ISSN: 0976-3031

Available Online at http://www.recentscientific.com

CODEN: IJRSFP (USA)

International Journal of Recent Scientific Research
Vol. 8, Issue, 7, pp. 18227-18235, July, 2017

International Journal of Recent Scientific Research

DOI: 10.24327/IJRSR

Research Article

SYNTHESIS, CHARACTERISATION AND SOLVATOCHROMISM OF SOME 3-NITRO-1,5-DIARYLFORMAZANS

Sanjeev Kumar* and Rajeev Sharma

Department of Chemistry, Multani Mal Modi College, Patiala-147001, Punjab (India)

DOI: http://dx.doi.org/10.24327/ijrsr.2017.0807.0472

ARTICLE INFO

Article History:

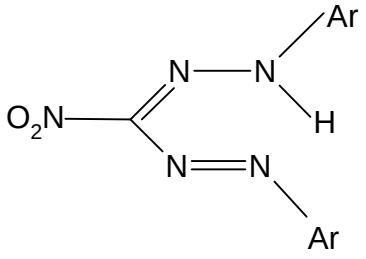
Received 15th April, 2017
Received in revised form 25th May, 2017
Accepted 28th June, 2017
Published online 28th July, 2017

ABSTRACT

3-nitro-1,5-diarylformazans are synthesized by reacting ice cold solution of aryl diazonium salt with alkaline solution of nitromethane in cold. The so synthesized 3-nitro-1,5-diarylformazans have been characterized on the basis of cryoscopic studies, elemental analysis, UV-visible, IR, Mass, ^{1}HNMR and ^{13}CNMR spectral studies. The present studies clearly reveal that the 3-nitro-1,5-diarylformazans have intra molecularly hydrogen bonded symmetrical six membered chelate ring structure. The so synthesized and characterized compounds have been explored for their solvatochromic behavior in various organic solvents of different polarities. The spectral shifts in UV-visible profiles have been revealed using linear solvation energy relationship (LSER) based upon Kamlet-Taft equation.

INTRODUCTION

3-nitro-1,5-diarylformazans, I, constitute a special class of formazan compounds, containing a characteristic chain of atoms and a nitro group (-NO_2) at position 3 (meso position).[1]



I

Where **Ar and Ar'** may be same or different

If Ar= Ar', it is called symmetric 3-nitro-1,5-diarylformazans and if Ar= Ar', it is called unsymmetrical 3-nitro-1,5-diarylformazans. 3-nitro-1,5-diarylformazans are generally prepared by the action of aryldiazonium salts on arylhydrazones or the compounds containing active methylene group like nitromethane[2-10] (CH_3NO_2).

The chemistry and applications of colour change phenomenon commonly known as chromic phenomena such as photochromism, ionochromism, thermochromism, electrochromism and solvatochromism, as well as the lesser popular ones such as tribochromism, piezochromism, vapochromism, and halochromism (figure 1) have been an interesting area of study since the last few decades[12-25]. These chromic phenomena attracted the attention of chemists and find applications in various fields like thermochromic temperature indicators, fax paper, photochromic spectacle lens, smart windows, mirrors and visual displays.[26-28]

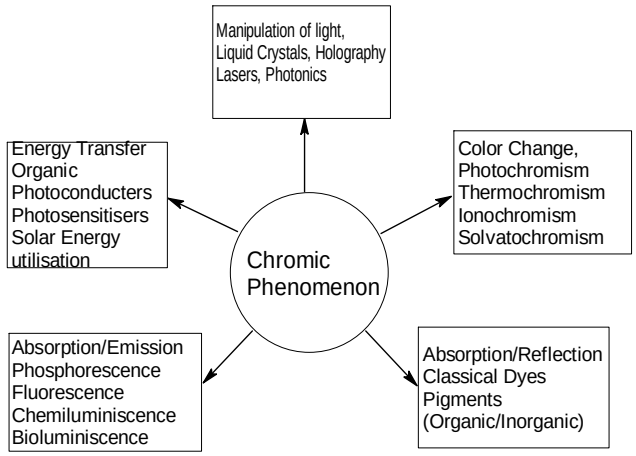


Fig 1 Classification of Chromic Phenomenon

Solvatochromism is described as the phenomenon whereby a compound undergoes a color change on dissolving in different organic solvents either by change in absorption or emission spectra of the molecule[29]. This phenomenon has indispensable scope for the applications of colored compounds in a variety of

Corresponding author:* **Sanjeev Kumar
Department of Chemistry, Multani Mal Modi College, Patiala-147001, Punjab (India)

outlets, especially where changes in the polarity of the medium are a part of the process.

In solvatochromism, the shifts in the maxima of the absorption or emission spectra of molecules are observed owing to differences in the solvation energies of the ground (E_S^0) and excited states (E_S^1) due to the different nature of the solvent, as shown in figure 2.This leads to two observable phenomena:

If the ground state is less polar than the excited state, stabilization of excited state is favored by more polar solvents leading to a decrease in transition energy and a bathochromic shift in the spectrum (positive solvatochromism, as shown in figure 2a).

On the contrary, when the ground state is more polar than the excited state, then a hypsochromic shift (blue shift) in the spectrum (negative solvatochromism, as shown in figure.2b) is observed when the solvent polarity is increased. The type of the solvatochromism exhibited by a compound depends on the difference in dipole moment of the ground and excited states of the chromophore.

The solvatochromic effect is related to a strong dependence of absorption and emission spectra on the solvent polarity. Since polarities of the ground and excited state of a chromophore are different, a change in the solvent polarity will lead to different stabilization of the ground and excited states, and thus, a change in the energy gap between these electronic states. Consequently, variations in the position, intensity, and shape of the absorption spectra are directed by the specific interactions between the solute and solvent molecules.

assumption that attractive solute-solvent interactions are frequently of two kinds: (i) nonspecific dipolarity/polarizability and (ii) specific hydrogen-bond complex formation. Class (ii) is further subdivided, on the basis of the capability of solute and solvent to act as hydrogen accepter or donor into (HBD)/solvent hydrogen-bond acceptor (HBA) complexing and solute HBA/solvent HBD complexing. LSER further assumes linear free energy or electronic energy relationships for each of the contributing terms to the observed solvent effects. Molecular properties like dipole moments, spectroscopic solvent shifts, or molecular affinities etc. are also influenced by the factors affecting the molecular structure of the solvents. The solvatochromic behavior of 3-cyano-1,5-diarylformazans have been investigated by Sanjeev *et al*.[35]

