CHAPTER - II

EXPERIMENTAL WORK

CHAPTER - II

EXPERIMENTAL WORK

CHMICALS :

1) 4,4'-Diaminostilbene 2,2'-disulphonic acid :

This compound was purified by recrystallization from acetone-alcohol and its purity checked by spectral methods and M.P. 228°C

2) Cyanuric chloride :

Cyanuric chloride was used of West-German Degaüsse Company.

3) Metanilic acid :

B.D.H. (A.R.) grade was used.

4) 6-Amino-uracil :

It was used of B.D.H. (A.R.) grade.

5) Benzoic acid hydrazide :

It was prepared and purified by recrystallization using ethanol M.P. was taken.

6) Diethanol amine :

It was used of B.D.H. (A.R.) grade.

7) Benzoyl Chloride :

It was used of B.D.H. (A.R.) grade.

8) Sodium carbonate :

B.D.H. (A.R.) grade was used.

9) Sodium chloride :

B.D.H. (A.R.) grade was used.

Instruments used for spectral study :

1) U.V. - Double beam spectrophotometer.
Hitachi - UV - 330 spectrophotometer.

2) I.R. spectra were recorded in KBr pellets on a " Perkin-Elmer -783 infrared spectrophotometer"

3) Fluorescence Shimadu-Double Monochromator Spectrofluorophotometer RF - 540.

SCHEME I : SYNTHESIS OF 4,4'-DIAMINOSTILBENE-2,2'-DISULPHONIC ACID :

The synthesis of 4,4'-diaminostilbene-2,2'-disulphonic acid has been reported.[83] This was prepared by three-step synthesis from p-nitrotoluene. The latter was first sulphonated with 26% oleum at 55-60°C to give 4-nitrotoulene-2-sulphonic acid.

A paste of 4-nitrotoluene-2-sulphonic acid was dissolved in a larger amount of water and neutralised with sodium hydroxide solution. The sodium salt of 4-nitrotoluene-2-sulphonic acid was then oxidized with a solution of sodium hypochlorite at 75-80°C under simultaneous addition of sodium hydroxide solution.

After termination of the oxidation process the reaction mixture was neutralised with concentrated hydrochloric acid, cooled and salted out. The separated product was isolated by filteration on a filter press. The paste of 4,4'-dinitrostilbene-2,2'-disulphonic acid was then reduced by adding it gradually into an aqueous suspension of iron filings, etched with hydrochloric acid, at a temperature of about 100°C.

The reaction mixture was made alkaline with sodium hydroxide and freed of the iron-containing sludge on á filter press. From the filtrate 4,4'-diamino stilbene-2,2'-disulphonic acid was precipated by acidification with sulphuric acid. The product was filtered off. For further work product was usually used directly in the form of paste.

Preparation of sodium salt of 4,4'-diaminostilbene-2,2'-disulphonic acid :

4,4'-Diaminostilbene 2,2'-disulphonic acid (11 gms.) was added in 25 ml distilled water in 250 ml beaker. The mixture was well stirred and equimolar quantity of sodium carbonate (17.2 gms.) was added. The mixture was stirred and heated till clear solution obtained.

Yield - 80% Decomposes - 226-228°C

Analytical data :

	C	H	N
Calculated :	40.30	3.60	7.22
Found	40.30	3.80	7.21

Spectral data :

1) U.V. - A = 210 nm, B = 335 nm

2) I.R. - NH_2 - 3450 - 3250 cm^{-1}

C = C - 1600 - 1500 cm^{-1}

-C-N 1200 - 1020 cm^{-1}

C-H- stretching 3030 - 3080 cm^{-1}

3) Fluorescence - 435 nm.

U V ABSORPTION SPECTRUM OF SODIUM SALT OF 4,4'-DIAMINO STILBENE 2,2'- DISULPHONIC ACID.

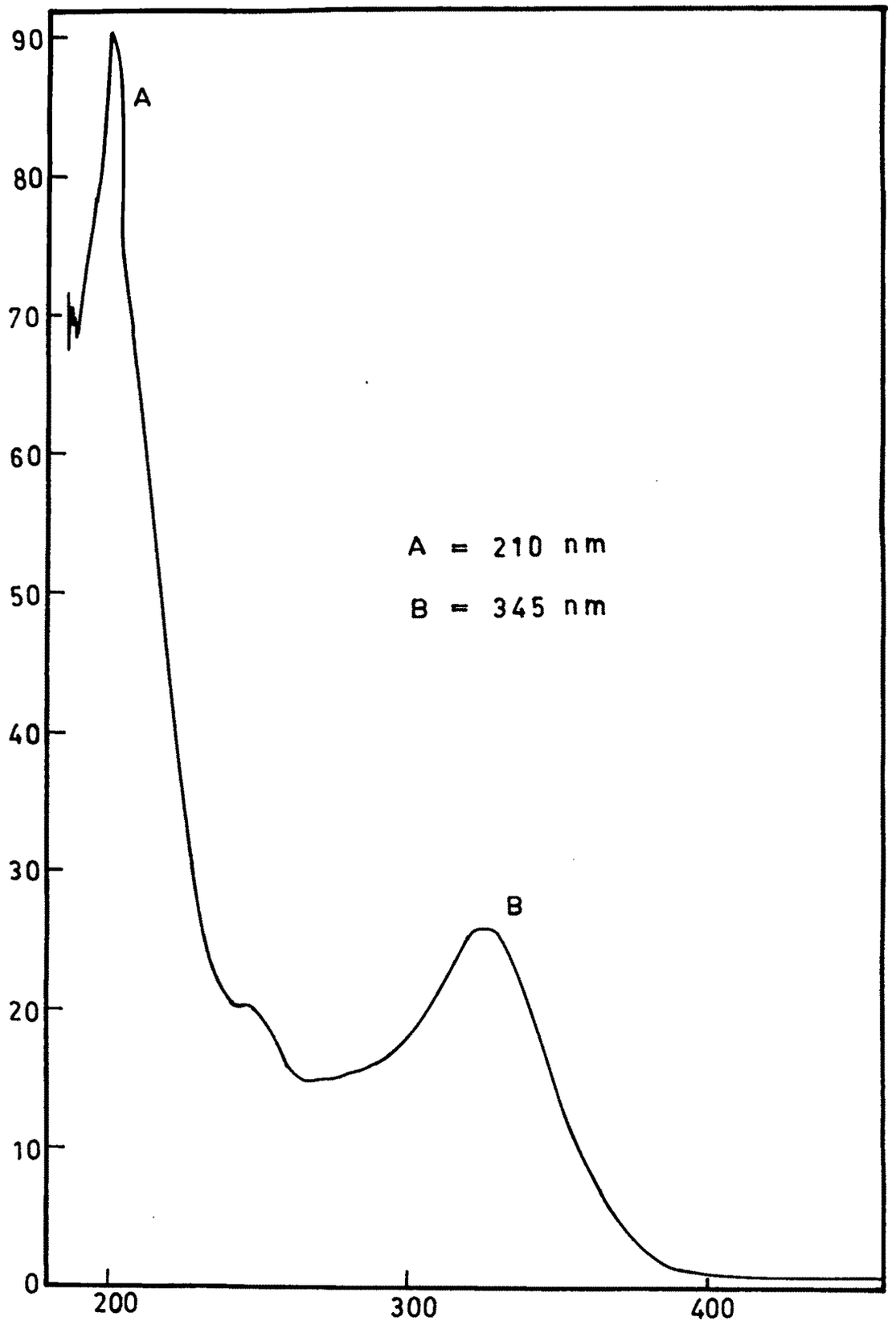


FIG.

I R SPECTRUM OF SODIUM SALT OF 4,4′-DIAMINOSTILBENE-2,2′-DISULPHONIC ACID .

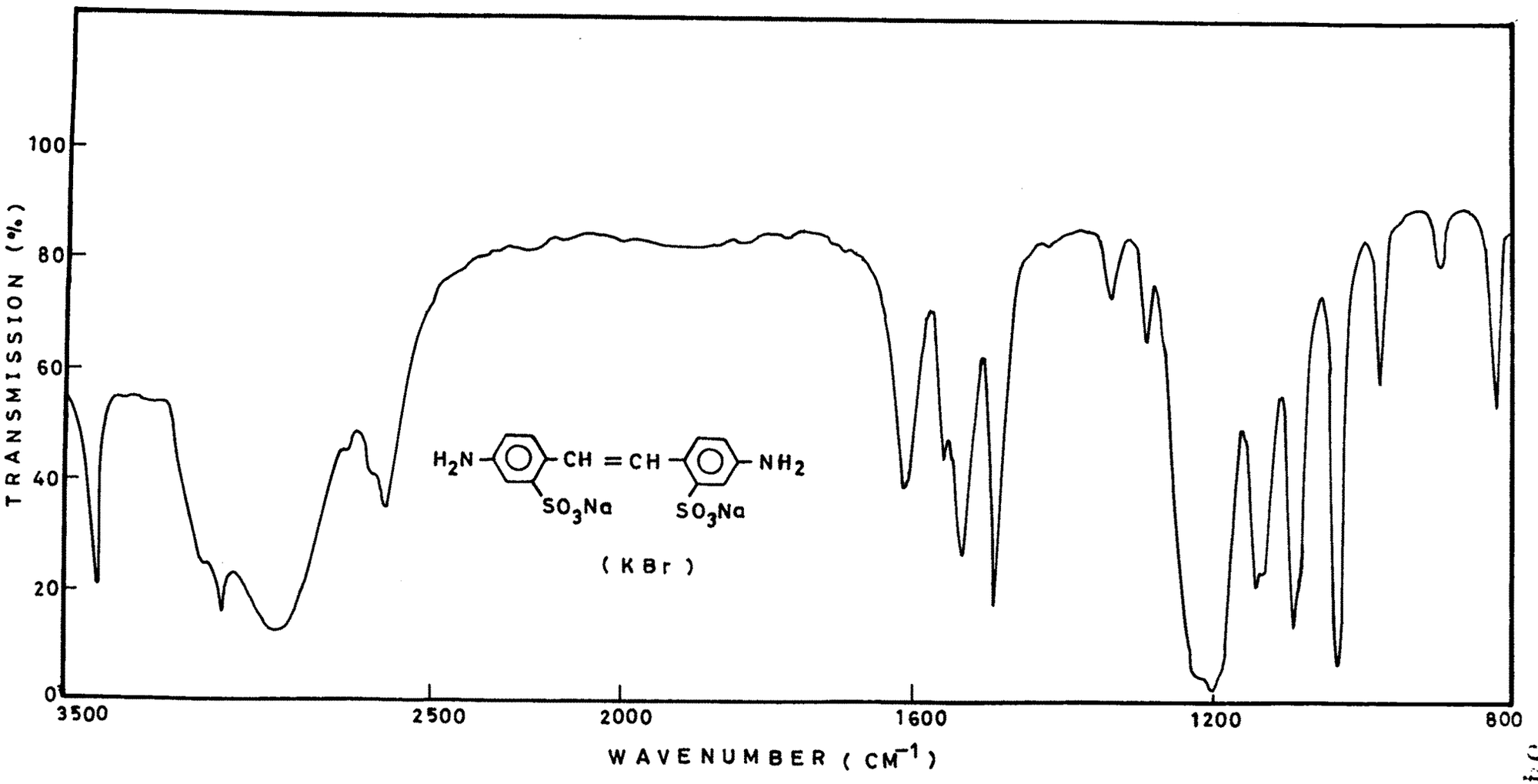


FIG.

