

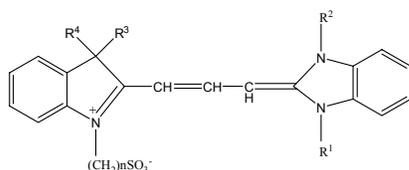
Synthesis, Characterization and Sensitometric Properties of Unsymmetrical 1,1'-dimethyl-N-propylsulfo-indo-N-dimethyl-amino-ethyl-benziimidazole-carbocyanine sensitizing dye in Photographic Emulsion

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Abstract

This paper reports synthesis method of a novel and unsymmetrical imidazole-indole carbonic cyanine. The structural of the novel compound is characterized by element analysis, IR, MS, NMR. In addition the properties in various emulsion were determined sensitometrically.

A novel asymmetric class of sensitizing dye whose general formula is indicated below:

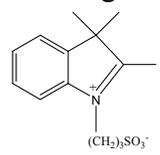


Where R^1, R^2, R^3, R^4 = alkyl group, normally $-CH_3$ or ethyl groups had been discovered and synthesized in series in our laboratory^{[1][2]}. The preliminary applied test in different emulsion, especially in emulsion of printing demonstrated that the sensitizing dye with the structure ($n=3, R^1=R^2=C_2H_5, R^3, R^4=CH_3$ etc) is featured by the high sensitizing efficiency, lower fog and without color residues left in developed and dried emulsion layer.

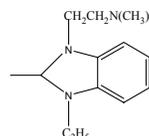
From the contemporary concepts of spectral sensitization, between the crystal lattice of silver halide microcrystals and the supermolecules of aggregating sensitizing dyes, depending on the site occupation, there must be geometric correspondence and the energetically prior well-matched in band gap involved.

Being as the second step, we are to prepare a new sensitizing dye of this class with $R^2 = -(CH_2-CH_2)_n-N-(CH_3)_2$ such a design of molecular attached to nitrogen atom is of prime importance for the reasons as follows: (1) Firstly we used the $-(CH_2-CH_2)_n-N-(CH_3)_2$ with somewhat electron expelling capacity to fine-tune the sensitizing peak to

some extent to bathochromic shift as compared with the primitive sensitizing dye with $R^2 = C_2H_5$. (2) Secondly the existence of $-(CH_2-CH_2)_n-N-(CH_3)_2$ enables the aggregated dye supermolecule possess 2 occupied sites, one is the original, it is the



the another is



It means that such a sensitizing dye will be certain to have more probability to make occupied size selection, leading to higher sensitizing efficiency.