Experimental Section

All the reagents used were of AR grade.
The 3-nitro-1,5-diarylformazans were prepared by the method already reported in literature[8,11]. The method of preparation of one of the representative ligand i.e. 3-nitro-1,5-di-p-phenitylformazans is as follows:

p-Phenitidine (14.5 mL) was added in a mixture of 75mL of conc. HCl and 40 mL of water and was dissolved by heating. Sodium acetate (15g) was added to it and the solution was cooled to 0°C by keeping it in ice-bath. This ice-cold solution was then diazotized by adding an ice-cold solution of sodium nitrite (15g in minimum quantity of water) taking care that the temperature does not rise above 0°C. Nitromethane (6 mL) was separately dissolved in cold aqueous solution of sodium

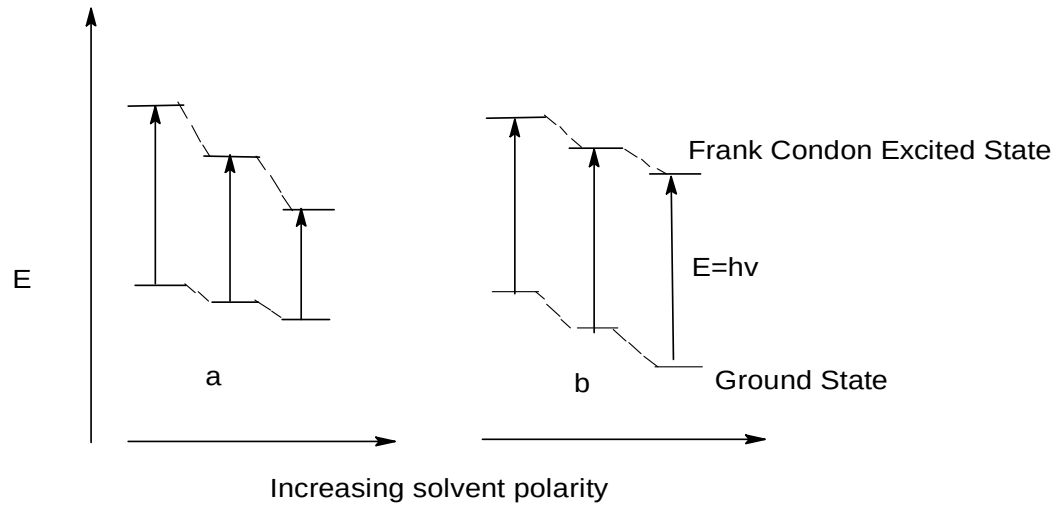
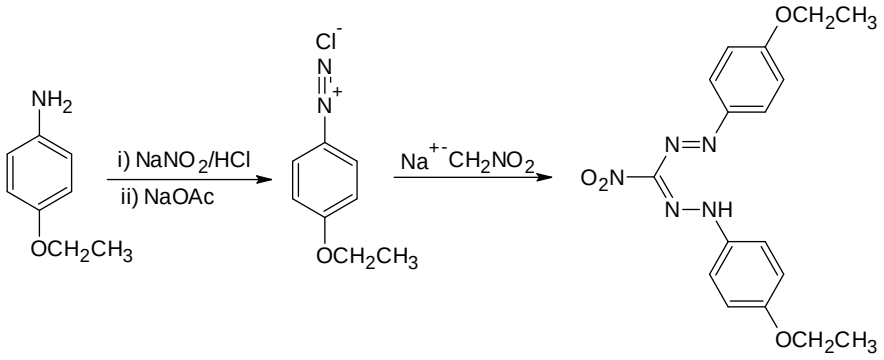


Fig 2 Schematic representation of effect of solvent polarity on the UV-visible transition energy

Positive solvatochromism: With the increase in solvent polarity, the UV-visible transition energy shifts to longer wavelength thus exhibiting bathochromic effect

Negative solvatochromism: With the increase in solvent polarity, the UV-visible transition energy shifts to shorter wavelength thus exhibiting hypsochromic effect
The effect of solvent polarity and hydrogen bonding on the absorption spectrum is interpreted by linear solvation energy relationship method (LSER) concept. Taft *et al*.[30-34] introduced the term linear solvation energy relationship for generalized treatment of solvation effects, which is based on the

hydroxide (8g in minimum quantity of water) keeping the temperature below 10°C. The alkaline solution of nitromethane was then added to the diazotized solution of p-phenitidine in small amounts with constant stirring and keeping the temperature below 5°C. The crude dark red coloured material was formed it was filtered and washed with water. The product was crystallized from ethanol and recrystallized from chloroform-hexane (1:1) mixture. The reaction occurred according to the scheme- I:



Scheme - I

3-nitro-1,5-diphenyl-formazan, 3-nitro-1,5-di-*p*-tolylformazan, 3-nitro-1,5-di-*o*-tolyformazan, 3-nitro-1,5-di-*p*-anisylformazan, 3-nitro-1,5-di-*o*-anisylformazan, 3-nitro-1,5-di-*p*-bromophenyl formazan, 3-nitro-1,5-di-*p*-chlorophenylformazan, 3-nitro-1,5-di-*m*-nitrophenylformazan, 3-nitro-1,5-*p*-nitrophenylformazan and 3-nitro-1,5-di-*o*-phenitylformazan were prepared following the similar procedure.

Physical Measurements

The IR spectra of the so synthesized, purified and recrystalized 3-nitro-1,5-diarylformazans were recorded in KBr and in carbon tetrachloride, on Cary eclipse 630 FTIR spectrophotometer.

The ^{1}HNMR and ^{13}CNMR spectra of 3-nitro-1,5-diarylformazan ligands were recorded in $CDCl_3$ on Bruker Advance II 400 MHz Spectrometer. The mass spectral studies were carried out using Agilent 6200 TOF/6500 series, Version Q-TOF B.05.00.

