, ethyl acetate and alcohol for the removal of the organic impurities, filtered off when it was hot and dried in oven. The solid is dissolved in 5 mL dimethylsulfoxide and acetone was added to the solution for the precipitation of the product. The product was filtered off, washed with acetone for 4–5 times for the removal of DMSO and dried in oven. The dye structures are shown in Scheme 2. Yield: 74–99%.

3. Results and discussion

UV–visible spectra of the concentrated and dilute solutions of the azo compound obtained in DMSO



X: (o- , m- , p-) -H, -OH, $-NO_2$, $-CH_3$, $-OC_2H_5$, -COOH

Scheme 2.

were recorded. The dilute solution was separated into two parts. To one part was added 1–2 drops of piperidine and to the other was added 1–2 drops of glacial acetic acid. The spectra of both parts were taken again separately in order to examine the effect of concentration, acid and base upon the resulting spectra.

3.1. Investigation of the effect of concentration, acid and base upon the visible spectra

The investigation of the absorption spectra with concentration revealed that (Table 1) the absorption maxima of *m*- and *p*-substituted compounds was generally unchanged. The adsorption maxima of (the UV–visible spectra of 2,6-bis(2-ethoxyphenylazo)-*s*-hydrindacene-1,3,5,7-tetrone is given in Fig. 1. as an example) changed when it was substituted with electron donating groups. Since tautomeric equilibrium is known to be not significantly affected by electron donating groups in *o*-substituted compounds one can talk about ionic as well as the tautomeric equilibria.

There was a hypsochromic shift in both acidic and basic solutions when electron donating groups were attached to *p*-position. Electron withdrawing groups on the other hand did not change λ_{max} in acidic solutions but showed a bathochromic shift in basic solutions. In *m*-substituted compounds electron donating hydroxy and etoxy groups did not change λ_{max} in acidic solutions. However, hydroxy groups caused a bathochromic and etoxy group caused a hypsochromic shift in basic solutions. Methyl group shifted λ_{max} bathochromically in acidic and hypsochromically in basic solutions. Carboxy groups resulted in bathochromic shift in acid and hypsochromic shift in basic solution while with nitro group there was no change in acidic solutions but bathochromic shift in basic solutions.

Table 1
The UV–visible spectral data of the concentrated, dilute and, acidic and basic solutions of [2,6-bis(*o*-, *m*-, *p*-substituted phenylazo)-*s*-hydrindacene-1,3,5,7-tetrone]

Substituent	Concentrated	Dilute	Acidic	Basic
H	461	467	484	454
o-OC_2H_5	477	469	473	434
m-OC_2H_5	455	455	455	433
p-OC_2H_5	476	476	466	422
o-OH	461	479	484	457
m-OH	388	388	388	416
p-OH	469	469	461	413
o-COOH	501	501	492	502
m-COOH	446	446	451	437
p-COOH	447	447	447	455
o-CH_3	570	553	571	541
m-CH_3	477	477	487	457
p-CH_3	454	454	454	435
o-NO_2	487	487	487	479
m-NO_2	403	409	409	464
p-NO_2	481	481	481	470

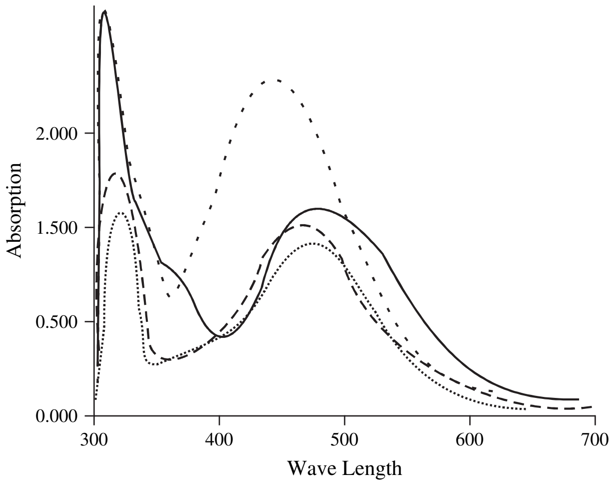


Fig. 1. UV–visible spectra of 2,6-bis(2-ethoxyphenylazo)-*s*-hydrindacene-1,3,5,7-tetrone (—) concentrated, (- - -) dilute, (——) basic, (...) acidic.

These data indicate that there was no regular change in λ_{max} values of the compound in acidic and basic solutions. It also reveals that the existing equilibrium and the stability of the anion are highly dependent upon the substituents. In *o*-substituted compounds electron donating groups cause a hypsochromic shift in basic and bathochromic shift in an acidic solution. This shows that the electron donating groups destabilize the anion when attached to *o*-position. Electron withdrawing groups on the other hand do not cause a significant change in λ_{max} values which indicates that these compounds are not very sensitive towards acids and bases. This can be explained by the formation of strong intra molecular H-bonds.