FLUORESCENCE SPECTRUM OF SODIUM SALT OF 4,4′-DIAMINO STILBENE 2,2′ DISULPHONIC ACID.

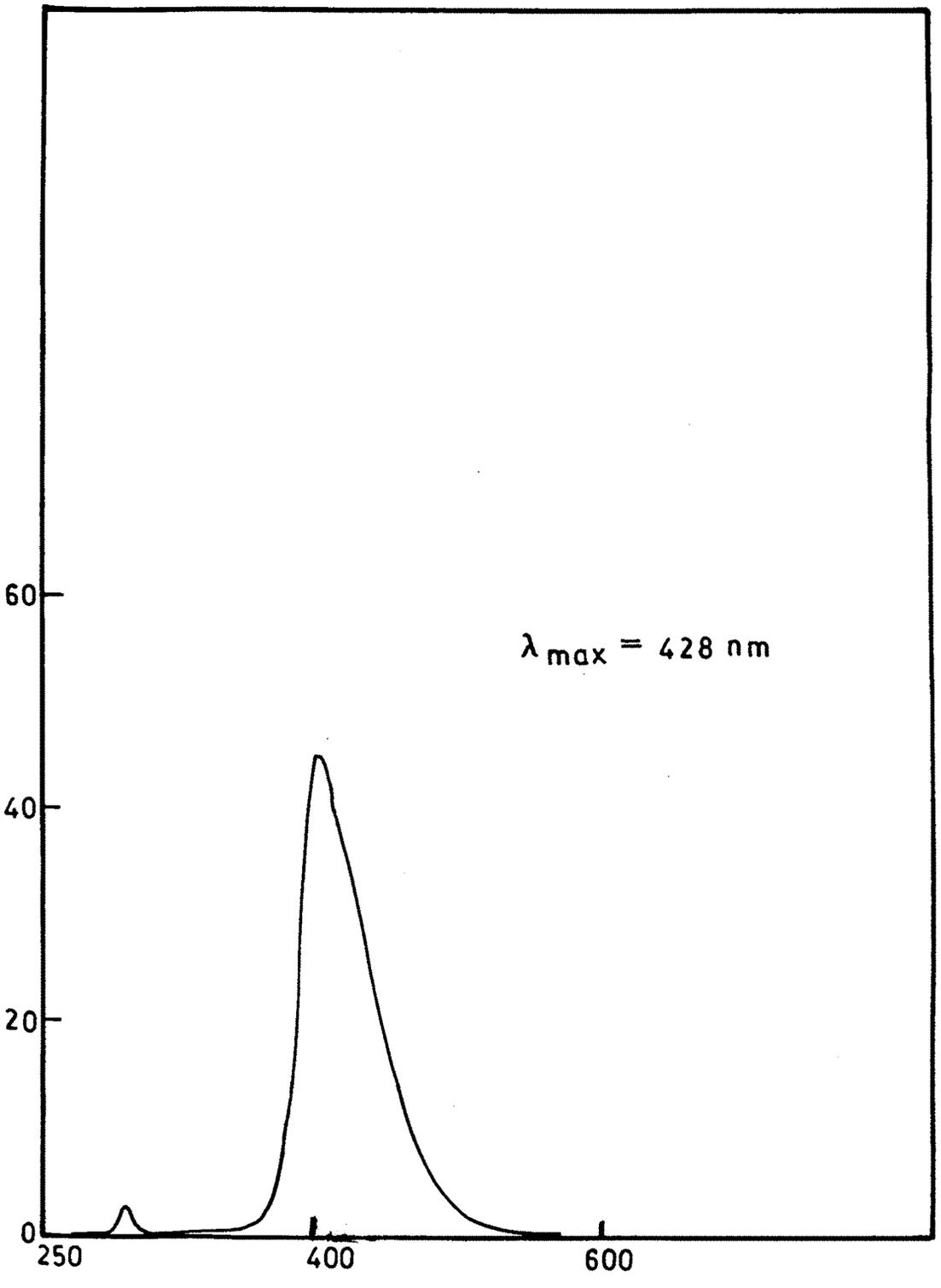
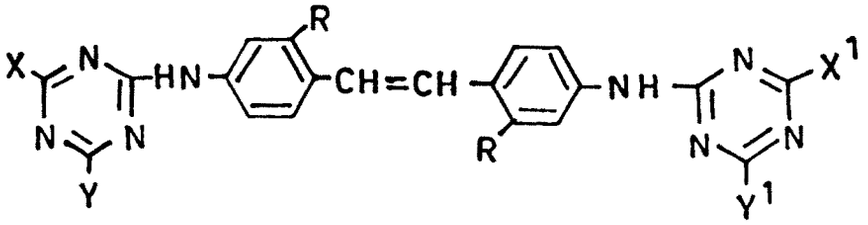


FIG.

FLUORESCENT BRIGHTENING AGENTS

General Structure :



$X = X^1$, $Y = Y^1$, $R = SO_3Na$

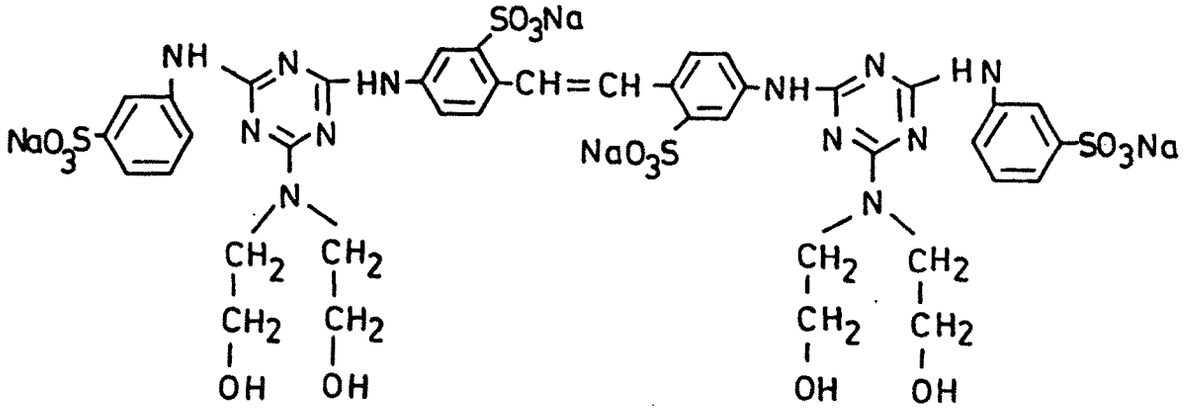
Symmetrical fluorescent brightening agent, where $X = X^1$, $Y = Y^1$ [84]

This type of fluorescent brightener was storage stable at -30 to + 50°C and suitable for use on cellulosic fibers or in the paper making.

FLUORESCENT BRIGHTENER NO. 1

This fluorescent brightener (FBA 1) was commercially available and was supplied by spark chemicals in 98% purity.

STRUCTURE OF FBA 1



Analytical data : Microanalysis of element :

	C	H	N
Found :	40.75	3.15	14.90
Calculated :	40.67	3.14	14.84

Spectral Analysis :

1) U.V - A = 276 nm, B = 330 nm

2) I.R. - NH-(streching)- 3400 cm-1

-NH_ (bending) -1200 cm^{-1}

-OH- 2800-3000 cm^{-1} C=C - 1670 cm^{-1}

3) Fluorescence - 430 nm

UV ABSORPTION SPECTRUM OF F B A NO-1.

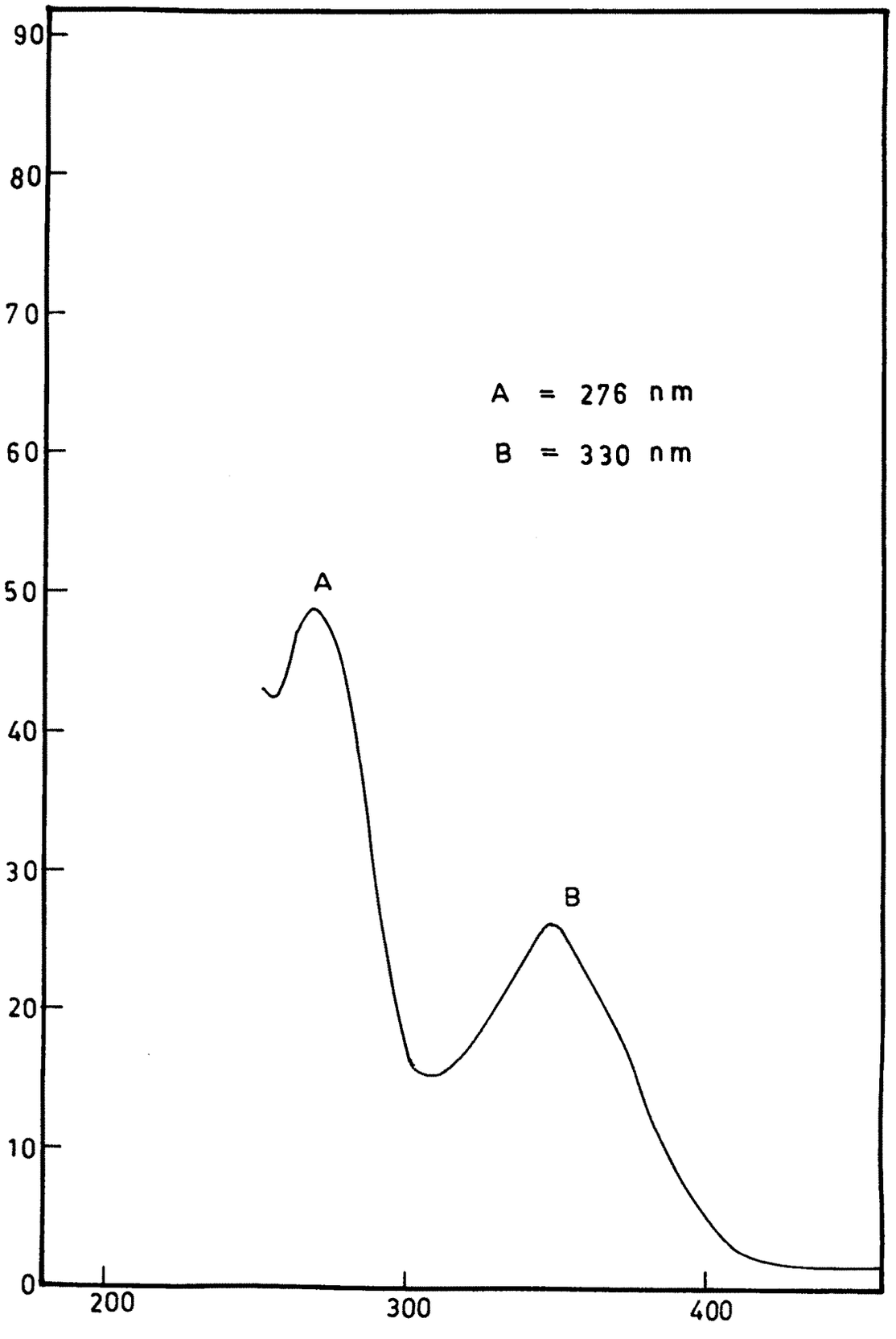


FIG.