MATERIALS AND METHOD

The organic compound with different characteristics- methanol, ethanol, tetrahydrofuran (THF), acetonitrile (ACN), dichloromethane (DCM), dimethylformamide (DMF), dimethylsulphoxide (DMSO), chloroform, cyclohexane, 1,4-dioxane, ethylacetate and acetone were used as the solvents. These solvents were of analytical grade. The deionized doubly distilled water was used. The stock solutions of 1.292 X 10^{-5} M compounds were prepared in different organic solvents. The UV-visible spectrums of the solutions were scanned in the range 330-600nm using Thermo Scientific 2600 UV-Visible Spectrophotometer. All measurements were carried out at room temperature. The values of dielectric constant ε, refractive index n and other solvatochromic parameters α, β and π* were taken from the literature.163. The spectral data for the various compounds is summarized as below:

3-nitro-1,5-di-phenylformazan: Blood red color, Yield=50% M.p.:162-163°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 15.10 (s, 1H, NH), 7.2-7.8 (m, 8H), ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.0, 144.1, 130.2, 130.0, 120.4 ppm. FT-IR (KBr): 1550 (s), 1352 (s), 1285 (s), 750 (s) cm^{-1}. UV-vis ($CHCl_3$): λ_{max} 325 nm (ε = 11500 L mol^{-1} cm^{-1}), 452 nm (ε = 23750 L mol^{-1} cm^{-1}). MS (EI): *m/z* 269 (M+, 25 %). Anal.Calcd for $C_{13}H_{11}N_5O_2$: C, 52.52; H, 4.11; N, 26.21. Found C, 51.09; H, 3.85; N, 26.16.

3-nitro-1,5-di-p-tolylformazan: Maroon Red, Yield=46% M.p.: 122-124°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 15.40 (s, 1H, NH), 7.2-7.6 (m, 8H), 2.42 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.1, 144.7, 141.4, 131.0, 120.3, 21.7 ppm. FT-IR (KBr): 3276, 1546 (s), 1509, 1352 (m), 1281 (s), 815 (m) cm^{-1}. UV-vis ($CHCl_3$): λ_{max} 265 nm (ε =8250 L mol^{-1} cm^{-1}), 340 nm (ε = 14000 L mol^{-1} cm^{-1}), 464 nm (ε = 27500 L mol^{-1} cm^{-1}).MS (EI): *m/z* 297 (M+, 15 %). Anal.Calcd for $C_{15}H_{15}N_5O_2$: C, 60.60; H, 5.09; N, 23.56. Found C, 60.61; H, 5.06; N, 23.43.

3-nitro-1,5-di-p-anisylformazan: Dark Red, Yield=42% M.p.: 118-120°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 15.12 (s, 1H, NH), 6.0-8.0 (m, 8H), 2.0-2.80 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.0, 160.8, 152.3, 140.4, 130.8, 120.9, 20.2 ppm. FT-IR (KBr): 3432, 1536 (s), 1340 (m), 1275 (s), 798 (m) cm^{-1}. UV-vis ($CHCl_3$): λ_{max} 265 nm (ε =8250 L mol^{-1} cm^{-1}), 340 nm (ε = 14000 L mol^{-1} cm^{-1}), 464 nm (ε = 27500 L mol^{-1} cm^{-1}).MS (EI): *m/z* 329 (M+, 15 %). Anal.Calcd for $C_{15}H_{15}N_5O_2$: C, 54.71; H, 2.73; N, 21.27. Found C, 55.02; H, 2.93; N, 21.56.

3-nitro-1,5-di-p-chlorophenylformazan: Cherry red color, Yield=52% M.p.:146-148°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 15.20 (s, 1H, NH), 6.4-8.4 (m, 8H), ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.2, 143.1, 140.7, 138.3, 129.2, 120.1, 119.7 ppm. FT-IR (KBr): 3196, 1552(s), 1355(s), 1310 (s), 750 (s), 625cm^{-1}. UV-vis ($CHCl_3$): λ_{max} 365 nm (ε = 13000 L mol^{-1} cm^{-1}), 452 nm (ε = 23500 L mol^{-1} cm^{-1}). MS (EI): *m/z* 338 (M+, 27 %). Anal.Calcd for $C_{13}H_9N_5Cl_2O_2$: C, 46.15; H, 2.66; N, 21.71. Found C, 45.55; H, 2.05; N, 20.92.

3-nitro-1,5-di-p-bromophenylformazan: Poppy Red color, Yield=50% M.p.:180-182°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 14.8 (s, 1H, NH), 6.0-8.0 (m, 8H), ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.9, 149.3, 142.9, 139.6, 137.4, 125.6, 122.4, 118.6 ppm. FT-IR (KBr): 3202, 1554(s), 1598, 1358(s), 1310 (s), 750 (s), 559 cm^{-1}. UV-vis ($CHCl_3$): λ_{max} 342 nm (ε = 12500 L mol^{-1} cm^{-1}), 452 nm (ε = 25000 L mol^{-1} cm^{-1}). MS (EI): *m/z* 427 (M+, 30 %). Anal.Calcd for $C_{13}H_9N_5Br_2O_2$: C, 36.53; H, 1.17; N, 16.04. Found C, 37.47; H, 1.17; N, 16.40.

3-nitro-1,5-di-p-phenitylformazan: Red color, Yield=45% M.p.:110-112°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 14.7 (s, 1H, NH), 6.3-7.9 (m, 8H), 3.6-4.2 (m, 4H), 2.5-2.9 (m 6H) ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.9, 148.8, 132.2, 127.7, 115.4, 63.7, 15.0 ppm. FT-IR (KBr): 3033, 1598(s), 1569, 1360(s), 1257(s), 747(s), 559 cm^{-1}. UV-vis ($CHCl_3$): λ_{max} 315 nm (ε = 11000 L mol^{-1} cm^{-1}), 452 nm (ε = 22500 L mol^{-1} cm^{-1}). MS (EI): *m/z* 357 (M+, 28%). Anal.Calcd for $C_{17}H_{19}N_5O_4$: C, 57.14; H, 5.32; N, 19.60. Found C, 58.02; H, 4.99; N, 20.16.

LSER concept-Kamlet -Taft

Kamlet-Taft equation was used to describe multiple intermolecular solute-solvent interactions

$$\nu_{max} = \nu_0 + s\pi^* + b\beta + a\alpha \qquad \text{(I)}$$

where α, β and π^* are solvent parameters and s, b and a are solvatochromic coefficients.

in terms of the parameters such as π^* (a measure of solute/solvent dipolarity/dielectric effect), β (a measure of hydrogen bond acceptor basicity) and α (a measure of hydrogen bond donor acidity) contribute to the UV-visible spectral shifts to the different extent. Thus Kamlet-Taft equation-I helps to unravel, quantify, correlate and rationalise multiple inteacting solvent effects as many types of physico-chemical properties.

