Nitrophenyl Hydrazine Derivatives (Formation, Characterization, Physical and Polarized Optical Behavior)

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Abstract--- The organic compounds have a wide applications in more than field like (formation of drugs, preparation of antimicrobial compounds , as a ligands in coordination chemistry, as a reagents , as liquid crystals ,…) for this reason, we reported preparation of novel compounds from (azo or amide)- crystals and their identification via many instrumental systems like (I.R , H.NMR , Polarized optical measurements, physical characterizations).

Keywords--- Hydrazine, Liquid Crystal, Polarized Optical, AZO, Amide.

I. Introduction

Most of organic compounds have a liquid crystal properties and can be appeared both in the natural world and with technological uses[1-5] and applications. Some of biocompounds like, many proteins are liquid crystals and soapsolutions and kinds of detergents, other materials[6-17]:

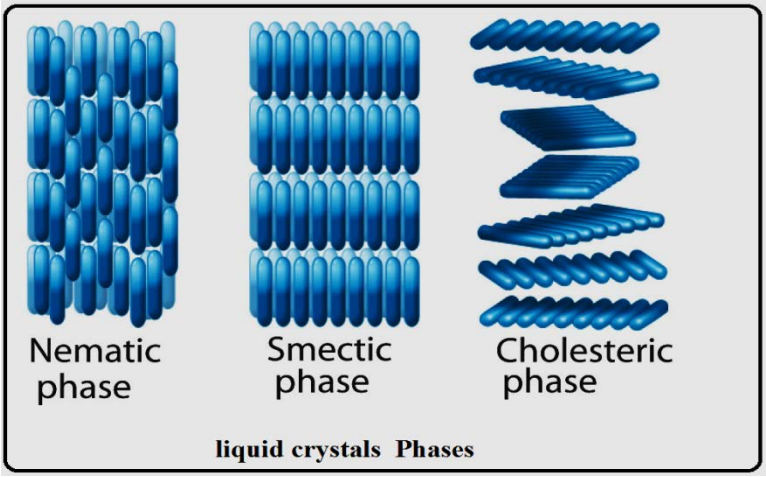

Fig. 1: Liquid crystals Phases

The measurements of liquid crystals[18-27] are investigated and detected via two main methods, the essential method was use of microscopy for thermal optical measurements , in which some organic compounds were placed between two crossed polarizers; the compound was heated then cooled[28-35].While the second method depends on differential scanning calorimetry measurements[36-45](DSC) which allow for more precise determination of phase transitions .

II. Experimental Part

Hydrazine-azo derivatives were prepared , then characterized via FT-IR spectra (FT-IR 8300 Shimadzu) in the range (400-4000) cm^{-1} with KBr discs., 1H.NMR– Spectra in DMSO–solvent., and Polarized Optical analysis (POM) for chemical compounds:

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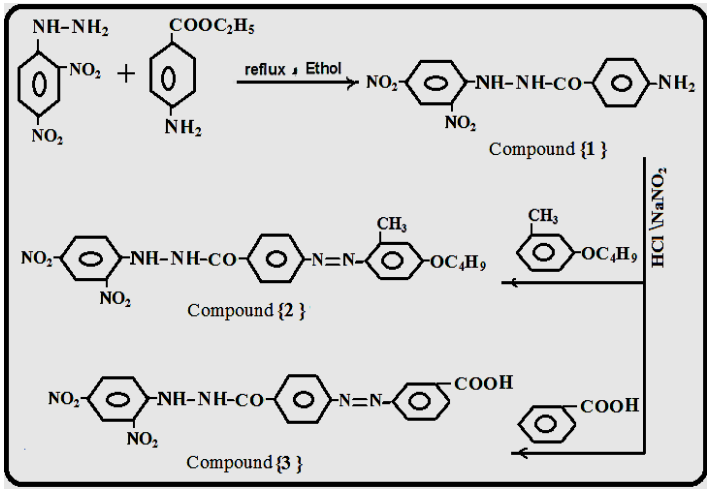
Procedures

Preparation of Hydrazine-Amide{1}

Dinitrophenyl hydrazine(0.01 mole) refluxed in first step with para-aminoethylbenzoate (0.01mole) for (3hrs) by flowing procedures[16, 17]with (3 drops) of acetic acid(glacial),to format precipitation, filtered , dried and re crystallized to givehydrazin-amidederivative{1}.

