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

By

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DEPARTMENT OF CHEMISTRY

SUBMITTED IN
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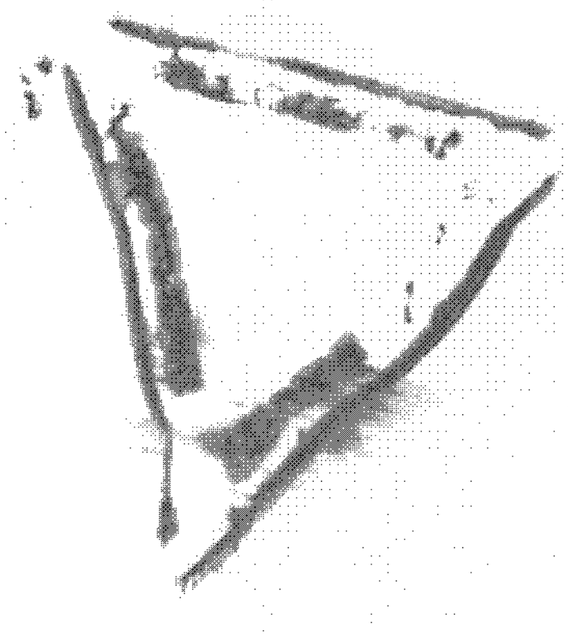

C E R T I F I C A T E

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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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 -CH=(methine group) abstract the proton from the -CH=, 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 $-\overset{O}{\overset{\|}{C}}-$ bond as compared to that of $-\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}-$ bond, which has resulted in the intermolecular interaction (H-bonding) between the $-\overset{O}{\overset{\|}{C}}-$ of one molecule with the -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.

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