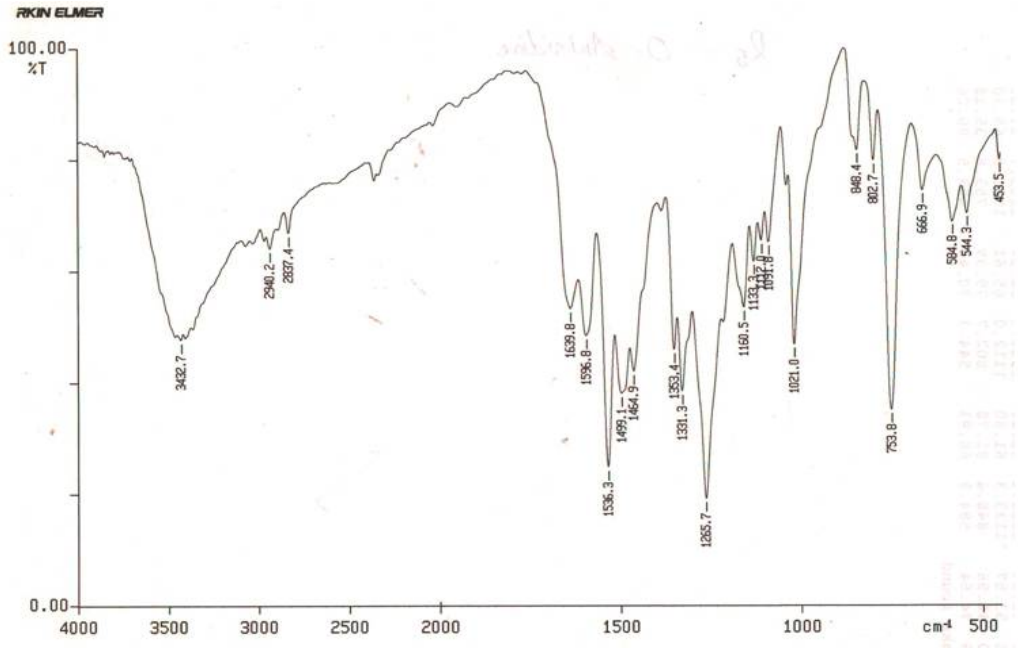


Fig. 3a FTIR spectrum of 3-nitro-1,5-di-*p*-anisylformazan

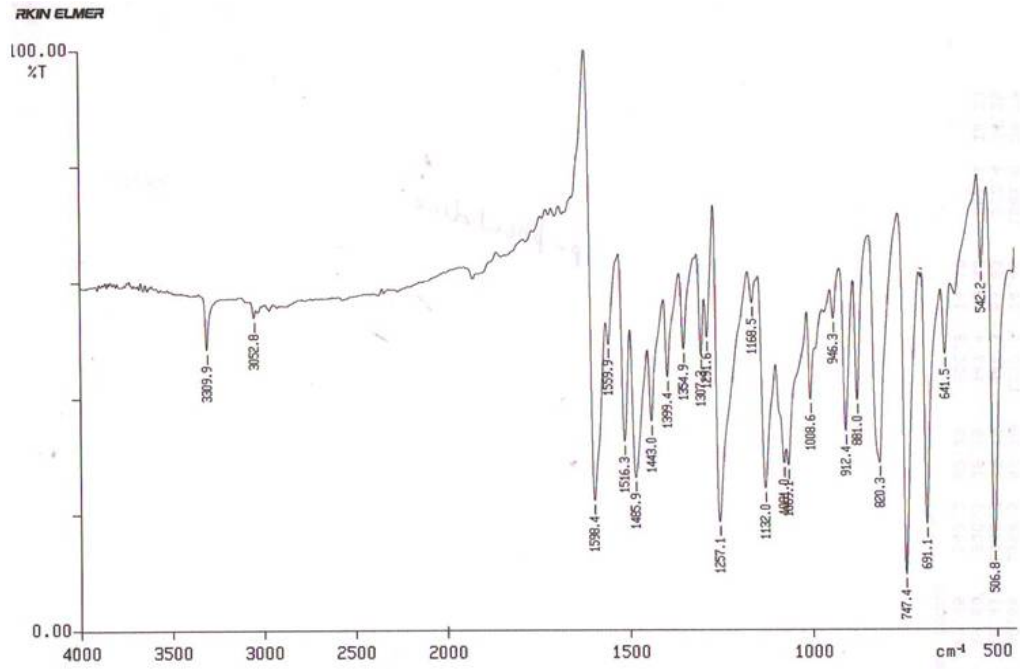


Fig 3b FTIR spectrum of 3-nitro-1,5-di-*p*-phenitylformazan

The above generalized equation is intended for use in the Linear Solvation Energy Relationships (LSER) describing the solute-solvent interactions. The multiple parameter correlations involving different physico-chemical properties of the solvents

RESULTS AND DISCUSSION

FTIR Studies

All the 3-nitro-1,5-diarylformazans studied here are found to be monomeric on the basis of cryoscopic studies in benzene. The IR of 3-nitro-1,5-diarylformazans in KBr phase shows υ_{N-H} as a very broad band between 2900-3200cm^{-1}. This band shifts slightly towards higher frequencies i.e. between 3360-3000 cm^{-1} when the IR is recorded in CCl_4 solution. But no new sharp band appears around 3400 cm^{-1} due to υ_{N-H} (unassociated) nor does υ_{N-H} shifts its position even on changing the concentration of 3-nitro-1,5-diarylformazans.[8,25] This suggest an intramolecular hydrogen bonding for 3-nitro-1,5-diarylformazans.

The IR spectra[11,12] of the 3-nitro-1,5-diarylformazans show group frequency bands that are typical of 'formazyl' group. These group frequencies are different from those observed in the compounds containing isolated azo or hydroazo group. This is because of the high degree of conjugation in formazans. Additional absorption bands appear due to $C-NO_2$ group.

FTIR spectrum of 3-nitro-1,5-diarylformazans have been shown in the figure 3a-3b

^{1}HNMR studies

The proton magnetic resonance (PMR)/^{1}HNMR studies of 3-nitro-1,5-diarylformazans show aromatic protons as multiplet between 6.0-8.0 ppm and imino proton as a very broad signal between 14.0-16.0 ppm from TMS in $CDCl_3$ (figure 4).