Preparation of Hydrazine-Azo-Amide {2, 3}

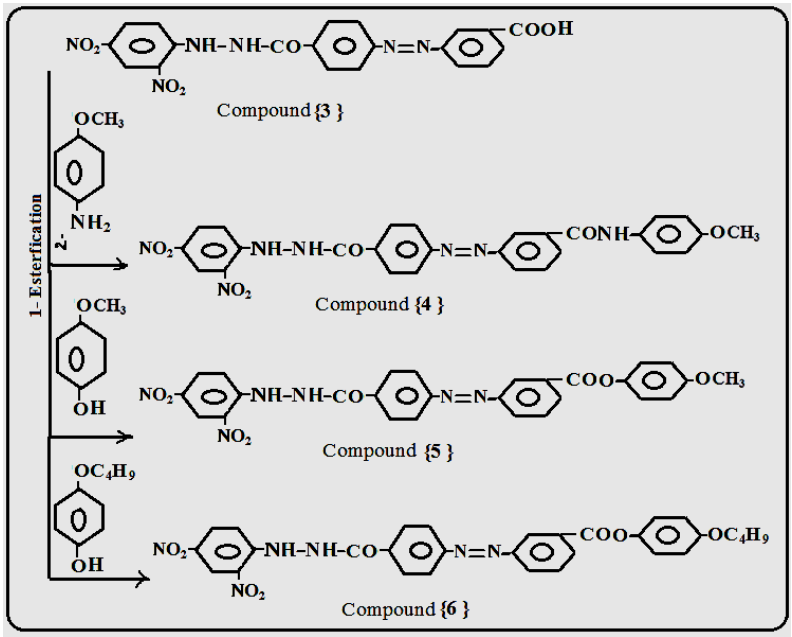
Dinitrophenyl hydrazine{1} (0.01 mole) dissolved in (HCl) and solution of sodium nitrite in second step , then coupling step toluene ether derivative or with benzoic acidby flowing procedures[20-22]to format precipitation, filtered, dried and re crystallized to givehydrazin-amid- azo derivative{2} and {3}.



Scheme 1: Formation of Hydrazine-Azo-Amide {1- 3}

Preparation of Hydrazine-Azo-Amide {4, 5, 6}

Dinitrophenyl hydrazine {3} from first step (0.01 mole) refluxed with para-methoxy aniline or with para-methoxy phenol or with para-hydroxy phenyl ether (0.01mole) for (3 to 4 hrs) by flowing procedures[20-22]to format precipitation, filtered , dried and re crystallized to givehydrazin-amide-Azo derivatives { 4 , 5, 6}.



Scheme 2: Formation of Hydrazine-Azo-Amide {4 ,5,6}

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III. Results and Discussion

Our derivatives identified with variety spectral and chemical techniques like (FT.IR ,H.NMR) spectra with Polarized Optical Measurements:

Spectral Investigations

FT.IR- Spectraof Hydrazine- Derivatives: The spectra of derivatives gave many absorption bands at (NH_2) amine group : (3370 , 3345) ., (CO-N-) carbonyl of amide: 1678 .,(NO_2)nitro groups : (1350, 1510) in compound {1} , but other bands appeared in derivative {2} at (CO-N-) carbonyl of amide: 1680 .,(NO_2) nitro groups :(1317, 1543) ,(-N=N)azo group: (1410 ,1477) , (C-O-C-) ether : 1174 in compoundin derivative {2} , but other bands appeared in derivative {3} at (CO-N) carbonyl of amide: 1666 .,(NO_2)nitro groups :(1355, 1510) ,(-N=N)azo group[27 ,28]: (1422 ,1533) , (COO-) carboxyl group (1701) , (OH) of carboxyl group : (2600-3070) in compoundin derivative {3} , while compound {4} at (CO-N) carbonyl of amide: 1765 .,(NO_2) nitro groups :(1356 , 1532) ,(-N=N)azo group: (1461 ,1512) ,(NH): (3289) , (C-O-C)ether: 1185 ., but compound {5} at (CO-N) carbonyl of amide: 1773 .,(NO_2) nitro groups :(1347 , 1518) ,(-N=N)azo[27, 280] group: (1439 ,1526) ,(NH): (3265) , (C-O-C)ether: 1171 , (COO) carbonyl of ester : 1709 , the last compound{ 6} bands (CO-N) carbonyl of amide: 1790 .,(NO_2) nitro groups :(1358 , 1510) ,(-N=N)azo group: (1421 ,1519) ,(NH): (3211) , (C-O-C)ether: 1167 , (COO) carbonyl of ester : 1713, while other bands appeared in figs (2 ,3) .