IR SPECTRUM OF 4,4′-BIS-[6-METANILO-4-DIETHANOL AMINO-1,3,5-TRIAZIN-2-YL] AMINOSTILBENE-2,2′-DISULPHONIC ACID.

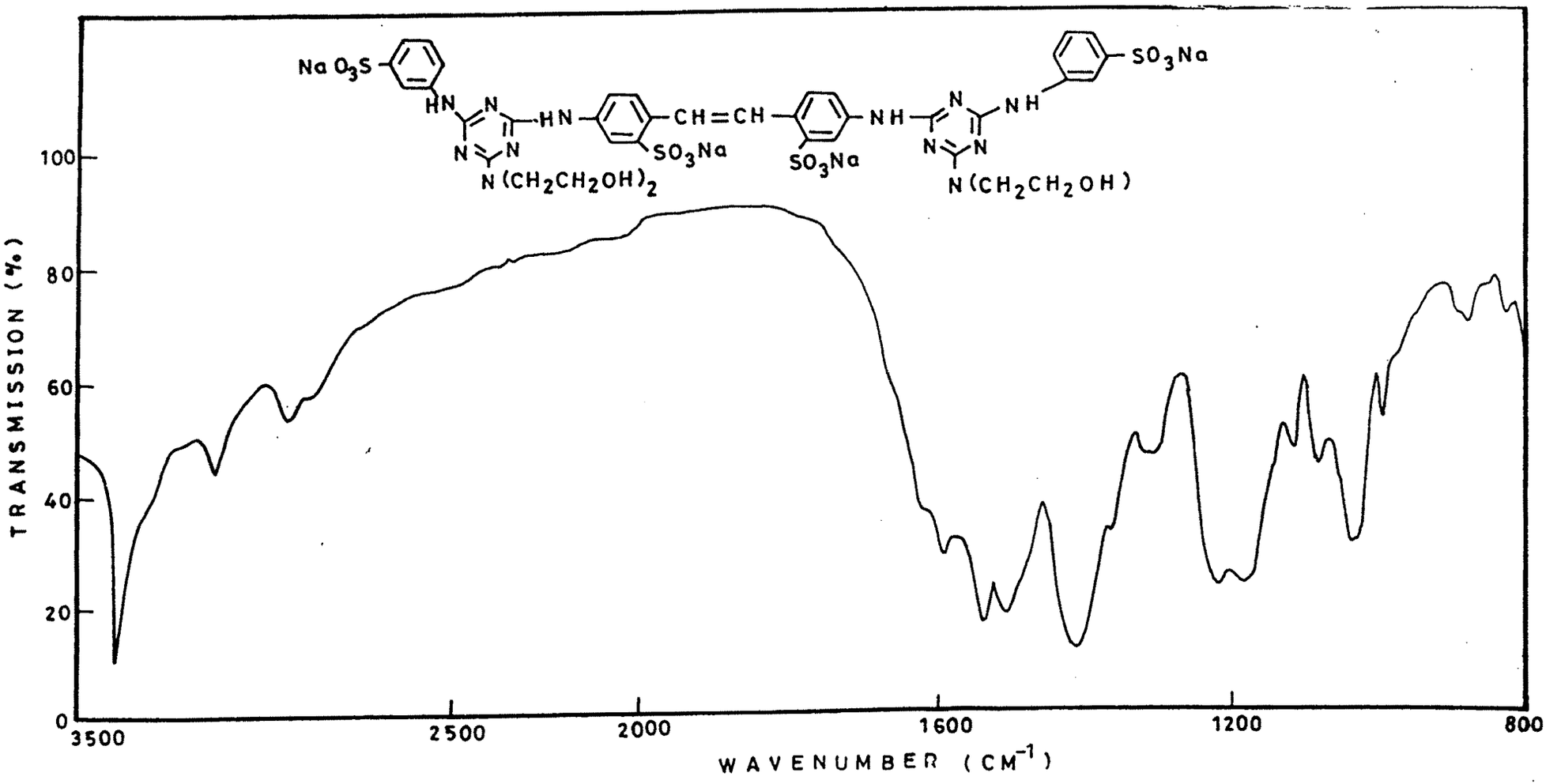


FIG.

FLUORESCENCE SPECTRUM OF FBA NO. 1

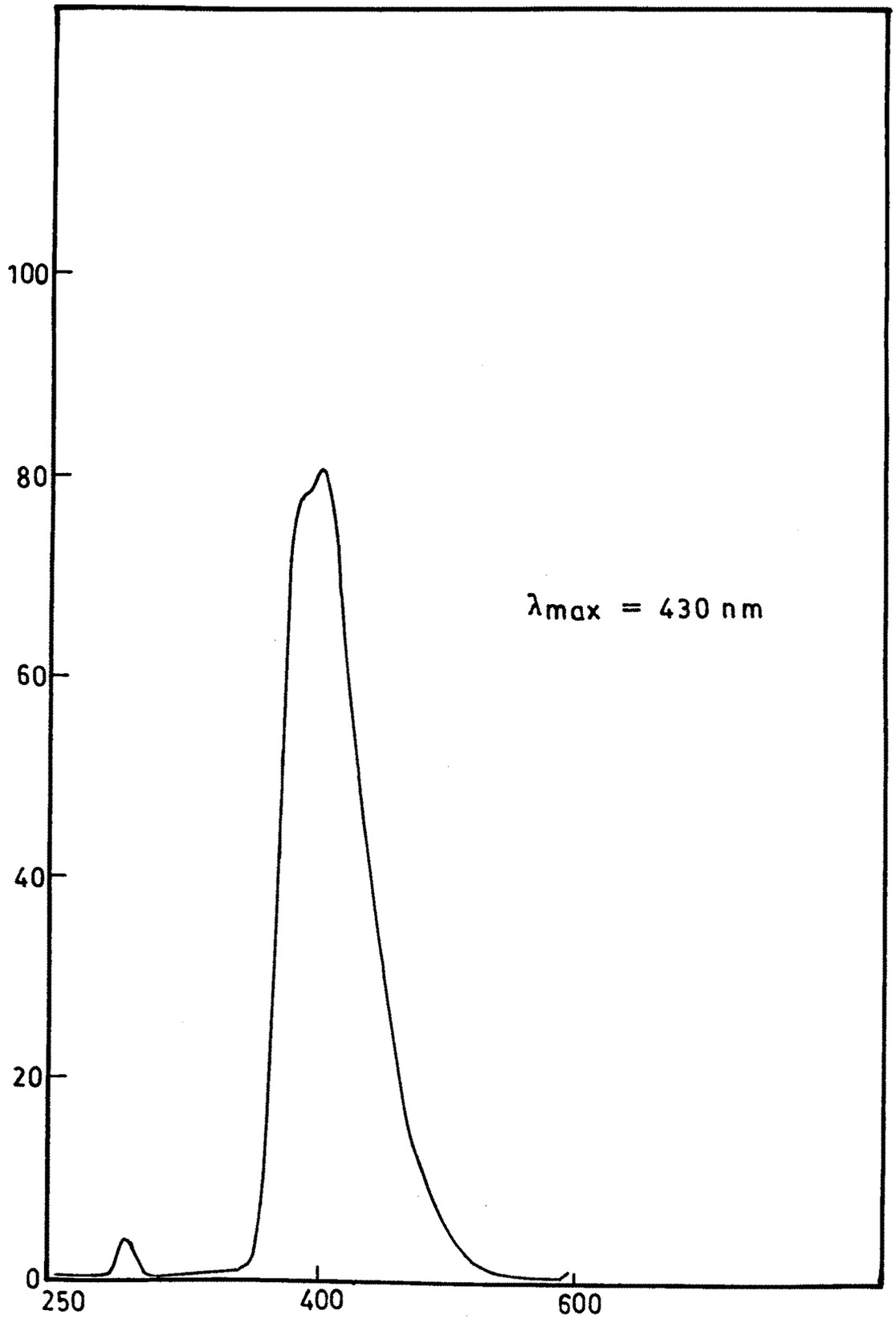


FIG.

SYNTHESIS OF FLUORESCENT BRIGHTENER NO. 2

STEP I - SYNTHESIS OF 6-(6-AMINOURACILO)-2,4-DICHLORO-1,3,5-TRIAZINE

Cyanuric chloride (10 gms, 2 mole) was dissolved in aqueous acetone (25%, 25 ml), maintaining temperature at 0-5°C. Beaker was equipped with mechanical stirrer, 6-Aminouracil (8 gms, 2 mole) was added in small quantity at a time and reaction was stirred vigorously. Reaction was continued after adding all quantity of 6-aminouracil (pH 4-5). The reaction mixture was stirred for an hour.

STEP II - SYNTHESIS OF 4,4'-BIS [6-(6-AMINOURACILO)-4-CHLORO-1,3,5-TRIAZIN-2-YL] AMINOSTILBENE-2,2'-DISULPHONIC ACID

A paste of sodium salt of 4,4'-diaminostilbene-2,2'-disulphonic acid (8 gms, 1 mole) was added to the above reaction product at room temperature. Addition was made slowly and dropwise with continuous stirring. The completion of reaction [condensation of primary amine with cyanuric chloride] was checked by testing unreacted aromatic primary amine by diazotization method.

STEP III - SYNTHESIS OF 4,4'-BIS [6-(6-AMINOURACILO)-4-DIETHANOLAMINO -1,3,5-TRIAZIN-2-YL] AMINOSTILBENE-2,2'-DISULPHONIC ACID

Reaction mixture was heated to 85-90°C. Diethanolamine (6 ml, 2 mole) was added dropwise. Stirring was continued for 30-40 minutes (pH 8.6). Reaction mixture was cooled. It was salted out with sodium chloride and filtered, washed with acetone, dried and the crude

product was weighed. Fine yellow coloured granular powder was obtained with good fluorescence.

Yield = 24 gms.

M.P. = Decomposed above 305°C

Analytical data = Percentage of elements.