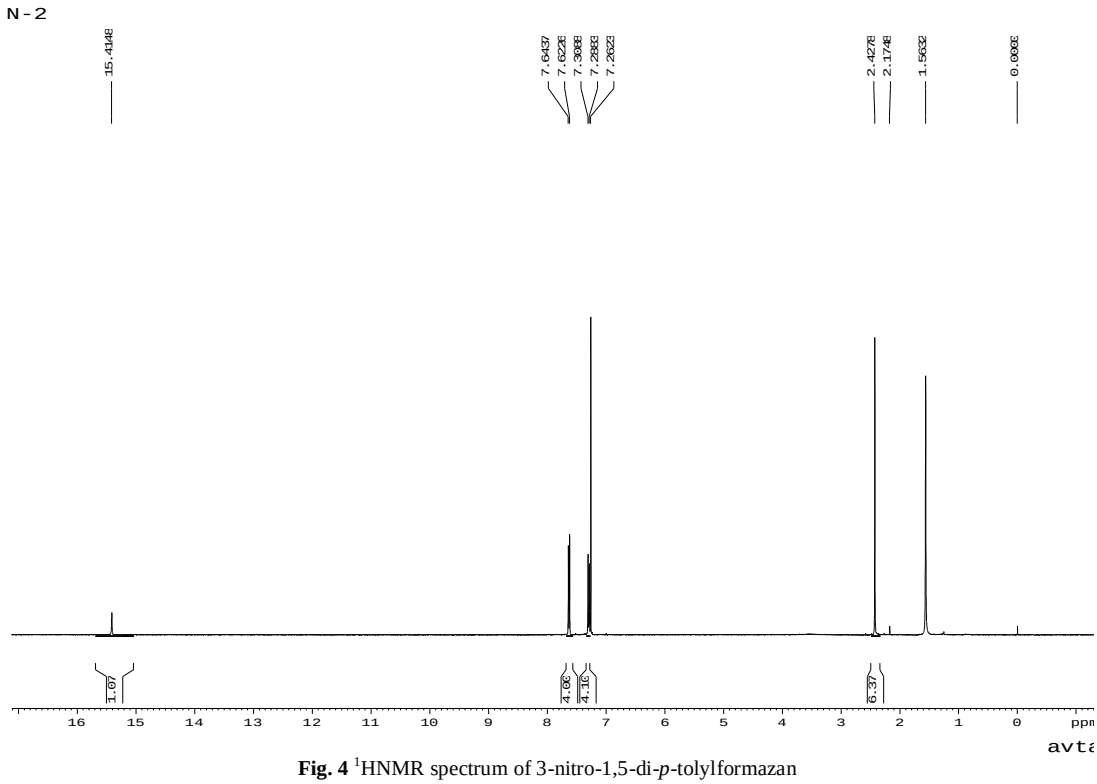


Fig. 4 ^{1}HNMR spectrum of 3-nitro-1,5-di-*p*-tolylformazan

The position of this signal does not shift even if the concentration of a particular 3-nitro-1,5-diarylformazans in solution is varied example, in case of concentration dependent studies on 3-nitro-1,5-di-p-phenitylformazan, the NH signal was observed 14.97 ppm from TMS in $CDCl_3$ between the concentration range 0.06 m.moles/ml to 0.01 m.moles/ml of $CDCl_3$. The concentration dependent studies of this compound in deuterated DMSO again give NH signal at a constant position i.e. 14.97 ppm from TMS. This fact strongly supports the previous conclusion that the imino hydrogen is strongly chelated between the two N-aryl groups.[8]

Also single -CH_3 signal is observed for the methyl groups in case of 3-nitro-1,5-di-*o*-tolylformazan and 3-nitro-1,5-di-*p*-tolylformazan at 2.54 and 2.38 ppm, respectively, from TMS in $CDCl_3$.

^{13}CNMR Spectral Studies

^{13}CNMR spectra of the 3-nitro-1,5-diarylformazans exhibit characteristic peak due to the formazyl carbon from 155-165 ppm, the peak due to phenyl carbon is observed at 115-130 ppm. In addition to the above peaks, the compound 3-nitro-1,5-di-*p*-tolylformazan exhibit the peaks at 15-25ppm which corresponds to -CH_3 group . Similarly in the compound 3-nitro-1,5-di-*p*-phenitylformazan, the peaks appearing at 60-65ppm and those at 15-20ppm correspond to -*o*-CH_2 and -CH_3 group respectively (figure 5).

Mass Spectral Studies

The formazan moiety possesses $-N^1=N^2-\underset{|}{C^3}=\underset{|}{N^4}-N^5-$ as the basic structural unit in its molecule. The fragmentation mode of a compound as studied by mass spectrometer mainly depends upon the nature of the bonds that are present between the atoms and nature of the group present on the terminal carbons. Azo hydrazone

tautomerism exhibited by azo compounds is prevented during mass spectral studies due to the electron bombardment.

