Synthesis of Liquid crystals with terminal polar groups and study their mesomorphic and spectroscopic properties.

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ABSTRACT

Synthesis new Schiffs bases substituted with polar groups CI . Br , F , $N0_2$, CH_3 , OCH_3 , $COCH_3$ in para position or aniline moiety, and derived Cu (II) complex from the Schiff base which substituted with $COCH_3$. The Schiffs bases substituent with CH_3 , OCH_3 exhibited Nematic phase but the other Schiff bases and Cu (II) complex exhibited Smectic phase (Sc) only. Molecular complexes of Cu (II) complex with various nitrogen bases were studied spectrophotometrically in benzene solvent at different temperatures. All these complex show a new broad charge transfer band in the visible region of the electromagnetic spectrum.

All the donors are known to form I: I complex with the acceptor and their stoichiometry was unaffected by the variation of temperature over a small interval. The thermodynamic and spectroscopic parameters were evaluated. The order of donor strength followed the sequence:

Butyl amine> 4 - methyl pyridine > N,N – dimethyl aniline.

Introduction:

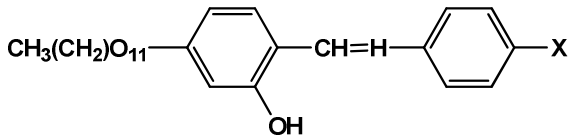
The mesomorphic behavior of an organic molecule is sensitive to its molecular structure. A slight change in the molecular geometry could cause a considerable change in its mesomprphic properties.

Many mesomorohic homologues series comprising different terminal groups in the same molecule have been studied[1-5]. The Smectic and Nematic mesophase determined by the ratio of the lateral to the terminal attractive forces . If the lateral cohesion are very strong, the temperature to which the Smectic mesophase persists is high, and the thermal vibrations needed to destroy the layer arrangement are sufficiently intensc to disrupt the molecular structure completely. The isotropic liquid crystal is then obtained, if on the other hand, the lateral attraction arc relatively easily overcome the break down of the smetic order occurs at a lower temperature ,at which it is more likely that a nematic arrangement or the molecules will persisl[6].

The donors molecules which form donor - acceptor complexes may be divided into two groups: Hydrocarbon donors as olefins and aromatic hydrocarbons (π - donors) and compounds which contain heteroatoms such as oxygen or nitrogen atoms with lone – pair electrons (n - donors) generally speaking, the latter group has stronger donating properties than the former and especially aliphatic amines.[7]

Cu (II) complexes is one of the acceptor molecules and it is known to form molecular complexes with a wide range of electron donors[8]

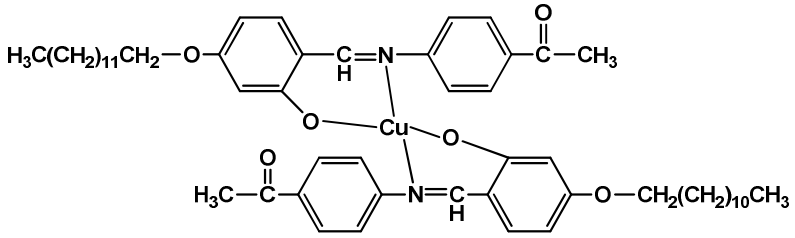
In this paper we continue this line of research in order to study the relation between molecular structure and mesogenic activity in depth. We report the mesogenic properties of a new family of Schiffs bases derived from imines with terminal polar groups in the amine part with the general structure DNX :



X =H,CH_3 ,OCH_3, Cl ,F ,Br ,I ,$N0_2$,COH_3

DNH, $DNCH_3$, $DNOCH_3$. DNCl ,DNF ,DNBr ,DNI , $DNN0_2$, DNAc

The Cu (II) complex derived from imine with polar group $COCH_3$. And study the adduct formation between both liquid crystalline Cu (II) complex (Acceptor): Bis [4 - (dodecyloxy) - N - (4 - acetyl phenyl) - 2 – hydroxyl benzalimine] cu (II) and different donors butyl amine, 4 - methyl pyridine and N , N - dimethyl aniline.