	C	H	
Found :	51.80	4.00	14.53
Calculated :	51.81	4.09	14.52

Spectral Analysis :

1) U.V. - A = 280 nm, B = 380 nm

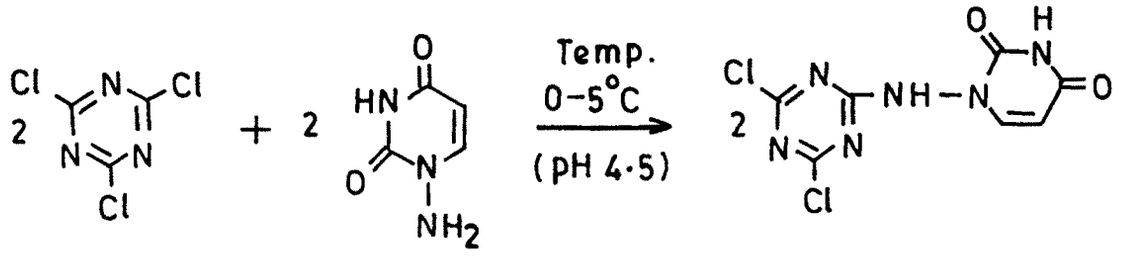
2) I.R. - -NH-3400 cm^{-1} C = O-1665 cm^{-1}

-OH-3200, C = C - 1500-1600

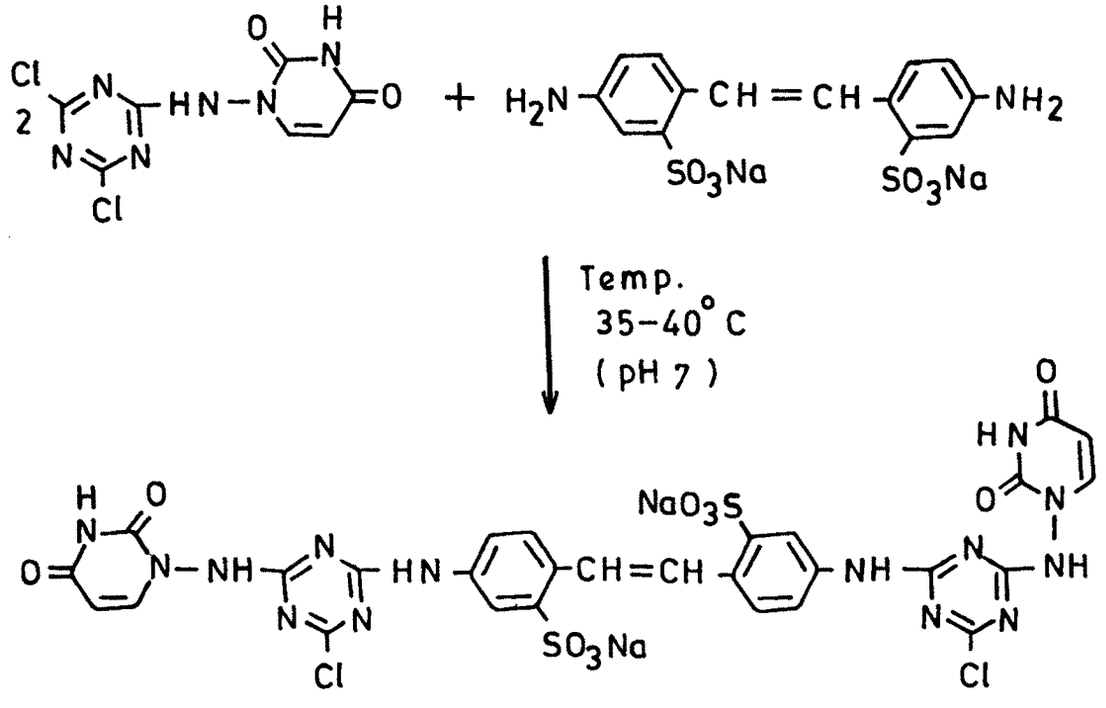
3) Fluorescence - 445 nm

REACTIONS OF FLUORESCENT BRIGHTNER NO. 2

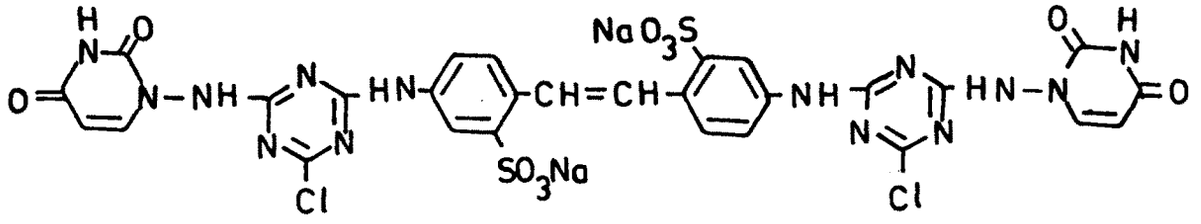
STEP I – SYNTHESIS OF 6-(6-AMINOURACILO)-2,4-DICHLORO-1,3,5-TRIAZINE.



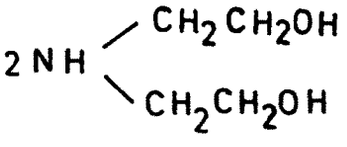
STEP II – SYNTHESIS OF 4,4′-BIS-[6-(6-AMINOURACILO)-4-CHLORO-1,3,5-TRIAZIN-2-YL] AMINOSTILBENE-2,2′-DISULPHONIC ACID.

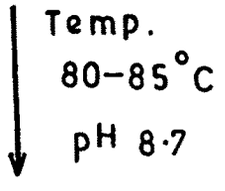


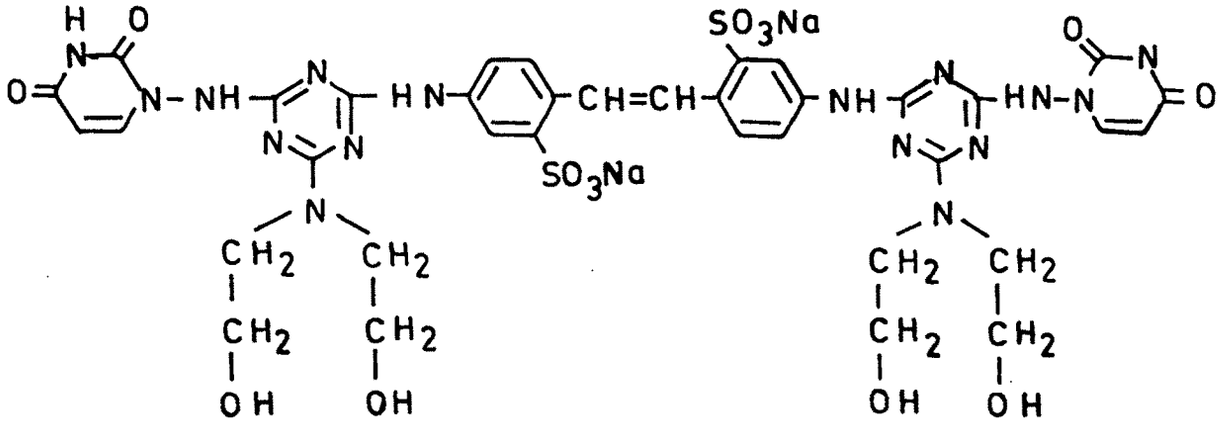
STEP III -SYNTHESIS OF 4,4'-BIS-[6-(6-AMINOURACILO)-4-DIETHANOLAMINO-1,3,5-TRIAZIN-2-YL] AMINOSTILBENE-2,2'-DISULPHONIC ACID.



+







FLUORESCENT BRIGHTNER NO. 2

U V ABSORPTION SPECTRUM OF F B A NO-2

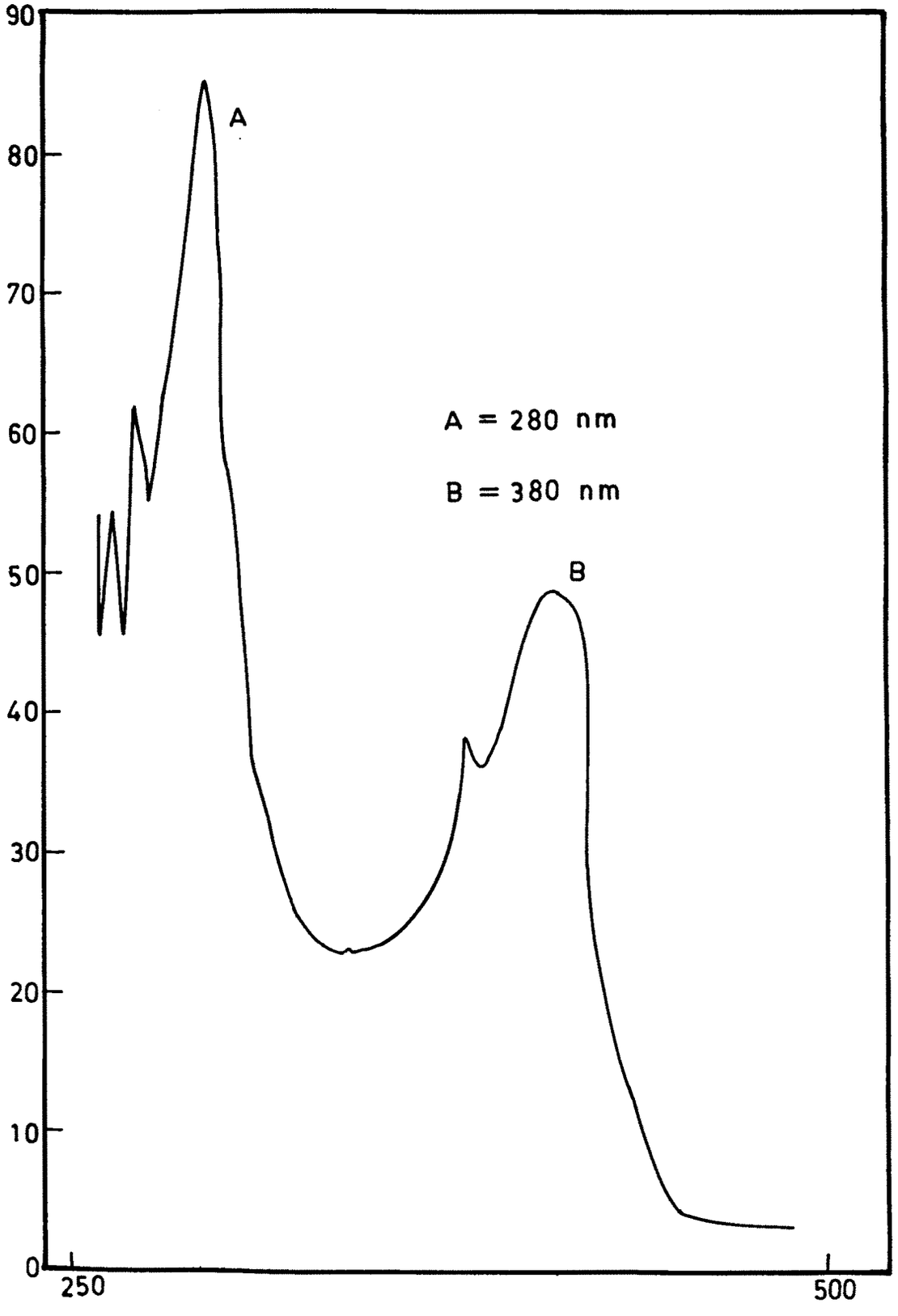


FIG.

IR SPECTRUM OF 4,4′-BIS-[6-(6-AMINOURACILO)-4 DIETHANOL AMINO — 1,3,5-TRIAZIN-2-YL] AMINOSTILBENE-2,2′-DISULPHONIC ACID.