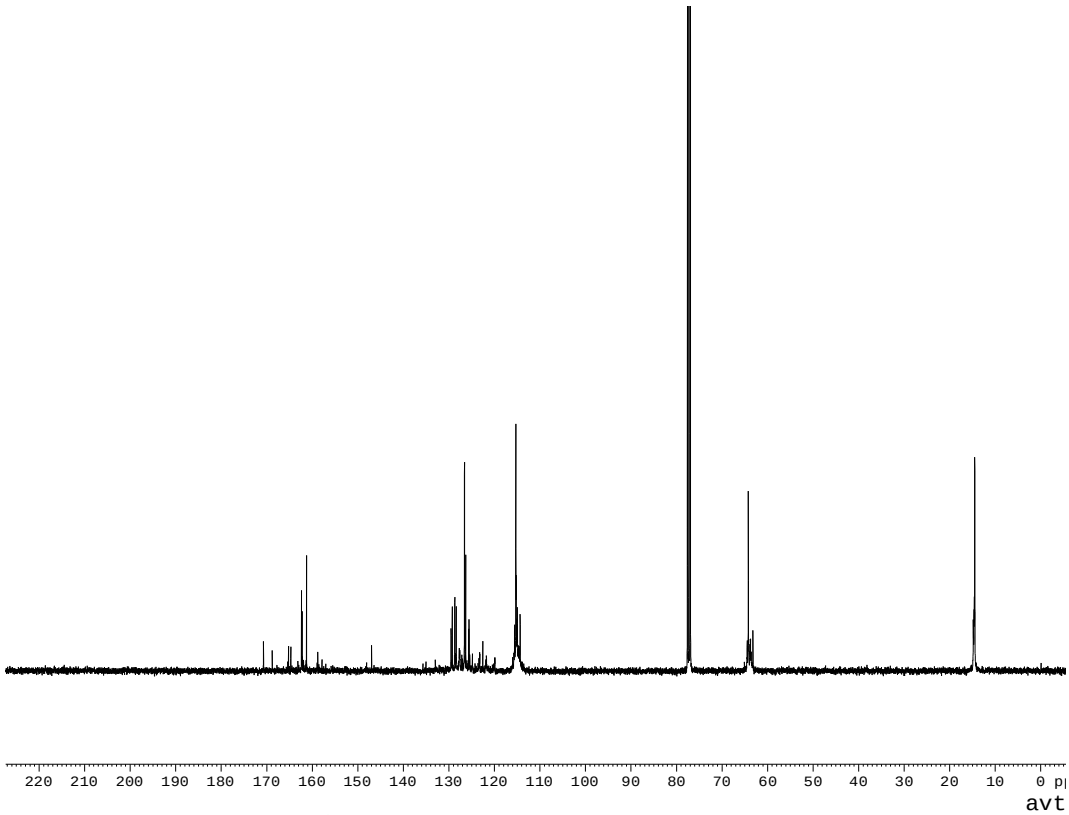


Fig 5 ^{13}CNMR spectrum of 3-nitro-1,5-di-*p*-phenitylformazan

Hence mass spectrum reflects the actual structural arrangement of the molecule in gaseous state. In case of formazan cleavage occurs on both sides of N=N group and also for the hydrazone carbon at $-N-N=$ bond. The characteristic peak formed due to the elimination of N_2 in case of azo compounds is also observed. There are different peaks observed due to different fragmentation modes observed in formazan (figure 6). In case of azo compounds the cleavage occurs in both sides of N=N function and for the hydrazone at the =N-N= bond. The peaks obtained in the mass spectra of 3-nitro-1,5-di-*p*-phenitylformazan are due to Ar, $ArNH^+$, ArN_2^+.

3-nitro-1,5-di-*p*-phenitylformazan exhibit intense parent peak at $(M+1)^+$ (m/z= 358). Moreover, the striking feature in the spectra of the given compound is the presensce of the peak at m/z= 77, 136, 208 and 250.

Solvatochromic Behavior of 3-nitro-1,5-diarylformazans

The UV-visible spectra of the 3-nitro-1,5-diarylformazans under consideration were recorded in twelve different organic solvents which possess different values of solvent parameters and solvatochromic parameters (table 1). Their absorptions generally appear in the range 395-520nm depending upon the nature of the molecule. The formazan molecule absorption appearing in the above region corresponds to $\pi \rightarrow \pi^*$ transition. It was observed that the compounds under study exhibit positive solvatochromism or bathochromic effect while moving from least polar solvent (cyclohexane) to most polar solvent (DMSO) (figure 1 - 3). The energy changes corresponding to $\pi \rightarrow \pi^*$ electronic transition occuring in the compounds namely 3-nitro-1,5-di-p-anisylformazan, 3-nitro-1,5-di-p-tolylformazan and 3-nitro-1,5-di-p-chlorophenyl formazan are $\Delta E_{max} = +8.89$, $\Delta E_{max} = +9.26$, $\Delta E_{max} = +10.12$.

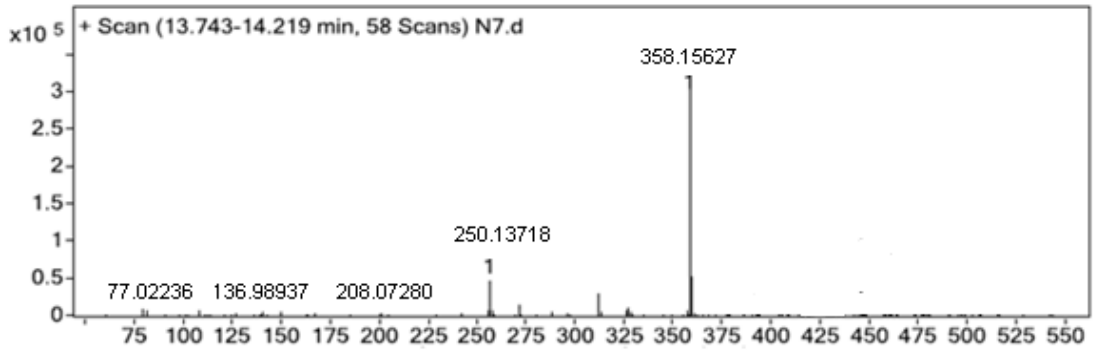


Fig 6 Mass spectrum of 3-nitro-1,5-di-*p*-phenitylformazan

The positive values of ΔE_{max} indicate that the molecules exhibit significant bathochromic shift (table 3). This can be explained on the basis of hydrogen donating tendency of the molecule and hydrogen accepting ability of the polar solvents. With the increase in the polarity of the solvent, its hydrogen accepting ability increases.

The λ_{max}values for various substituted formazans in DMSO follow the order:

p-Cl> p-OCH_3> p-CH_3

The bathochromic effect observed is explained on the basis of stabilization of excited state in the presence of polar solvent. The $\pi \rightarrow \pi^*$ transitions, characteristic of the formazan moiety, shift to longer wavelength in the presence of polar solvents. Since DMSO is highly polar it stabilised the excited state due to dipole-dipole interactions. Electronic effect of the substituents gives rise to the above mentioned order of λ_{max} in DMSO.

Multiple Linear Regression Analysis

The parameters governing the contribution of the influence of wide solvent parameters upon spectral shifts in terms of specific and non-specific interactions have been evaluated using Kamlet-Taft equation.

$$\nu_{max}=\nu_{max,0} +a\alpha +b\beta +s\pi^*$$

Where ν_{max} is maximum absorption wavenumber of the given compound processed experimentally, $\nu_{max,}$ was calculated by the regression method, the other parameters i.e. the Kamlet-Taft coefficients a, b and s were also calculated using regression analysis method. These coefficients on their percentage basis as evaluated on the basis of values of regression coefficients contributed differently, predicted the type of solute-solvent interactions and solvatochromic behavior.