Cu $(DNAc)_2$

Experimental:

1.Synthesis

Synthesis of 4 - dodecayloxy - 2 - hydroxy benzaldehyde[9]

These were prepared from 2,4 - hydroxy benzaldehyde (I mmol) anhydrous potassium carbonate(1 mmol) and the dodecayl bromide (1 mmol) in acetone. The reaction mixture was heated under reflex for 24h , the hot mixture was filtered then removal of acetone and finally yielded the alkoxy as a yellow oily liquid.

Synthesis of Schiffs bases[9]

The respective Schiffs bases were synthesized using a well known method by mixing an ethanolic solution of (I mmol) of 4 - decayloxy - 2 -

hydroxy benzaldehyde with(I mmol) of appropriate amine and 2 drops of acetic acid as catalyst. The reaction mixture was heated under reflex for (2h) , the solution was allowed to cool, the yellow precipitate was separated by filtration and finally repeated recrystallization (several times) from heptane yielded the pure Schiffs bases.

Synthesis of Cu (II) complex[11]

The synthesis of copper (II) complex Cu ($DNAc)_2$ was carried out by the addition of an ethanolic solution (20 ml) containing copper (II)acetate (I mmol) to a hot solution of ligand (DNAc) in ethanol, the solution was refluxed for(I - 2h) . After cooling the precipitate was collected by filtration and recrystallized from ethyl acetate. Produced crystals have brown clolor.

2.Apparatus :

The HNMR was carried out by (NMR - 400MHz Bruker) . IR were recorded on FTIR - 8400S spectrophotometer. and the elemental analysis were recorded by elemental Micro - analysis.

The absorption band of the ligand and molecular complex were carried out by using Philips - PU 8620 UV Vis. The spectrophotometer is equipped with a cell holder through which water from thermostatic bath is continuously circulated. Temperature is maintained with (t 0.1 $\overset{\circ}{C}$) .The measurements are carried out in 1 cm path length quartz cell. The concentration of complex (accepter) being kept constant (3 x 10 - 3 M) while the concentration of donors are much greater than that of acceptor.

(0.1 - 0.4 M) to fulfill the condition of Rose - drago equation for I: I complexes. Equilibrium constants were determined using the Rose - Drago method[12]

$$K^{-1} = \frac{C_A C_B}{A - A_0} \quad (\epsilon_C - \epsilon_A)(C_A - C_B) + \frac{A - A_0}{\epsilon_C - \epsilon_A}$$

Where CA is the initial chelate concentration, CB is the initial base

concentration, A The phase transitions were observed with a Leitz Laborlux 12 Pol optical microscope with polarized light in orthomat camera. Measurements of transition temperatures were made using a Perkin - Elmer DSC 50 differential scanning calorimeter with a heating rate of 10°C $min^{(-1)}$.

Result and discussion:

1. Characterization

The HNMR spectral data for these Schiff's bases show broadly similar spectral characteristics and the data for (DNCI) compound (fig. I) representative of the compounds: (ppm , CDCl3) 13.9 (S , IH , 0H) . 8.51 (S , IH , CH = N) 7.3 - 6.5 (m , 7 H , ring protons) , 4.0 (t , 2H . OCH2) , 2.0 - 2.1 (m , 20H , CH_2) 0.92 (t, 3H .CH_3).

IR spectral (cm^{-1}. KBr) 3040 -3070 (C - H aromatic). 2820 - 2900 (C - H aliphatic) 1630 - 1650 (CH = N), 1615 -1630, 1570 - 1575 (two bands for aromatic C = C), 1290 (C- 0).

The UV spectral (nm , $CHCl_3$) of the Schiffs bases was almost identical contained two bands for π - π^* transition the first one at (325 - 345 nm) for the transition between azomethine group and aromatic ring (ph-C) . the second one approximately constant at λ maX (277 - 281) for the transition... between ~ azomethine group and aromatic ring which is substituted with different polar groups (ph - N) .

The complex was characterized by IR , UV , and elemental analysis .The IR spectra (cm^{-1}, KBr) : 3040(CH aromatic) , 2820 - 2900 (CH aliphatic) , 1620 (CH = N) , 1590 . 1580 (aromatic C = C). The C = N stretching vibration is shifted to lower frequencies for the complex compared to that of the free Ligand. This indicates that the azomethine N atom involved in metal nitrogen bond formation[11]

The Schiff bases and the complex had satisfactory elemental analysis

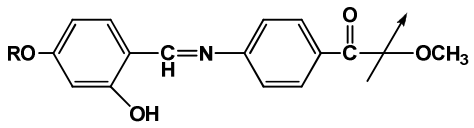
and are consistent with those expected (Table I) .

