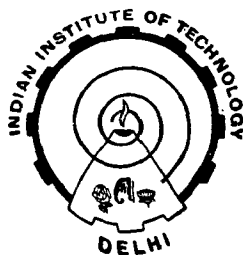


**STUDY OF PHOTOCHROMISM IN ORGANIC COMPOUNDS
(PHOTOCHROMISM IN SCHIFF'S BASES AND HYDRAZONES)**

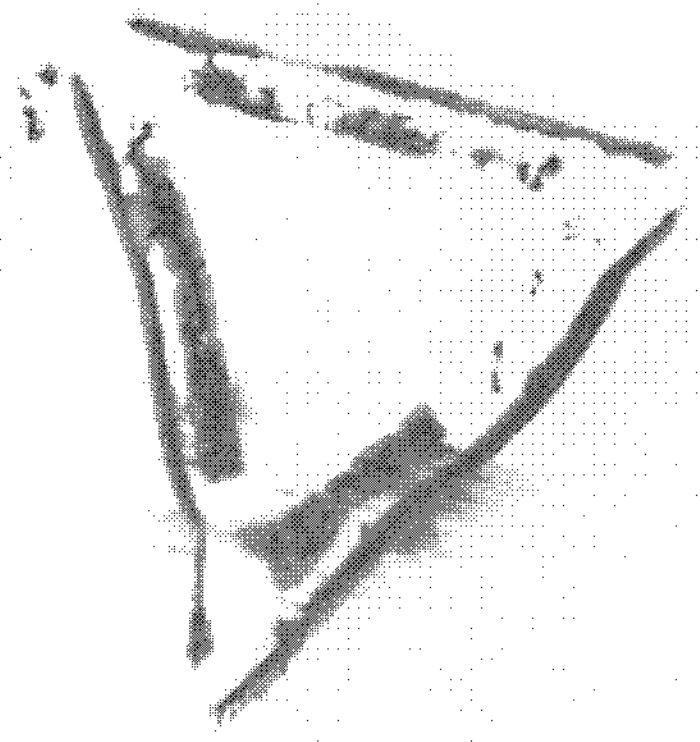
By
M.S.M. RAWAT
DEPARTMENT OF CHEMISTRY

SUBMITTED IN
FULFILMENT OF THE REQUIREMENTS OF THE DEGREE OF
DOCTOR OF PHILOSOPHY



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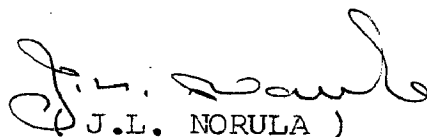


C E R T I F I C A T E

This is to certify that the thesis entitled, "Study of Photochromism in Organic Compounds (Photochromism in Schiff's Bases and Hydrazones)" being submitted by Mr. M.S.M. Rawat to the Indian Institute of Technology, Delhi, for the award of the degree of 'Doctor of Philosophy' in Chemistry, is a record of bonafide research work carried out by him.

Mr. Rawat has worked under my guidance and supervision, and has fulfilled the requirement for the submission of this thesis, which to my knowledge, has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or full, to any other University or Institute for the award of any degree or diploma.



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DEDICATED

TO MY

PARENTS

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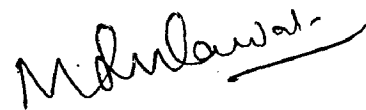
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(ii)

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(M.S.M. RAWAT)

ABSTRACT

The study of photochromic behaviour of dianils, hydroxylated polyazomethines and hydrazones were carried out in the present investigations.

Photochromic behaviour of these compounds was investigated by recording the absorption spectra in UV and visible region in rigid glassy solvents and PMMA films at low temperatures (-75°C & -180°C).

Dianils were synthesized by the condensation of (a) bis-salicylaldehydes with aromatic amines and (b) aromatic diamines with substituted salicylaldehydes.

Dianils of bis-salicylaldehyde 5,5'-sulphone with aromatic amines have shown absorption bands around 450-460 nm in rigid glassy media on cooling to low temperatures (-78°C & -180°C). Appearance of a band at about 450-460 nm can be attributed to the 'cis-keto' form of the dianils and showed fluorescence on irradiation (365 nm) in rigid media.

Most of the dianils showed a characteristic photochromic band at 480 nm at low temperatures (-75°C & -180°C) in rigid glassy solvents and PMMA films. While some of the dianils did not show the characteristic

photochromic bands at -75°C in liquid paraffin. It was considered that the lack of photochromic behaviour in liquid paraffin at -75°C may be due to the low temperature limit and high viscosity of the medium.

The process of photochromism in dianils was assumed due to the rotation of any of the moiety or both the moieties (bis-salicylaldehydic part or/and diamino part) during the photochemical isomerization to form the 'trans-keto' species from the 'enol'. Dianils showed the similar photochromic behaviour to that of salicylideneanilines, so a similar process seems to operate in the isomerization of salicylideneanilines.

It has been observed that the effect of the substituents on aldehydic and amino moieties are similar to that of salicylideneanilines as studied by previous workers.

All the dianils are thermochromic in solid state and showed luminescent behaviour on irradiation (365 nm).