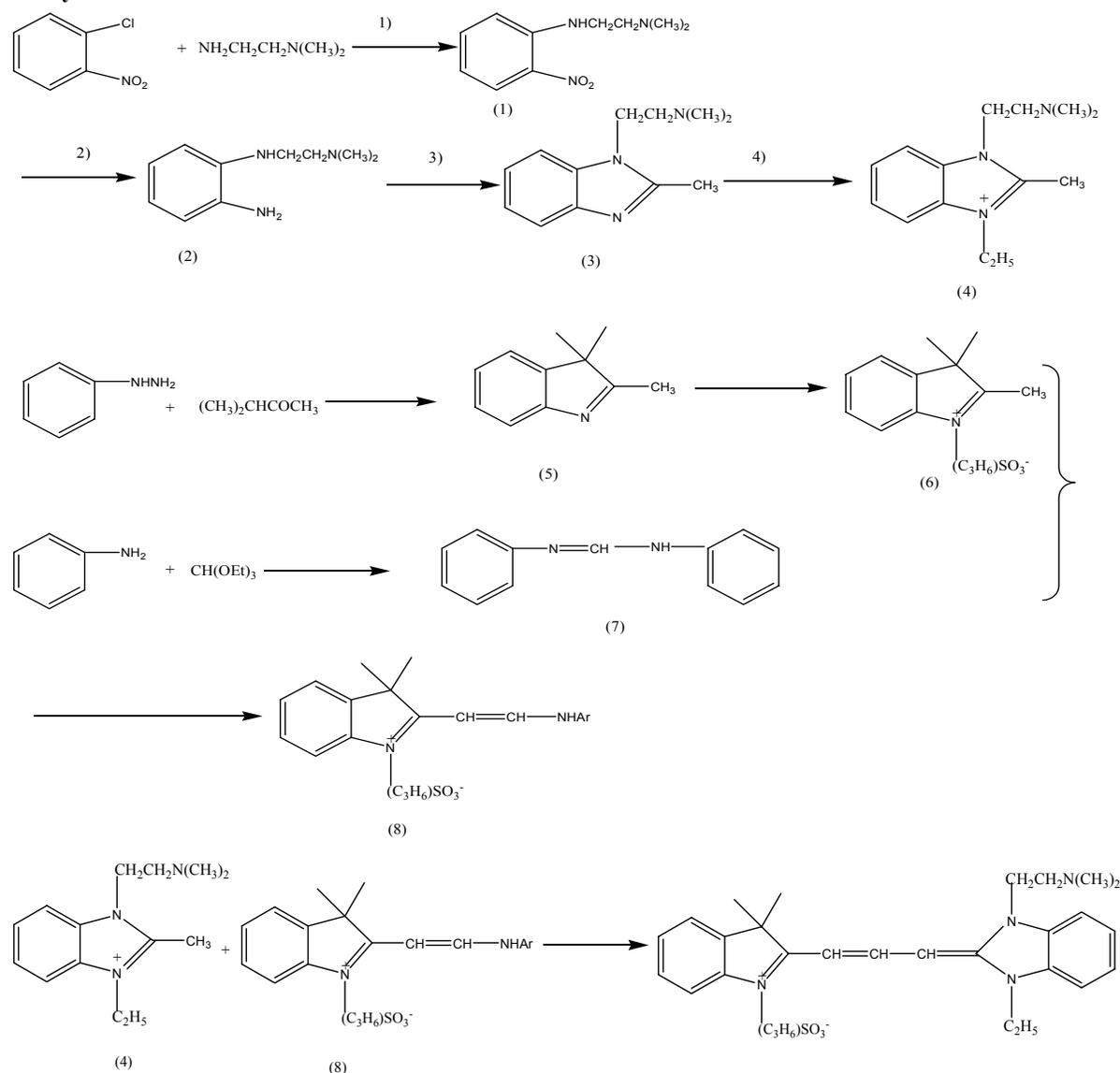
Below a preliminary synthesis, characterization (element analysis, Infra-red, MS and NMR etc) and the sensitometric measurements in various emulsion is given. It tells the fact that the said sensitizing dye is deserved to be concerned and worthwhile to be expanded in emulsions with different purposes.

Experimental

1. Instruments and reagents

All the reagents we used are CR. NMR(Nuclear Magnetic Resonance):VARIAN-CHMINI-300, Infrared spectrum :Bio-Red FTS165, MS(Mass spectrum):GC-MS; EA(Flash element analysis) :Carlo Erba 1106 and Flash EA1112; UV-Vis spectrum: Hitaci2001; Melting point: thermometer XT4(without any further correction).

2. Synthetic route:



3. Synthetic process:

3.1 synthesis of intermediate compound

1) *o*-(β -Dimethylaminoethylamino)-nitrobenzene(1)^{[3][4]}

A mixture consisting of 33.2g(0.283mole) of β -dimethylaminoethylamine, 57.2g(0.283mole) of *o*-chloronitrobenzene and 70g of anhydrous sodium acetate was stirred and heated at 140~150°C for ten hours. The mixture turned red after several minutes and near the end of the reaction became very viscous, making stirring impossible. The reaction mixture was cooled, diluted with about 500ml of water, acidified with hydrochloric acid and distilled. The residue (red solution) was allowed to cool and was basified by the addition of a cold 20%

potassium hydroxide solution. The solution was saturated with potassium carbonate, extracted with ether, the extract dried over anhydrous magnesium sulfate, the ether evaporated and the residue distilled in vacuo ;yield, 33.1g(50%) of a red oil, b.p.125~126°C (0. 2mm.)