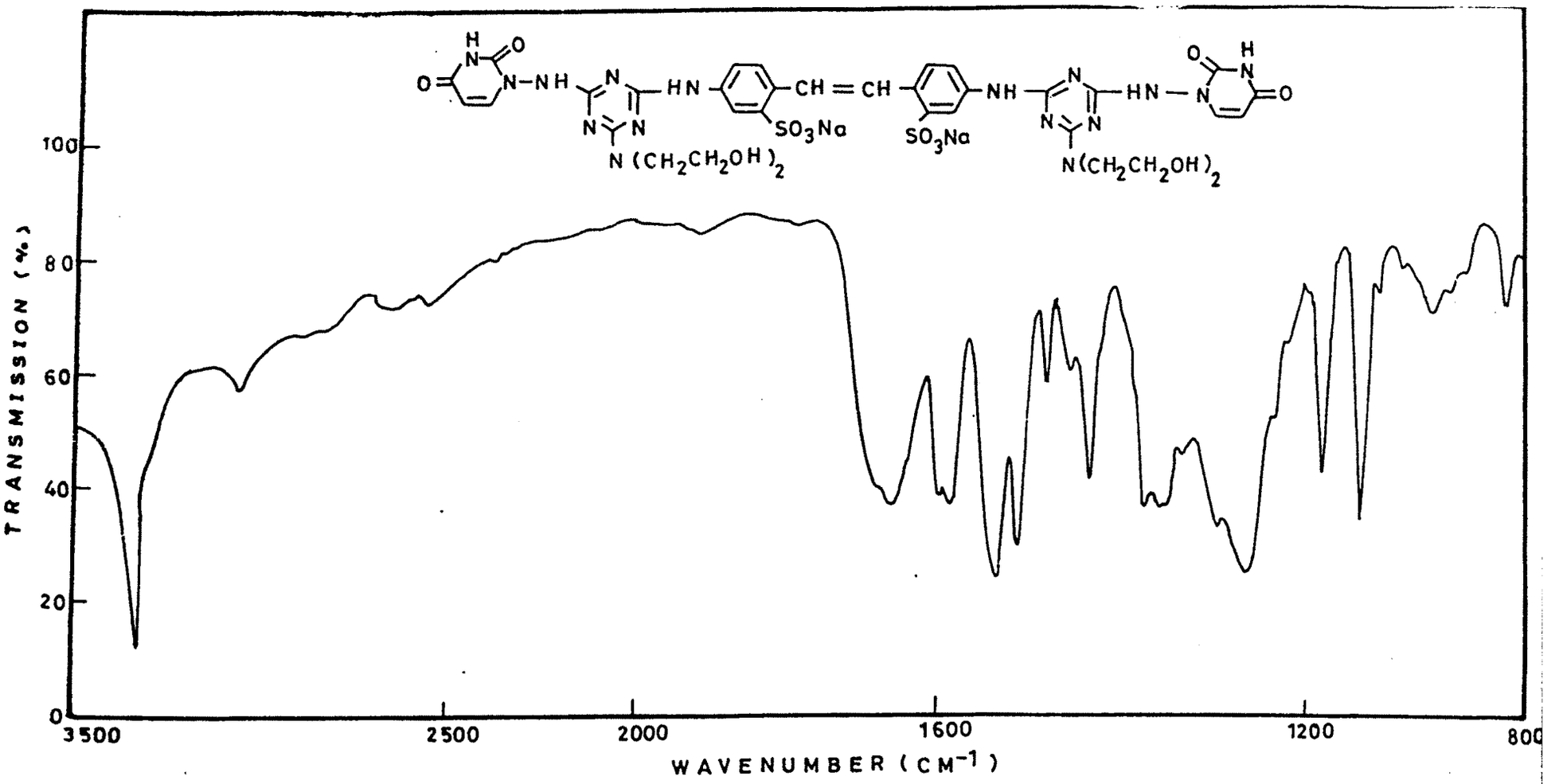


FIG.

FLUORESCENCE SPECTRUM OF FBA NO.2 .

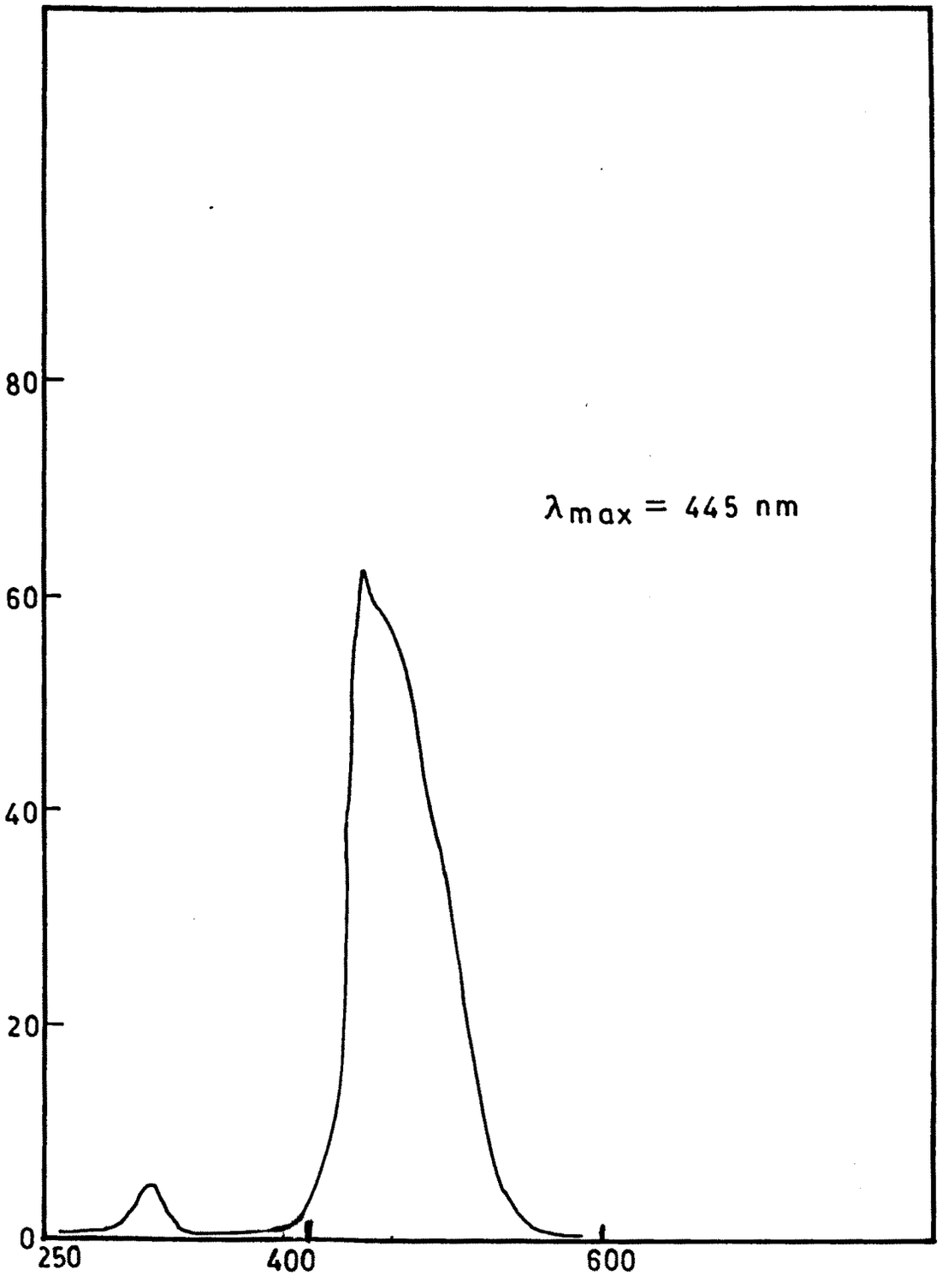


FIG.

SCHEME : SYNTHESIS OF BENZOIC ACID HYDRAZIDE :

The hydrazide was prepared[85] by refluxing equimolar quantities of p-methyl benzoate with hydrazine hydrate (BDH 99%), on water bath till the two layers disappeared and homogeneous solution was formed. The excess of hydrazine hydrate and other unreacted material were purified by recrystallization from slightly warmed ethanol.

Checked M.P.

M.P. - 112°C Yield - 85%

SYNTHESIS OF FLUORESCENT BRIGHTENER NO. 3

STEP I : SYNTHESIS OF 6-BENZHYDRAZIDO- 2,4-DICHLORO-1,3,5-TRIAZINE

Cyanuric chloride (8 grms, 2 mole) was dissolved in aqueous acetone (25%). It was cooled in a ice bath at 0-5°C . Beaker was equipped with mechanical stirrer. Benzoic acid hydrazide was added in small portion at a time and stirred vigorously. Reaction was continued for two hours (pH 4.5).

STEP II : SYNTHESIS OF 4,4'-BIS-[6-BENZHYDRAZIDO-4-CHLORO-1,3,5-TRIAZIN-2-YL] AMINOSTILBENE-2,2'-DISULPHONIC ACID

A paste of 4,4'-diaminostilbene-2,2'-disulphonic acid (5 gms, 1 mole) was added in a above reaction mixture at room temperature. Addition was made slowly and dropwise. Condensation of DASDA with cyanuric chloride required 2-3 hours, second chlorine atom was replaced at 35-40°C.

STEP II - To ensure reaction was completed [condensation of primary amine with cyanuric chloride] was checked by testing unreacted aromatic primary amine by diazotization method.

STEP III - SYNTHESIS OF 4,4'-BIS [6-BENZHYDRAZIDO-4-DIETHANOL AMINO 1,3,5-TRIAZIN-2-YL] AMINOSTILBENE-2,2'-DISULPHONIC ACID

Reaction mixture was heated to raise the temperature 85-90°C. As the third chlorine atom of cyanuric chloride was difficult to react Diethanol amine (6 ml, 2 mole) was added in dropwise, stirring was continued for an hour (pH 8.8). Reaction mixture was cooled. It was salted out with sodium chloride and filtered, dried with acetone. Weighed the crude product. Yellowish green powder with greenish fluorescence was obtained.

Yield - 12 gms. M.P. - Decomposes at 300°C

Analytical data : Percentage of Element.

	C	H	N
Experimental :	54.18	4.10	20.32
Calculated :	54.07	4.13	20.32

Spectral data :

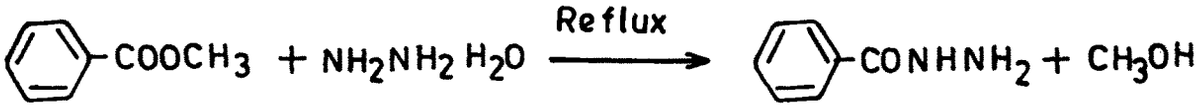
1) UV - A = 280 nm, B = 360 nm

2) I.R. - NH-3250-3300 cm^{-1}, -OH-3500 cm^{-1}
C=O 1675 cm^{-1} C=C 1500-1600 cm^{-1}
-NH-1580 cm^{-1}

3) Fluorescent spectra - 433 nm.