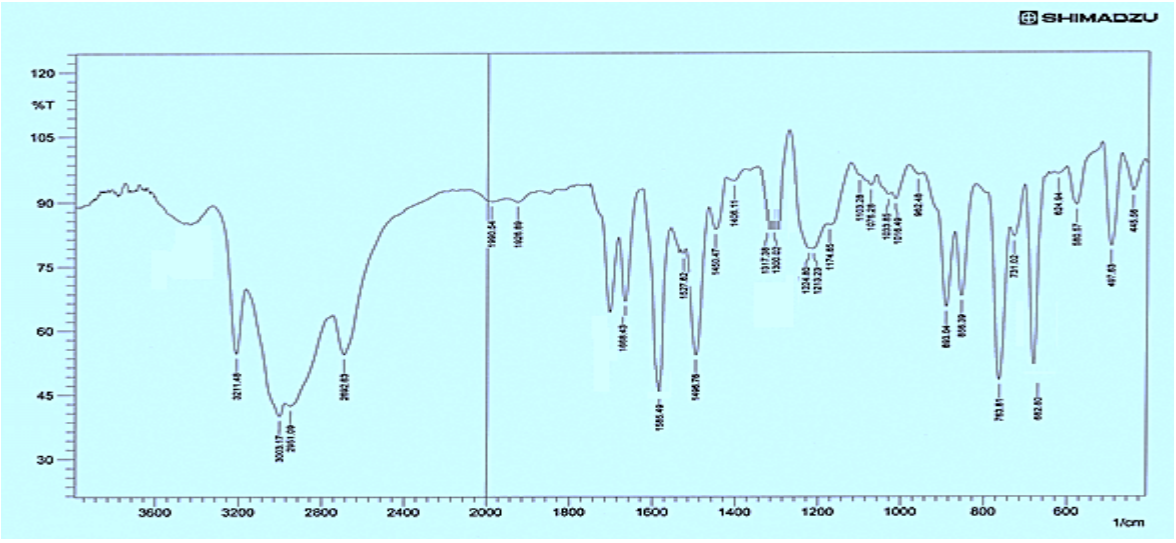

Fig. 2: I.R Spectrum of Hydrazine Derivative {2}

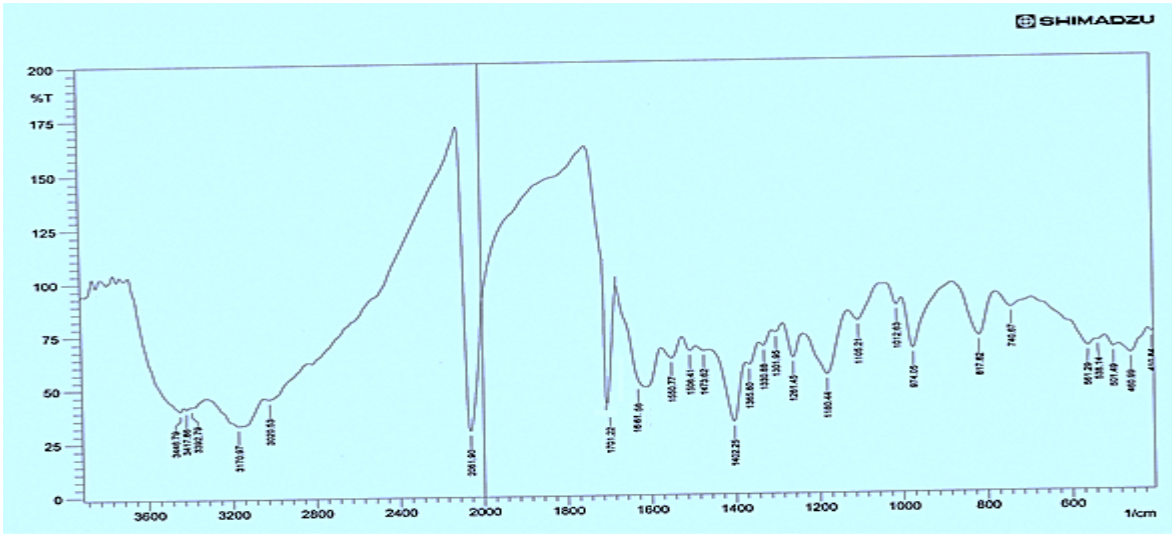

Fig. 3: I.R Spectrum of Derivative {3}

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[1]H.NMR- Spectraof Hydrazine Derivatives: all spectra of derivatives appeared good signals indicateat ƃ (NH_2) Protons of amine: 5.44 ., (CO-NH-)proton of amide : 9.15 ., Protons of Phenyl ring : (7.24 -7.96) in derivative { 1 } ., but other signals indicate at ƃ., (CO-NH-)proton of amide: 9.26 ., Protons of Phenyl ring: (6.80 -7.83) , (CH_3) protons of methyl : 1.20 , (OC_4H_9) : (93.04- 3.44) in derivative { 2 } ., signals indicate at ƃ (COOH): 12.70 ., (CO-NH-)proton of amide : 9.25 ., Protons of Phenyl ring : (7.23-7.81) in derivative { 3 } , in compound {4} noted other peaks at ƃ (CO-NH-)proton of amide: 9.38 ., Protons of Phenyl ring : (7.02-7.78) , (OCH_3) methoxy protons at : 3.05 ., in compound {5} gave other peaks at ƃ (CO-NH-)proton of amide: 9.41 ., Protons of Phenyl ring : (7.14-7.98) , (OCH_3) methoxy protons at : 3.11 ., in compound {6} appeared other peaks at ƃ (CO-NH-)proton of amide: 9.27 ., Protons of Phenyl ring : (6.92-7.47) , (OC_4H_9) protons at : (2.10- 3.40) ., other peaks in figs (4 , 5) .