2) *o*-(β -Dimethylaminoethylamino)-aniline(2)

To a solution of 13.0g(0.062mole) of *o*-(β -Dimethylaminoethyl amino)- nitrobenzene in 50ml of concentrated hydrochloric acid cooled to 5°C in an ice-bath was added, in portions with stirring, a solution of 50.0g of stannous chloride dihydrate in 72ml of concentrated hydrochloric acid. The temperature of the reaction mixture rose to 50°C and was allowed to remain at this temperature by removing the ice-bath occasionally. When the heat of the reaction had subsided the reaction mixture was allowed to cool to room temperature. After

standing over night the reaction mixture was cooled in an ice bath and made strongly basic with a cold 20% sodium hydroxide solution. The resulting mixture was extracted with ether, the ether extracts dried over anhydrous potassium carbonate and the solvent evaporated. Upon cooling the amber residue solidified. Yield of crude product, 10.8g (97%), m.p. 51-53 °C. Recrystallization from low-boiling petroleum ether gave almost colorless glistening plates melting at 52-53 °C.

3) o-(β-Dimethylaminoethyl)-2-methylbenzimidazole(3)

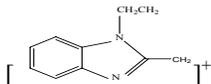
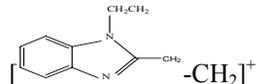
A mixture of 3.58g (0.02mole) of o-(β-Dimethylaminoethylamino)-aniline and 9.0ml of acetic anhydride was heated at about 100 °C for three hours and, when cool, was poured into water. The solution was basified with cold 20% sodium hydroxide solution and the resulting mixture worked up as described above for o-(β-Dimethylaminoethylamino)-nitrobenzene; yield, 3.0g (79%), b.p. 118 °C (0.3mm.).

4) o-(β-Dimethylaminoethyl)-2-methyl-3-ethylbenzimidazole(4)

A mixture of 3.0g (0.015mole) of o-(β-Dimethylaminoethyl)-2-methylbenzimidazole and 2.3g (0.015mole) of ethane iodide was heated up reflux for 48 hours. With the reaction time prolonged, the reaction mixture solidified and turned white. The reaction mixture was cooled to room temperature. Recrystallization from methanol gave white crystal melting at 235-237 °C, yield, 4.2g (80%).

Anal. Calcd. for C₁₄H₂₂N₃I: C, 46.80; H, 6.13; N, 11.70. Found: C, 46.25; H, 6.17; N, 10.99.

Anal. MS:

m/z	Molecular ion	Relative abundance(100%)
522	[M] ⁺	5
400	[M-(CH ₂) ₃ SO ₃] ⁺	1
371	[M-(CH ₂) ₃ SO ₃ -2(CH ₃)+H] ⁺	31
370	[M-(CH ₂) ₃ SO ₃ -2(CH ₃)] ⁺	100
356	[M-(CH ₂) ₃ SO ₃ -2(CH ₃)-CH ₃ +H] ⁺	23
341	[M-(CH ₂) ₃ SO ₃ -2(CH ₃)-C ₂ H ₅] ⁺	5
158		67
144		50

NMR: δ_H(CDCl₃): 7.4~7.61(4H,m,Ar-4H), 6.85~7.12(4H,m,Ar-4H), 6.51~6.57(1H,d,8-CH=), 5.94~5.98(1H,d,9-CH=), 8.05~8.15(1H,t,10-CH=), 4.3001~4.3340 (2H,t,N-CH₂CH₂), 4.6~4.62(2H,t, N-CH₂CH₂), 3.9696~4.0121(2H,t,-CH₂CH₂CH₂SO₃), 3.12~3.18(2H,q,N-CH₂CH₃), 1.644~1.713 (2H,m,-CH₂CH₂CH₂SO₃), 1.603(6H,s,C-(CH₃)₂), 1.26(6H,s,N-(CH₃)₂), 1.387~1.406 (3H,t,N-CH₂CH₃), 0.88~0.95(2H,t,-CH₂CH₂CH₂SO₃).

1-sulfopropyl-2-anilinvinyl-1,1-dimethylindole(8)

A mixture of 11.94g (0.042mole) of 1-sulfopropyl-1,1,2-trimethylindole(6)⁵¹, 16.46g (0.084mole) of dibenzo-amidine(7), 50ml of n-propyl alcohol, was stirring and heated up reflux for one hour. After cooling to room temperature, the reaction mixture was poured into ether and stirred. The residue was filtrated and dried. Recrystallization from ethanol twice gave red crystal melting 195-198 °C, yield, 7.9g (47.2%).