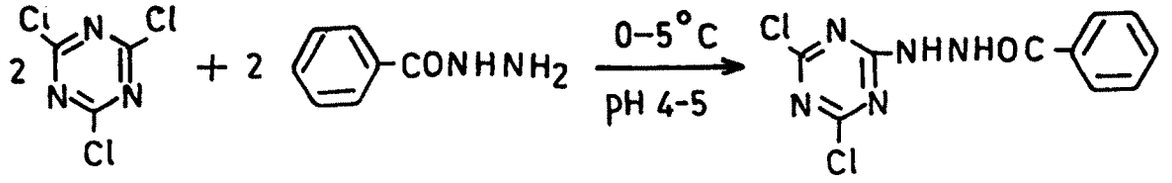
..CTIONS OF FLUORESCENT BRIGHTNER NO. 3

SYNTHESIS OF BENZOIC ACID HYDRAZIDE —

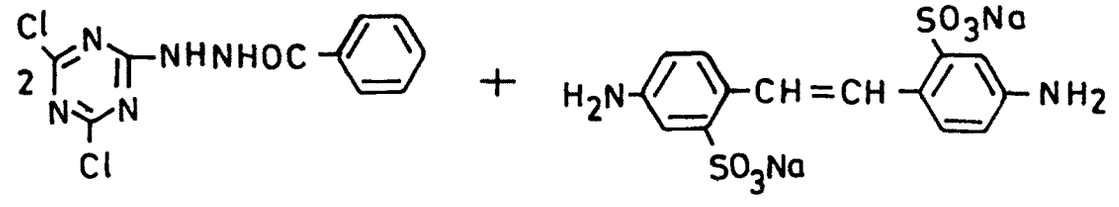


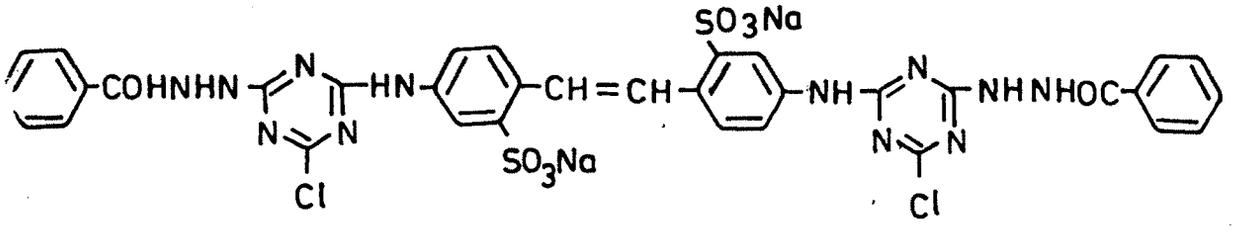
SYNTHESIS OF FLUORESCENT BRIGHTNER NO.3

STEP I — SYNTHESIS OF 6-BENZHYDRAZIDO-2,4-DICHLORO-1,3,5-TRIAZINE

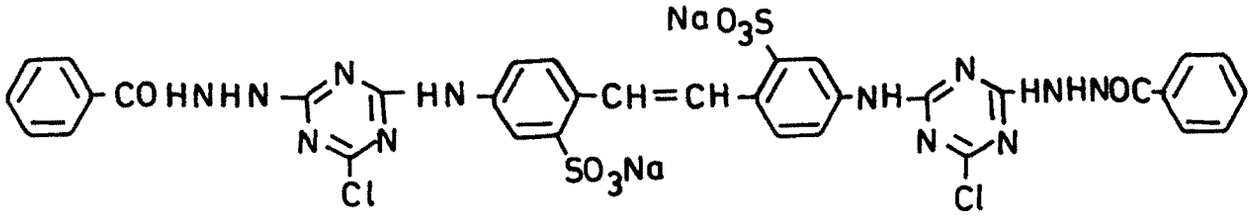


STEP II — SYNTHESIS OF 4,4'-BIS [6-BENZHYDRAZIDO-4-CHLORO-1,3,5-TRIAZIN-2-YL] AMINOSTILBENE-2,2'-DISULPHONIC ACID .

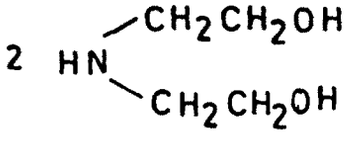




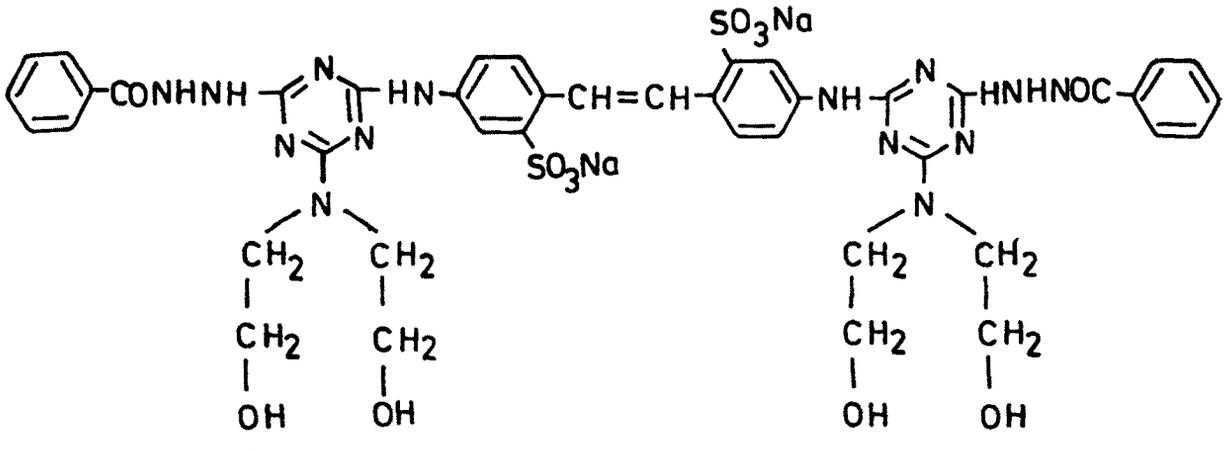
STEP III — SYNTHESIS OF 4,4'-BIS-[6-BENZHYDRAZIDO-4-DIETHANOLAMINO-1,3,5-TRIAZIN-2-YL] AMINOSTILBENE-2,2'-DISULPHONIC ACID.



+



Temp.
80-90° C
pH 8.7



FLUORESCENT BRIGHTNER NO.3

U V ABSORPTION SPECTRUM OF F B A NO. 3 .

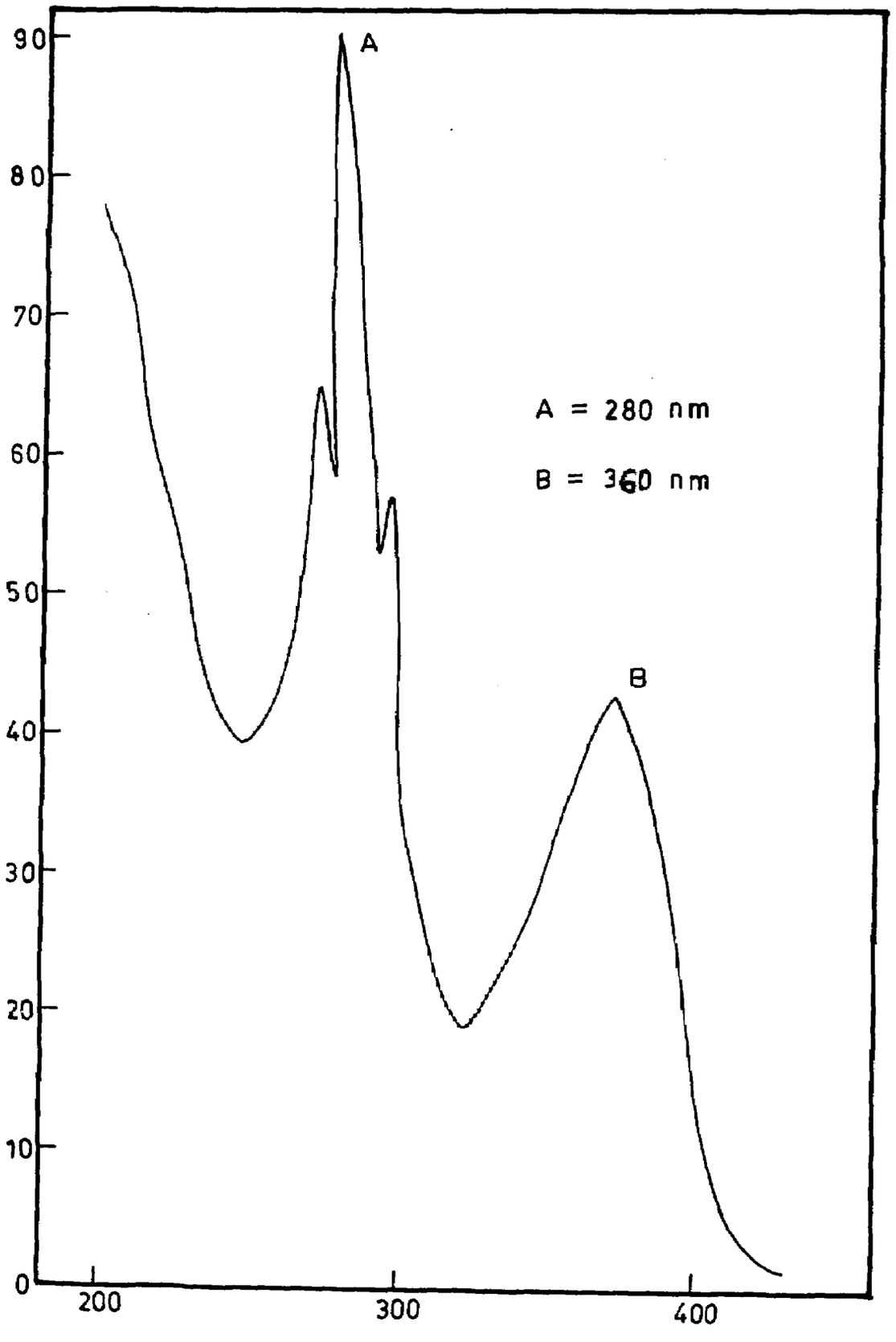


FIG.

TRIAZIN - 2-YL] AMINOSTILBENE - 2,2'- DISULPHONIC ACID .

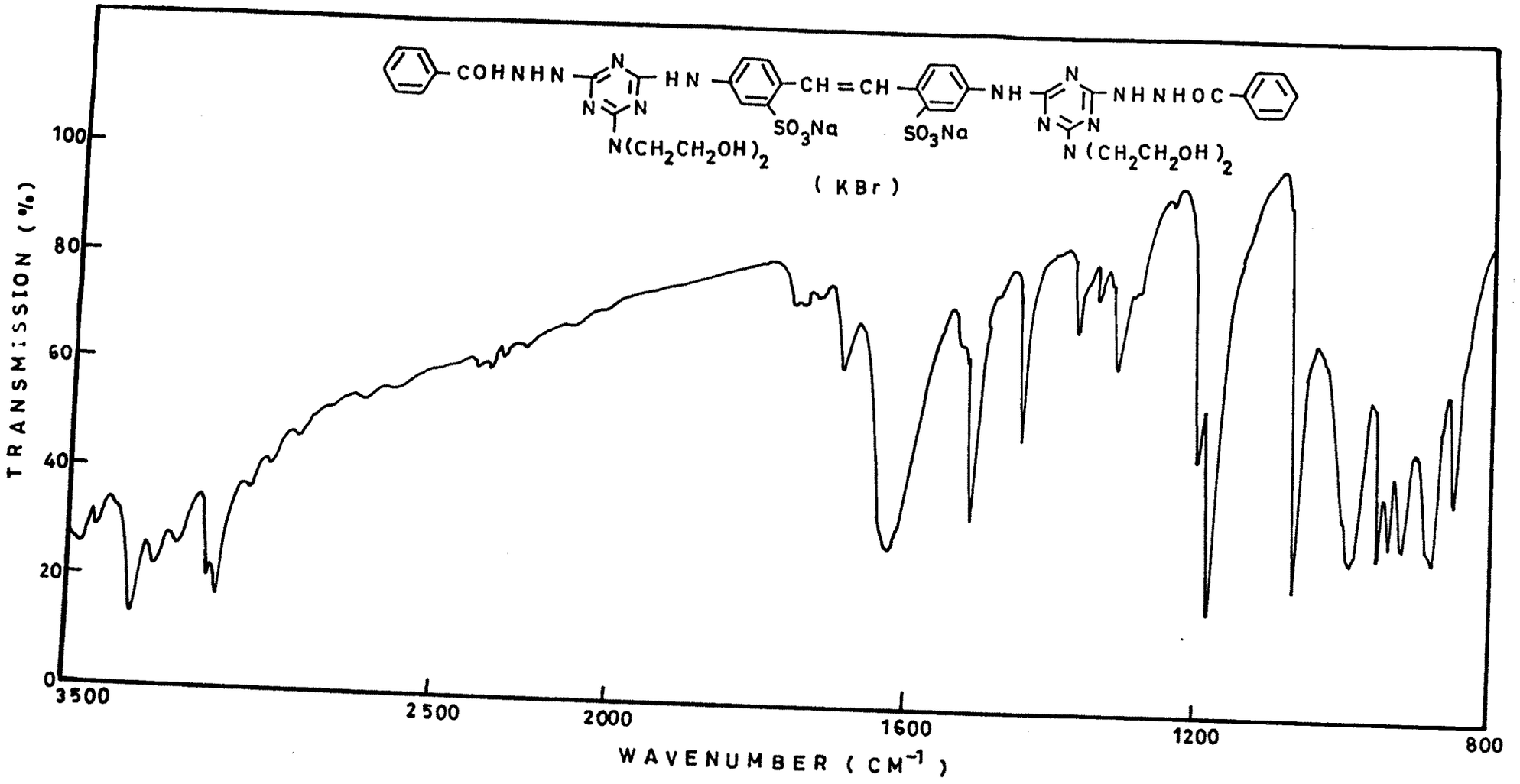


FIG .