Dianils of o-nitrobenzaldehyde with diamines are photochromic in solid state at room temperature and at liquid air temperature in PMMA films. On prolonged irradiation these dianils changed into irreversible forms.

o-Nitro group in the ortho position of the $-\text{CH}_2$ (methine group) abstract the proton from the $-\text{CH}_2$, to form the quinonoid forms. The irreversible form produced on irradiation for longer period can be attributed to the formation of o-nitrosobenzoyl derivatives of diamines and it was substantiated with the help of IR and Mass Fragmentation Patterns.

Arylidene aroyl hydrazines though structurally similar to benzene sulphonyl hydrazones did not show photochromic behaviour on irradiation in rigid media at low temperatures.

It was inferred that this is probably due to the more polar character of $-\overset{\text{O}}{\parallel}{\text{C}}-$ bond as compared to that of $-\overset{\text{O}}{\parallel}{\text{S}}-$ bond, which has resulted in the intermolecular interaction (H-bonding) between the $-\overset{\text{O}}{\parallel}{\text{C}}-$ of one molecule with the $-\text{OH}$ of the another molecule in polar solvents.

The structural elucidation of these compounds were carried out by elemental analysis, IR, UV and Visible and PMR spectroscopic techniques.

CONTENTS

	Page
List of Figures	(i) - (iv)
List of Tables	(v) - (vii)
 <u>CHAPTER - 1</u>	
INTRODUCTION	1-23
1.1 Definition	1-5
1.2 Fundamental Behaviour of Photochromic Systems	5-7
1.3 Historical Information	7-15
1.4 Photochromic Processes	15-19
1.5 Importance of Photochromic Compounds and Their Applications	19-23
 <u>CHAPTER - II</u>	
MECHANISM OF PHOTOCROMIC SYSTEMS	24-83
2.1 Dissociation	24-39
2.2 Isomerization	39-57
2.3 Reduction-Oxidation Systems	57-60
2.4 Changes in Physical Properties During Photochromic Processes	60-63
2.5 Mechanism of Photochromism in Hydroxyl-Azomethine (Schiff's Bases or Anils)	63-74
* 2.6 Scope of Present-Investigations	74-83

EXPERIMENTAL

Purification of Solvents for UV Spectroscopic Measurements and the Instruments Used	84-88
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CHAPTER - III

PREPARATION, CHARACTERIZATION AND STUDY OF PHOTOCROMISM IN ANILS OF BIS-Salicylaldehydes	89-101
3.1 Preparation of 5,5'-Methylene Bis-Salicylaldehyde	89-90
3.2 Synthesis of Bis-Salicylaldehyde 5,5'-Sulphone	90-92
3.3 Preparation of Dianils	92-94
3.4 Investigation of Photochromic and Thermochromic Behaviour	94-101
3.5 Results	101

CHAPTER - IV

PREPARATION, CHARACTERIZATION AND STUDY OF PHOTOCROMISM IN ANILS OF DIAMINES	102-131
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PART - A

4.1 Preparation of 5-Methylsalicylaldehyde	102-103
4.2 Preparation of 5-Bromosalicylaldehyde	103
4.3 Preparation of 5-Nitrosalicylaldehyde	103-104
4.4 Purification of Diamines	104-105
4.5 Preparation of Dianils of Diamines	105-106
4.6 Physical Data of Dianils	106-111
4.7 Investigation of Photochromic and Thermochromic Behaviour	112-115
4.8 Results	116-117

PART - B

4.9	Preparation and Physical Data of Dianils of O-Nitrobenzaldehyde with Diamines	118-119
4.10	Investigation of Photochromic Behaviour	119-123
4.11	IR Spectra of Irradiated Dianils	123
4.12	Mass Spectra	123-126
4.13	Results	126-127
	Charts of Mass Fragmentation Patterns	128-131

CHAPTER - V

	PREPARATION, CHARACTERIZATION AND STUDY OF PHOTOCHROMISM IN HYDROXYLATED POLYAZOMETHINES	132-146
5.1	Purification of Reagents	132
5.2	Method of Polymerization	132-134
5.3	Characterization of Polymers	134-145
5.4	Investigation of Photochromic and Thermo- chromic Behaviour of HPAM	145-146

CHAPTER - VI

	PREPARATION, CHARACTERIZATION AND STUDY OF PHOTOCHROMISM IN BENZENESULPHONYL HYDRAZONES	147-159
6.1	Preparation of Benzenesulphonyl Hydrazines	147
6.2	Preparation of p-Toluenesulphonyl Hydrazines	148-149
6.3	Preparation of o-Nitrobenzenesulphonyl Hydrazine	149-150

6.4	Preparation of Benzenesulphonyl Hydrazones	151-154
6.5	Investigation of Photochromic Behaviour of Hydrazones	154-158
6.6	Results	159

CHAPTER - VII

	PREPARATION, CHARACTERIZATION AND STUDIES OF PHOTOCHROMISM IN ARYLIDENE-AROYLHYDRAZINES	160-168
7.1	Preparation and Characterization of Arylidene- Aroylhydrazines	160-164
7.2	Investigation of Photochromic Behaviour	164-168
7.3	Results	168

CHAPTER - VIII

	DISCUSSION AND CONCLUSION	169-189
	Section A : Dianils	169-183
	Section B : Hydrazones	183-189
	REFERENCES	190-201