The above values (table 3) indicate the presence of non-specific dipole-dipole interactions which is dependent on the nature of the substituent attached to the aryl group.

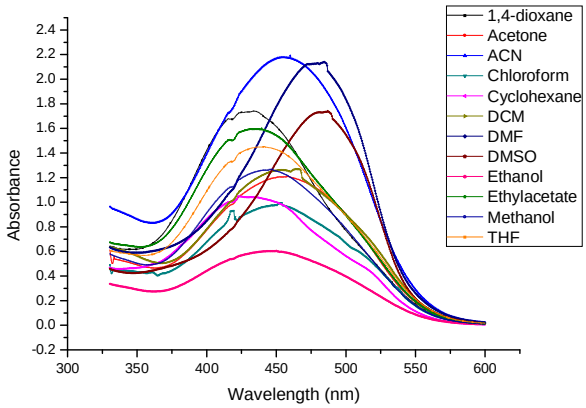


Fig 1 Absorption spectra of 3-nitro-1,5-di-p-anisylformazan

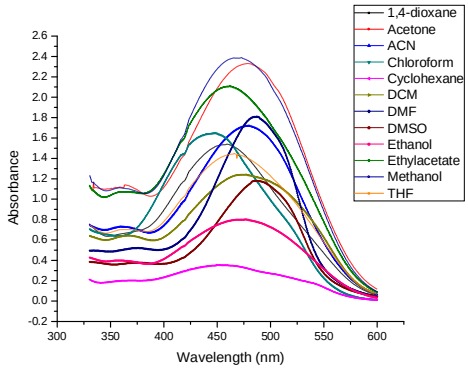


Fig 2 Absorption spectra of 3-nitro-1,5-di-p-tolylformazan

Table 1 λ_{max}(nm) values of the 3-nitro-1,5-diaryformazans in different organic solvents

Compound	Cyclohexane	1,4-Dioxane	Chloroform	Methanol	Ethanol	ACN	DMF	THF	Acetone	Ethyl Acetate	DCM	DMSO
3-nitro-1,5-di-p-anisylformazan	422.5	433.5	453.5	447.5	450.0	460.0	484.5	441.5	458.0	439.5	463.5	487.0
3-nitro-1,5-di-p-tolylformazan	419.0	435.0	448.0	473.0	476.0	479.5	482.0	466.0	474.0	460.0	477.0	485.0
3-nitro-1,5-di-p-chlorophenylformazan	421.0	433.0	449.0	472.5	478.0	479.0	491.0	472.0	482.0	463.0	476.0	495.0

Table 2 Kamlet-taft Parameters for 3-nitro-1,5-diarylformazan

Compound	ν_0 (x10^4)	a (x10^2)	b (x10^3)	s (x10^3)
3-nitro-1,5-di-p-anisylformazan	2.2356	+1.5791	-0.9876	-1.0158
3-nitro-1,5-di-p-tolylformazan	2.2015	+1.1123	-1.3663	-1.5601
3-nitro-1,5-di-p-chlorophenylformazan	2.6354	+2.9812	-1.4879	-2.3630

Negative values of both s and b (table 2) indicate that there is positive solvatochromism which means bathochromic shift with increase in solvent polarizability and solvent bond basicity.

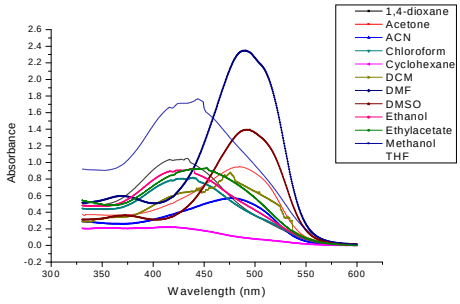


Fig 3 Absorption spectra of 3-nitro-1,5-di-p-chlorophenylformazan

Table 3 Contribution of Kamlet-taft Parameters for 3-nitro-1,5-diarylformazan

Compound	ΔE_{max} (kcal mol^{-1})	Solvatochromism	W_α (%)	W_β (%)	W_π (%)
3-nitro-1,5-di-p-anisylformazan	+8.89	Positive	7	45	48
3-nitro-1,5-di-p-tolylformazan	+9.26	Positive	4	45	51
3-nitro-1,5-di-p-chlorophenylformazan	+10.12	Positive	7	36	57

It is noticed that the contribution of 's' is maximum for 3-nitro-1,5-diarylformazans which establishes that the contribution of solvent-solute dipole-dipole interaction to bathochromic spectral shifts are more dominant than the specific interactions. Chlorine atom promotes orientation polarizations due to resonance effect and the methyl group diminishes orientation polarization. The radii of cavities emerging from the cavitation process were determined (table 4) and it was found that augmentation is less in non-protic solvents and higher in protic solvents like DMSO and DMF etc.

Table 4 Radii of cavities (Å) of 3-nitro-1,5-diarylformazans in different organic solvents

Solvent	3-cyano-1,5-p-anisylformazan	3-nitro-1,5-p-tolylformazan	3-cyano-1,5-p-chlorophenyl formazan
Methanol	0.09032	0.09642	0.06842
Ethanol	0.09042	0.09642	0.06947
Chloroform	0.08675	0.08086	0.07142
THF	0.09159	0.09626	0.06846
DCM	0.08660	0.09542	0.06449
DMF	0.12432	0.12580	0.09412
DMSO	0.11896	0.56173	0.09154
Cyclohexane	0.05325	0.05514	0.04640
1-4Dioxane	0.05806	0.06421	0.04486
Ethyl Acetate	0.09241	0.09765	0.07082
Acetone	0.10642	0.11421	0.08142
ACN	0.11842	0.12852	0.09442

CONCLUSIONS

From the above results and discussion it is concluded that:

1. 3-nitro-1,5-diarylformazans can be prepared by the action of nitromethane with diazotized aromatic amines in cold in an alkaline medium.
2. All the 3-nitro-1,5-diarylformazans synthesized are found to be intramolecularly hydrogen bonded.
3. On the basis of IR and PMR studies, it has been established that these 3-nitro-1,5-diarylformazans have a symmetric structure in which -N-N-C-N-N chain adopts the closed syn-s-cis configuration relative to formal double C=N and single C-N bonds.
4. ^{13}CNMR and mass spectral studies of 3-nitro-1,5-diarylformazans are also in agreement with the intramolecularly hydrogen bonded six membered chelate ring structure.
5. 3-nitro-1,5-diarylformazans show bathochromic shift.
6. The extent of bathochromic shift depends upon the nature of the group attached to the phenyl ring of the formazan moiety.
7. The contributions of various solvent parameters were investigated using multiple regression analysis.
8. The interaction between solute and solvent are non-specific in nature.