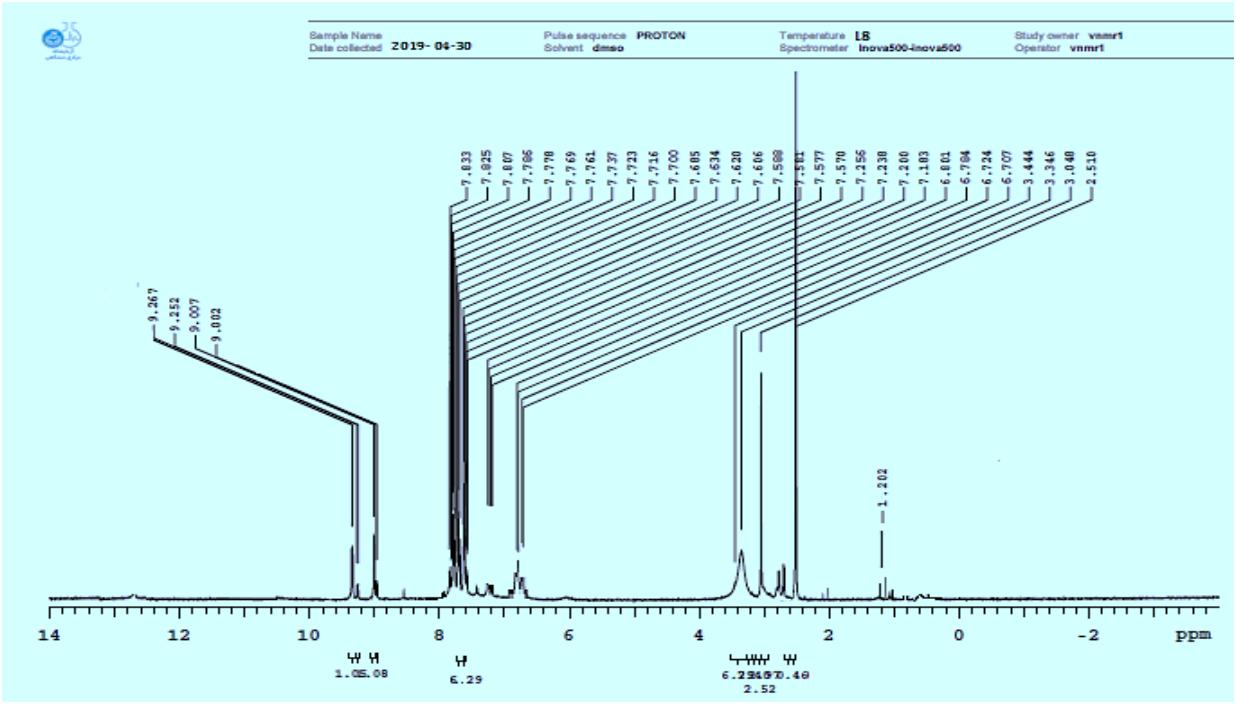

Fig. 4: H.NMR of Derivative {2}

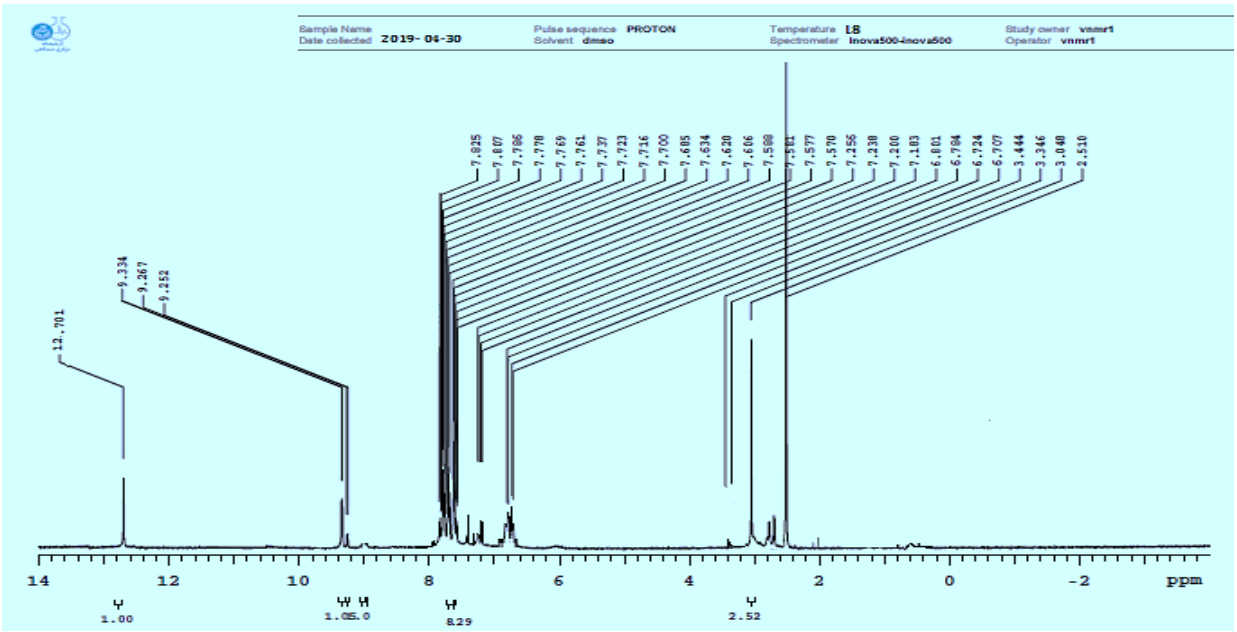

Fig. 5: H.NMR of Derivative {3}

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***Polarized Optical Measurements*[14]**

Hydrazine -amide azo derivatives were tested by optical microscopy via heating derivatives in