FLUORESCENCE SPECTRUM OF FBA NO.3 .

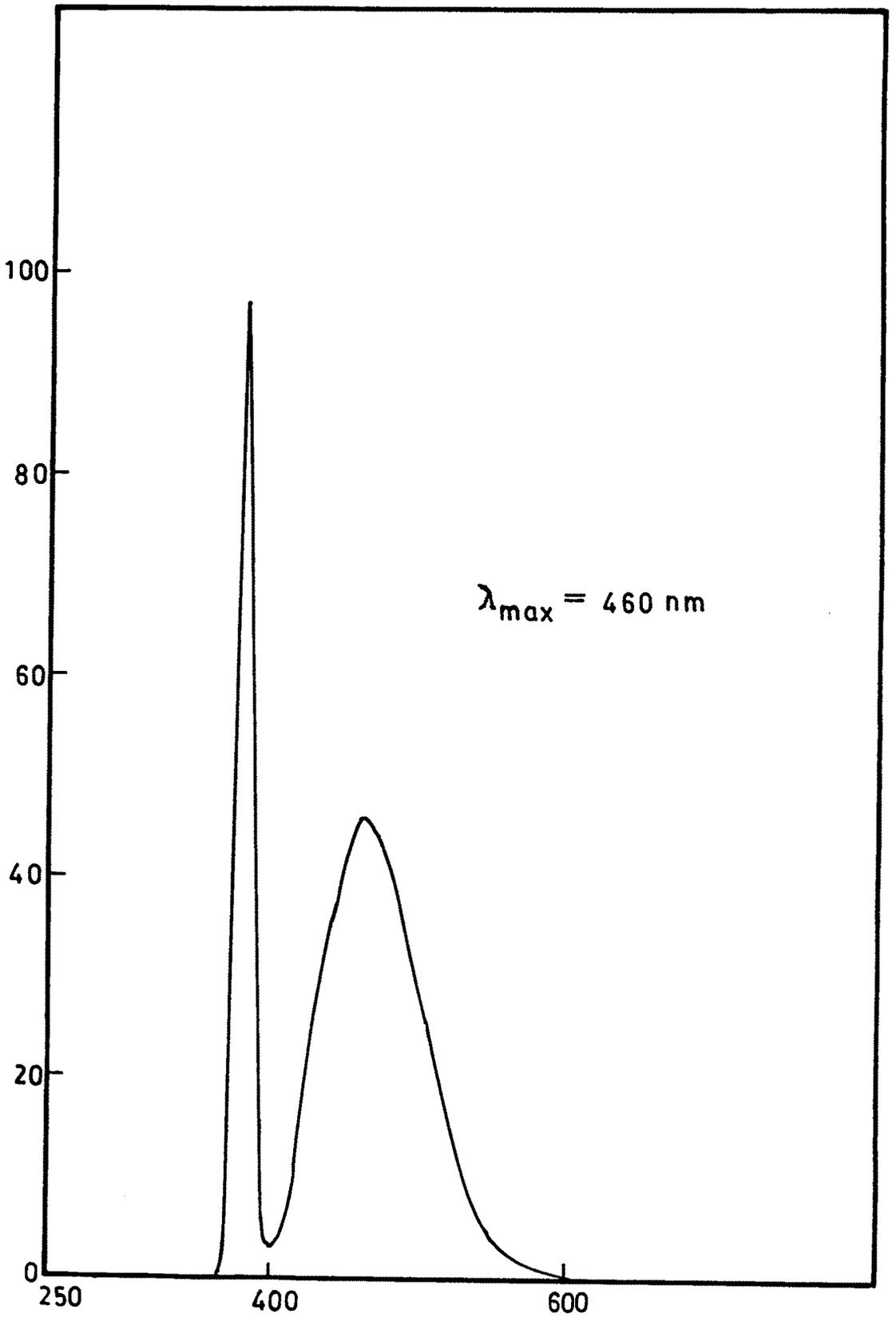


FIG.

SYNTHESIS OF FLUORESCENT BRIGHTENER NO. 4

STEP : SYNTHESIS OF SODIUM SALT OF 4,4'-DIAMINOSTILBENE 2,2'-DISULPHONIC ACID :

4,4'-Diaminostilbene-2,2'-disulphonic acid (11 gms.1 mole) was added in 25 ml distilled water in 250 ml beaker. The mixture was well stirred and equimolar quantity of sodium carbonate (17.2 gms) was added. The mixture was stirred and heated till clear solution obtained.

STEP II : SYNTHESIS OF BENZOYL DERIVATIVE OF 4,4'-BIS AMINOSTILBENE -2,2'-DISULPHONIC ACID :

A paste of sodium salt of 4,4'-diaminostilbene-2,2'-disulphonic acid was then cooled at 0-5°C. Benzoyl chloride (18 gms. 2 mole) was added slowly and dropwise with constant stirring, (pH 6-7). The pH of reacting mixture was kept at 6-7 by adding sodium bicarbonate. Benzoyl chloride was added in excess. The completion of reaction was checked by testing unreacted aromatic primary amine by diazotication method. Water was added and reaction continued at room temperature for 4-5 hours. The product was salted with sodium chloride and filtered. Washed first with water and then with acetone. Dried, and weighed.

Yield - 26 gms. M.P. - Decomposes above 289°C

Analytical data : (Microanalysis)

	Percentage of elements		
	C	H	N
Experimental	61.50	4.44	7.55
Calculated	61.50	4.45	7.55

Spectral data :

1) U.V. λ_A = 268 nm, λ_B = 318 nm

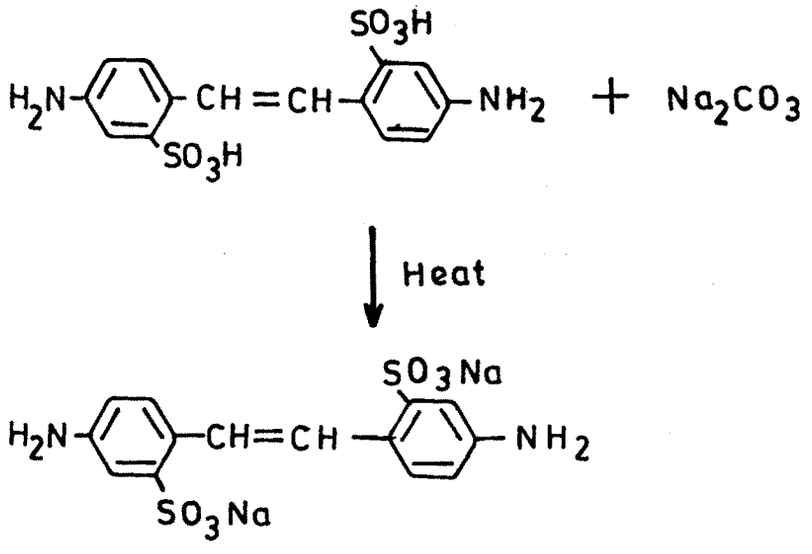
2) I.R. NH.(strec.) - 3400-3300 cm^{-1}

$C=O$ - 1750 cm^{-1} $C=C$ - 1600-1630 cm^{-1}

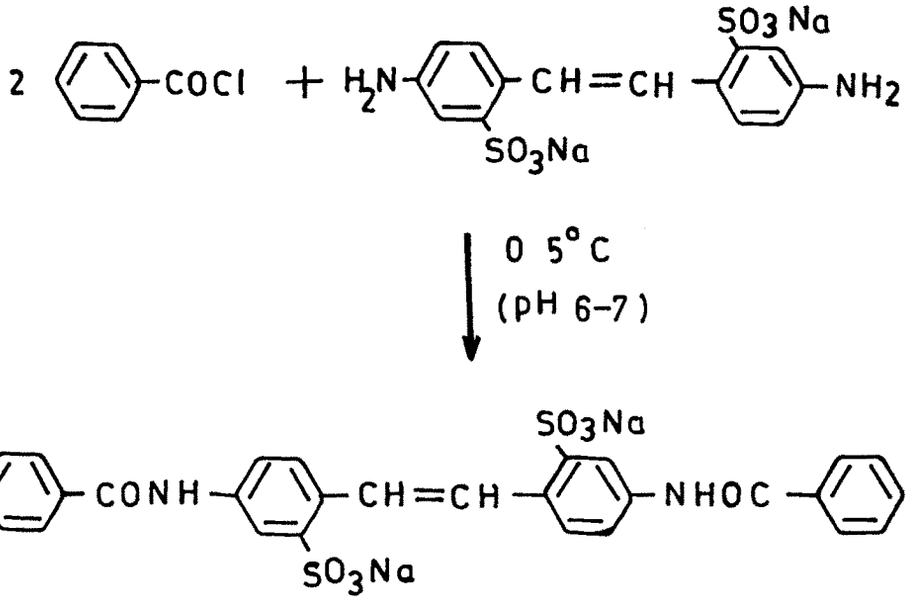
3) Fluorescence - 460 nm.

REACTIONS OF FLUORESCENT BRIGHTNER NO.4

STEP I – SYNTHESIS OF SODIUM SALT OF 4,4'-BIS-AMINO-STILBENE-2,2'-DISULPHONIC ACID :–



STEP II – SYNTHESIS OF 4,4'-BIS-(BENZOYL)-AMINO-STILBENE-2,2'-DISULPHONIC ACID :–



FLUORESCENT BRIGHTNER NO. 4

U V ABSORPTION SPECTRUM OF F B A NO. 4 .