References

1. Nineham A.W., *Chem. Rev*., (1955), 55, 355.
2. Freise P., *Ber.* (1875), 8, 1075.
3. Bamberger E., *Ber.*, (1894), 27, 155.
4. Bamberger E., Schmidt O. and Levinstein H., *Ber.*, (1900), 33, 2043.
5. Bamberger E. and Schmidt O., *Ber.*, (1901), 34, 574.
6. Bamberger E., Pandova R. and Ormerod E., *Ann.*, (1925), 446, 260.
7. Tarbell D.S., Todd C.W., Paulson M.C., Lindstrom E.G. and Wystrach V.P., *J. Am. Chem., Soc.*, (1948), 70, 138.
8. Kalia K.C. and Chopra S.L., *Ind. J. Chem.*, (1972), 10, 312.
9. Kalia K.C. and Kumar A., *Ind. J. Chem*., (1978), 16A, 52.
10. Gilroy J.B., Otieno P.O., Ferguson M.J., McDonald R. and Gicks R.G., *Inorg. Chem*., (2008), 47(4), 1279.
11. Huing S. and Boes, O., Ann., (1953), 579, 28.
12. Crano, J.C. Guglielmetti, R.J., Ed., Organic Photochromic and Thermochromic Compounds, Main Photochromic Families, Plenum Press, New York, 1999; Vol. 1.
13. Crano, J.C. Guglielmetti, R.J., Ed., Organic Photochromic and Thermochromic Compounds, Physicochemical Studies, Biological Applications, and Thermochromism, Plenum Press, New York (1999); Vol. 2.
14. Durr, H., Bouas-Laurent, H. Ed., Photochromism: Molecules and Systems, Elsevier, Amsterdam, 1990.
15. Suppan, P., Ghonheim, N., Solvatochromism, The Royal Society of Chemistry, Cambridge (1997), 79.
16. Nakazumi, H., Muthyala, R., Ed., Chemistry and Applications of Leuco Dyes, Plenum Press, New York, (1997), 1-45.
17. Maeda, S., Crano, J.C., Guglielmetti, Ed., Organic Photochromic and Thermochromic Compounds, Main Photochromic Families, Plenum Press, NewYork, (1999), 85-109.
18. Van Gemert, B., Crano, J.C., Guglielmetti, R.J., Ed., Organic Photochromic and Thermochromic Compounds, Main Photochromic Families, Plenum Press, New York, (1999), Vol. 1, 111-140.
19. Irie, M., Crano, J.C., Guglielmetti, R.J., Ed,, Organic Photochromic and Thermochromic Compounds, MainPhotochromic Families, Plenum Press, New York, (1999), Vol.1, 207-222.
20. M-G. Fan, L. Yu and W. Zhao, in Organic Photochromic and Thermochromic Compounds, Vol. 1, Main Photochromic Families, J.C. Crano and R.J. Guglielmetti (Eds.), Plenum Press, New York (1999), 141-206.
21. H. Durr, in Organic Photochromic and Thermochromic Compounds, Volume 1, Main Photochromic Families, J.C. Crano and R.J. Guglielmetti (Eds.), Plenum Press, New York (1999), 223-266.
22. V.A. Barachevsky, in Organic Photochromic and Thermochromic Compounds, Volume 1, Main Photochromic Families, J.C. Crano and R.J. Guglielmetti (Eds.), Plenum Press, NewYork (1999), 267-314.

23. V.I. Minkin, V.M. Komissarov and V.A. Kharlanov, in Organic Photochromic and Thermochromic Compounds, Volume 1, Main Photochromic Families, J.C. Crano and R.J. Guglielmetti (Eds.), Plenum Press, New York (1999), 315-340.
24. M. Inouye, in Organic Photochromic and Thermochromic Compounds, Volume 2, Physicochemical Studies, Biological Applications, and Thermochromism, J.C. Crano and R.J. Guglielmetti (Eds.), Plenum Press, New York, (1999), 393-414.
25. Chang G.; Xu M.; *Adv. Materials. Research*. (2013), 849, 373.
26. Michael A.; Rodgers J.; *J. Amer. Chem. Soc*. (2002), 124, 139.
27. Schueren L.V.; Clerck K.; *Adv. Sci. and Tech*. (2012), 80, 47.
28. Romulo A.A.; Nicholas P.W.; Paulo S.; Ricardo F.; Phys. Chem. *Chem. Phys*. (2009), 11, 7505.
29. Onsager, L. *J. Am. Chem. Soc*. (1936), 58, 1486.
30. Abboud, J.L.; Kamlet, M. J.; Taft, R. W. *Prog. Phys. Org.Chem.* (1981), 13, 485.
31. Kamlet, M. J.; Abboud, J.L.; M.; Abraham, M. H.; Taft, R. W. *J.Org. Chem.* (1983), 48, 2877.
32. Taft, R. W.; Abboud, J.L.; M.; Kamlet, M. J.; Abraham, M. H. *J. Solution Chem.* (1985), 14, 153.
33. Abboud, J. L.; Kamlet, M. J.; Taft, R. W. *J. Am Chem. Soc*. (1977), 99, 8325.
34. Taft, R. W.; Abbound, J.-L. M.; Kamlet, M. J. *J. Am. Chem. Soc*. (1981), 103, 1080.
35. Kumar S., Sharma R., Kumar S., Nitika, *Chem. Sci. Trans.* (2014), 3, 919-928.

How to cite this article:

Sanjeev Kumar and Rajeev Sharma.2017, Synthesis, Characterisation and Solvatochromism of some 3-Nitro-1,5-Diarylformazans. *Int J Recent Sci Res.* 8(7), pp. 18227-18235. DOI: http://dx.doi.org/10.24327/ijrsr.2017.0807.0472

****