various temperatures[14] , The results appeared that these compounds gave liquid crystals behavior , some figures for some hydrazine derivatives are shown :

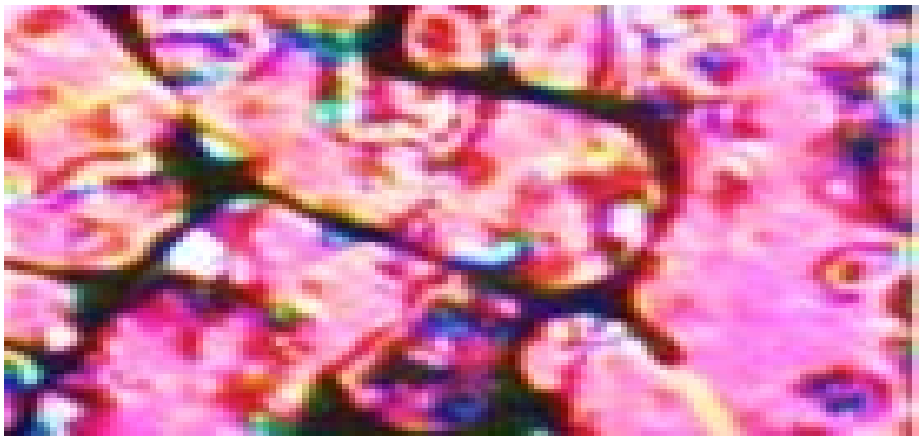

Fig. 6: Nematic Phase at (70C) for Compound[2]

Fig. 7: Nematic Phase at (75C) for Compound[3]

Fig. 8: Nematic Phase at (80 C) for Compound [4]