3.2. Effect of substituents upon the UV–visible spectra

When the absorption spectra of the compounds are taken into account looking at the spectra of the concentrated solutions, it is seen that each compound gives an adsorption at 461 nm. In peroxide substituted compounds it was found that values were dependent upon the position of the substituent. The λ_{max} values were 477 nm for *o*-, 455 nm for *m*- and 476 nm for *p*-position.

The λ_{max} values of hydroxy substituted compounds were 461 nm for *o*-position (no change), 388 nm for *m*-position and 412 nm for *p*-position. Carboxy substitution also gave different λ_{max} values according to its position as 501 nm for *o*-, 446 nm for *m*- and 447 nm for *p*-position. These values were 570 nm for *o*-, 477 nm for *m*- and 452 nm for *o*-position in methyl substitution. The λ_{max} values for *o*-, *m*- and *p*-substitution of nitro group were 487, 403 and 481 nm, respectively.

The change of Hammett substituent with λ_{max} in *m*- and *p*-series is given in Fig. 2. Although there is a partial correlation between Hammett coefficients and λ_{max} values for *m*-substitution there exists no such correlation for *p*-position. There are three different tautomeric structures possible for the synthesized compounds (azo–azo, azo–hydrazo, hydrazo–hydrazo). Since tautomeric equilibrium constants are highly dependent on the substituents and there exists different structure of the stable tautomer for different substituted compound which will change the ratios to each other, this an expected outcome. This is especially apparent for *p*-substituted compounds.

4. Conclusions

It was reported in previous studies that the synthesis of *s*-hydrindacene-1,3,5,7-tetrone was cumbersome [4]. It is stated that this compound could sometimes be synthesized and sometimes not giving a violet color polymer during the synthesis of diethyl *s*-hydrindacene-1,3,5,7-tetrone-2,6-dicarboxylate in spite of keeping all conditions the same. This was the case in our study as well. However, it was observed that polymerization could be minimized when the carboxylate compound was thoroughly dispersed in acetic acid before it dried up, stirred constantly when heating and cooled down rapidly in salt/ice bath. The diazo dyes obtained *s*-hydrindacene-1,3,5,7-tetrone are not soluble in any organic solvent, except DMSO. Some of them are even sparingly soluble in DMSO. That is they could not be recrystallized. Some of them were recovered by precipitation.

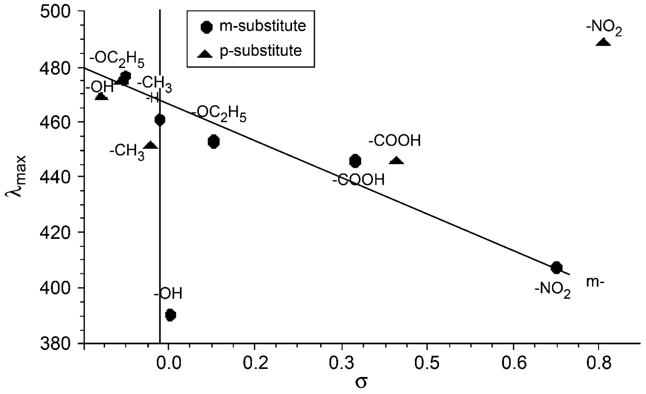


Fig. 2. The change of λ_{max} with σ (Hammett coefficient).

Acknowledgements

The authors are grateful to Research Foundation of Gazi University for supporting this study.

References

[1] Hocaoğlu N, Uyar T, Türker L. The synthesis of some novel 2-substituted phenylazo-1,3-indandiones. Dyes Pigments 1990;12: 87–95.

[2] Ertan N, Uyar T. The synthesis of some novel 2-methyl-2-substituted phenylazo-1,3-indandiones. Commun Fac Sci Univ Ank Ser B 1994;40:45–50.

[3] Ephraim F. Synthese von Indacen Derivaten. Ber 1901;34: 2779–94.

[4] Davies I. 1,3,5,7-*s*-Hydrindacenetetrone and its derivatives. Univ. Films (Ann Arbor, Mich.), Order no. 63–3572; 1963. p. 119. Dissertation Abstr. 23: 4531–2.

[5] Vavere M, Neiland O. 2,6-Diaryl-1,3,5,7-tetraoxo-5-hydrindacenes. Nov. Issled. Obl. Khim. Khim. Tekhnol. Mater. Nauchno-Tekh. Professorsko-Prepod. Sostava Nauchn. Rab. Khim. Fak. (Russ.) RPI (Pub. 1973); 1972. p. 9–10.

[6] Mosher WA, El-Zimaity T. 2,6-Diacyl-*s*-hydrindacene-1,3,5,7-tetrones and reaction with hydrazine. J Heterocycl Chem 1971; 8(6):1069–70.

[7] Ruggli P, Bücheler P. Uber die synthese eines linearen dioxo-dicyclopenteno-benzols. Helv Chim Acta 1947;30:2048–57.

[8] Arnold R, Rondestvedt E. Steric effect of methylene groups I. J Am Chem Soc 1945;67:1265–7.