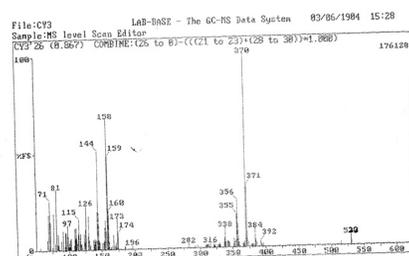
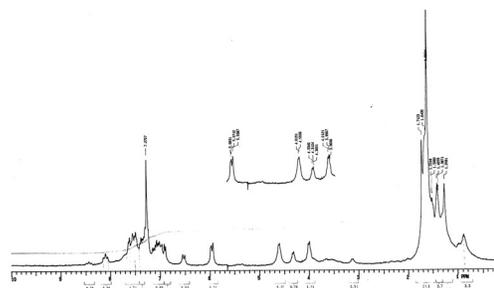
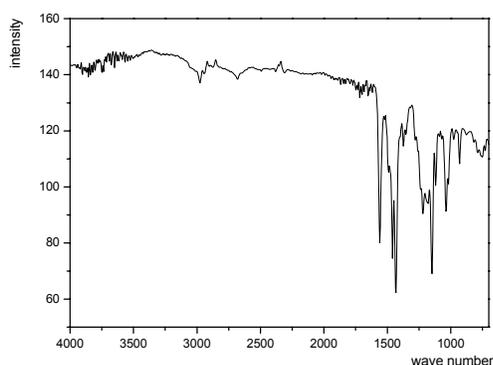
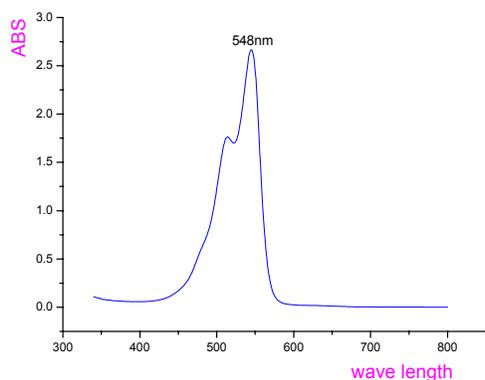
Anal. Calcd. for C₂₁H₂₄N₂SO₃: C, 65.62; H, 6.25; N, 7.29; Found: C, 65.38; H, 6.58; N, 7.35.

3.2 synthesis of Dye

A mixture of 4.0g (0.011mole) of o-(β-Dimethylaminoethyl)-2-methyl-3-ethylbenzimidazole(4), 4.22g (0.011mole) of 1-sulfuric acid propyl-2-anilinvinyl-1,1-dimethylindole(8) and 15ml nitrobenzene was stirred. Then, 3ml of triethylamine and 2ml acetic anhydride joined to the reaction mixture. The temperature of mixture rose slowly up reflux for four hours. After cooling to room temperature, the reaction mixture was poured into ether and stirred for 30 min. There would be purple solid separated out. The crude product was purified by column chromatography (silica gel, chloroform: ethanol=3:1(v/v); petroleum ether: ethanol=1:2(v/v)). Recrystallization from methanol gave mauve crystal melting 220-222 °C. λ_{max}^{Meoh}: 547.5nm

Element analysis(EA) Calcd. for C₂₉H₃₈N₄SO₃: C, 66.67; H, 7.26; N, 10.73; Found: C, 66.19; H, 7.38; N, 10.22.

the result of test :



All the EA,MS,and HNMR confirm that the synthesis of the synthesized dye is perfect.

4. Sensitometric property measurement

The iodobromide emulsion and chloride emulsion were prepared by double-jet with automatic control pAg and PH, coagulated re-dispersed in gelatin solution, chemically(S+Au) sensitized, spectrally sensitized by our new sensitizing dye(0.1% methanol), coated, dried, exposed (1/25 second), developed, fixed, and finally sensitometrically determined as usual.

Fig. Sensitometric property sensitized by our novel dye

Emulsion Type	Sensitizing condition	Sensitometric property					
		Before dyeing			After dyeing		
		Do	S(Din)	r	Do	S(Din)	r
AgBrI	0.1% methanol 1~5ml/50g	0.04	23~24	1.70	0.06	27~28	~
AgCl	0.1% methanol 1~5ml/50g	0.05	0~1	1.80	0.05	2~3	0.24

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