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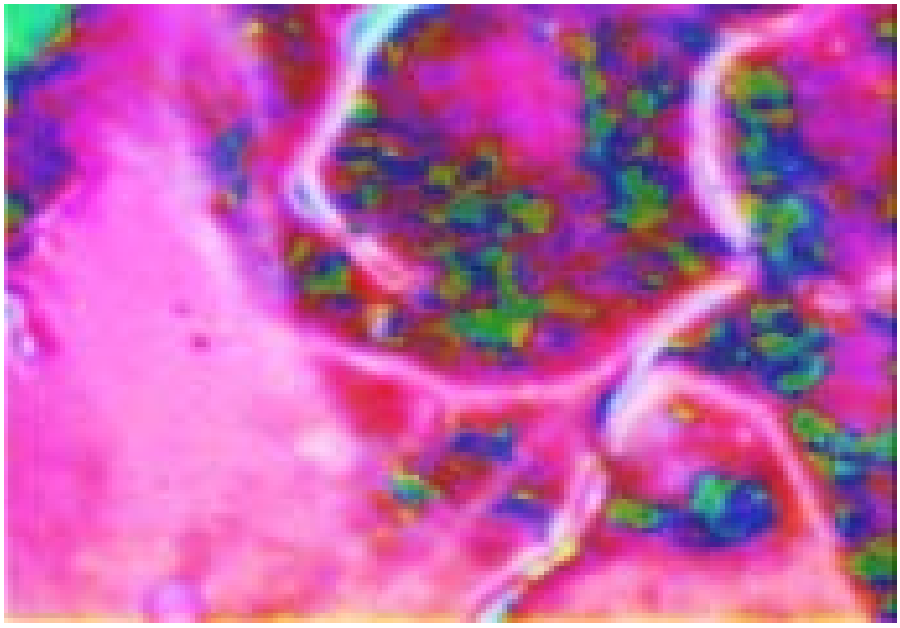

Fig. 9: Nematic Phase at (75C) for Compound[5]

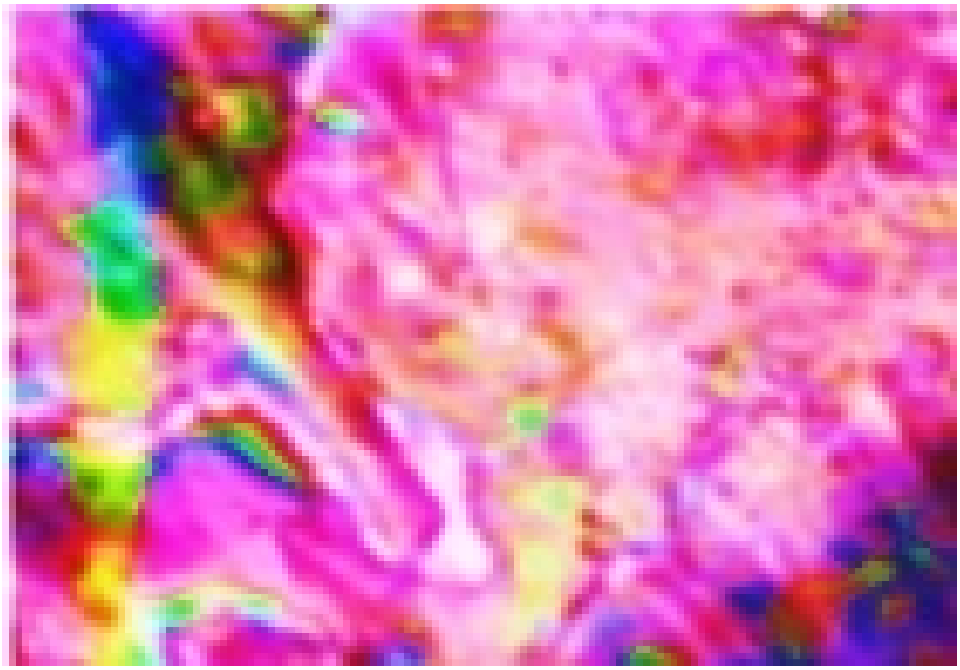

Fig. 10: Nematic Phase at (70C) for Compound[6]

Table 1: Physical and Chemical Characterization of Hydrazine Derivatives

Compounds	Colour of Compounds	Products %	Rf
{ 1}	Orange	70	0.64
{ 2}	Reddish Yellow	87	0.76
{3}	Reddish Orange	74	0.70
{4}	Pale Orange	70	0.58
{ 5}	Yellowish Orange	66	0.72
{6}	Reddish Orange	80	0.66

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