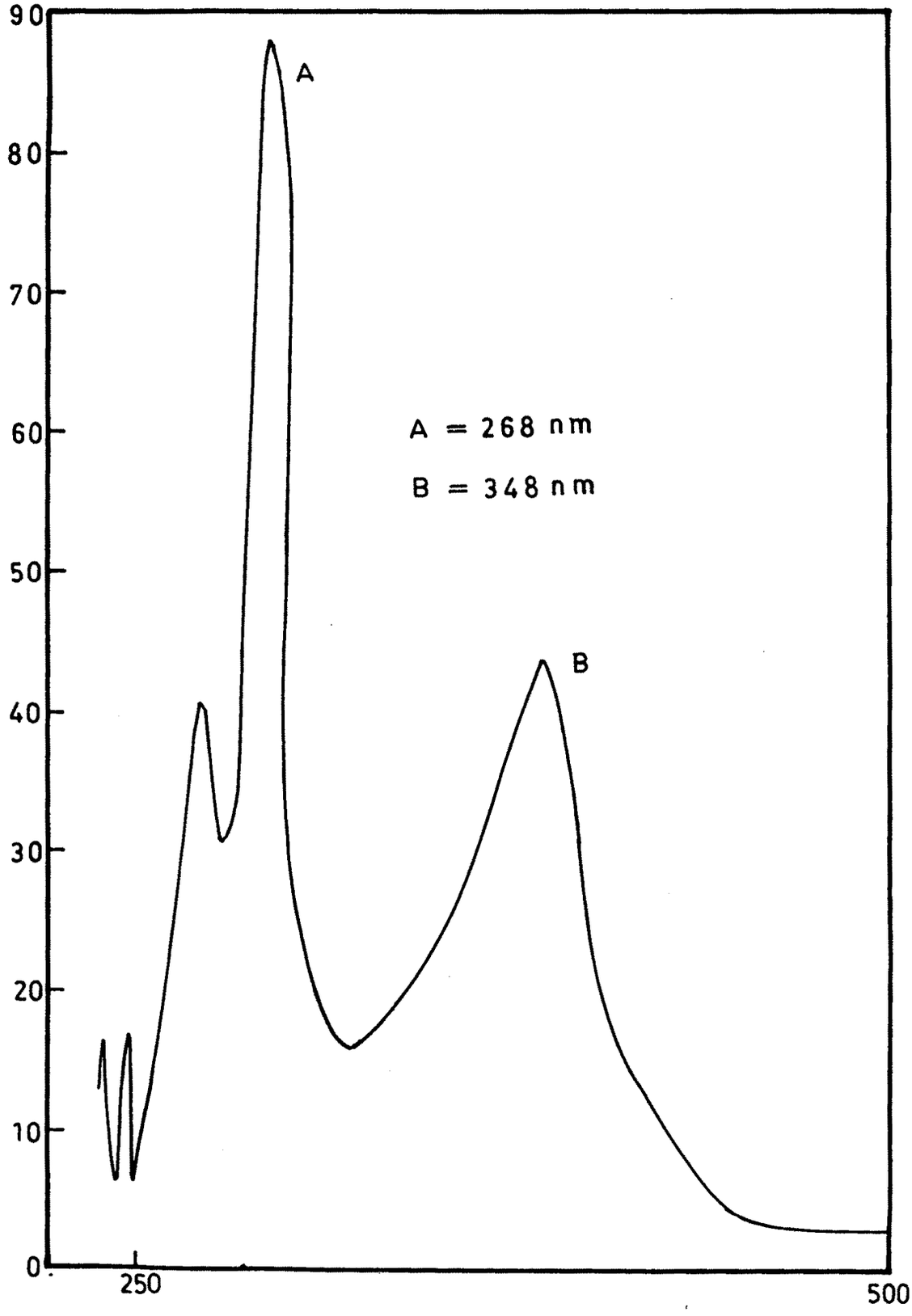
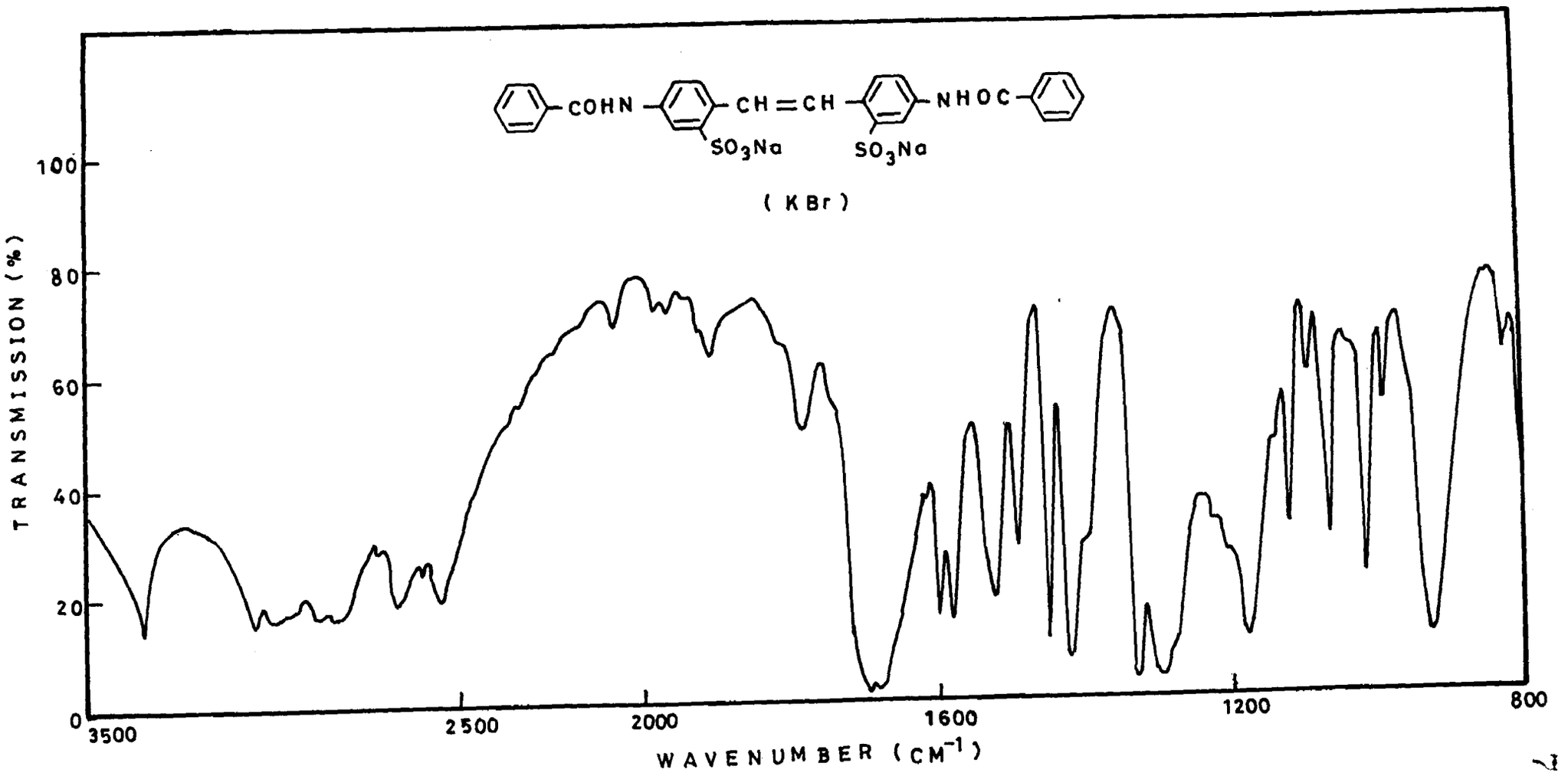


FIG.

I R SPECTRUM OF 4,4′-BIS-(BENZOYL)-AMINOSTILBENE-2,2′-DISULPHONIC ACID.



FIG

FLUORESCENCE SPECTRUM OF FBA NO.4 .

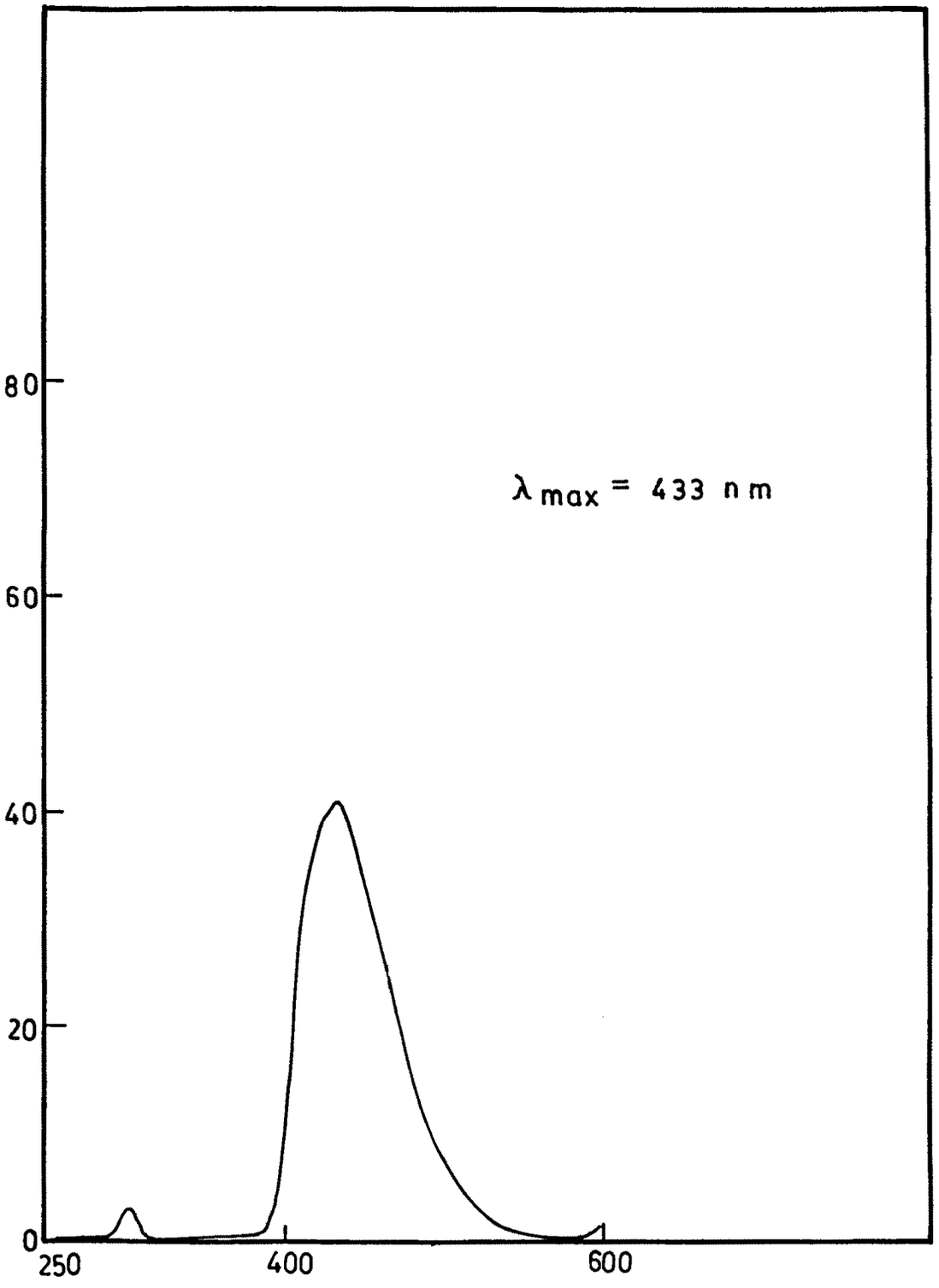


FIG.