Table 1. Elemental analytical data (calculated values in parentheses

Compound	Molecular formula	% C	% H	% N
DNH	$C_{25}H_{35}O_2N$	78.74 (78.94)	9.18 (8.95)	3.67 (3.45)
DNBr	$C_{25}H_{34}O_2NBr$	65.35 (35.55)	7.40 (7.39)	3.05 (2.94)
DNI	$C_{25}H_{34}O_2NI$	59.18 (59.48)	6.70 (6.65)	2.76 (2.69)
DNNO2	$C_{25}H_{34}O_4N_2$	70.42 (70.92)	7.98 (7.86)	6.57 (6.42)
DNCl	$C_{25}H_{34}O_2NCl$	72.20 (72.51)	8.18 (8.07)	3.36 (3.13)
DNMO	$C_{26}H_{37}O_3N$	75.91 (76.46)	9.00 (8.99)	3.40 (3.39)
DNM	$C_{26}H_{37}O_2N$	78.98 (79.21)	9.36 (9.29)	3.54 (3.33)
DNF	$C_{25}H_{34}O_2NF$	75.18 (75.58)	8.52 (8.41)	3.08 (2.95)
DNAc	$C_{27}H_{37}O_2NO_3$	76.558 (76.22)	8.80 (8.78)	3.30 (3.29)
$Cu(DNAc)_2$	$C_{54}H_{72}N_2O_6Cu$	71.37(71.17)	7.98 (7.89)	3.082 (3.06)

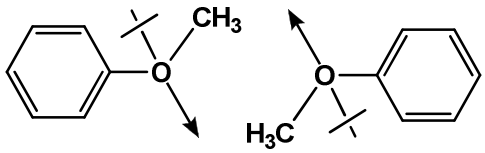
II. Mesogenic behavior

The results from optical microscope and differential calorimetry (DSC) listed in table (2), as it can be seen from the table all the Schiff bases and Cu(II) complex thermotropic liquid crystal compounds in heating and cooling (enantiotropic) fig. 1,2,3,4. The substituted Schiff s bases with dipole moment across the axes of molecul (DNCH), $DNOCH_3$) and DNAc) favorite the Semctic phase so the (DNAc) exhibited Semctic phase (Sc) because of this type of dipole moment enhance the lateral molecular attraction between molecules:



Dipole moment across the long axes of molecule

But in short alkyl and alkoxy chains (OCH) , CH_3) this dipole moment enhance the terminal intermolecular attraction and exhibited nematic phase.



Terminal attraction in short alkyl chains

However we should note that the thermal stability of the nematic phase of the $DNCH_3$ is considerably lower than that of the $DNOCH_3$ and this reminds us that the dipole of the ether group play some part in maintaining the parallel orientation in the nematic melt and the dipoles of the ether group probably enhance the terminal intermolecular attraction between the molecules[12].

The substituted Schiffs bases with (CI , F , Br , I , $N0_2$) exhibited Smectic phase Sc with different thermal liquid crystal range because of the presence different dipole moment a long the long axis of molecule in the terminal of molecules. That's dipole moment reduce the lateral intermolecular attractions. The enhance Smectic (Sc)properties in (DNCI , DNF , $DNN0_2$, DNI , DNBr) can be explained only if we imagine that molecules are tilted at an angle to the layer interfaces. As we tilt the molecules away from the perpendicular arrangement , the separations of the negative and positive charges of the C - X dipoles dipoles not necessarily increase, but we do bring the bouring dipole[6].

At some suitable angle, the attractive forces will outweigh the repulsive forces and the net energy of attraction will enhance the lateral attractions and the Smectic properties, so the substituent (CI , F , Br , I , $N0_2$) enhances the Smectic thermal stability relative to X = H .

The order of decreasing Smectic thermal stability of the compounds - in terms of the substituent X is :

DNAc> DNBr > DNCI > DNI > DNF > $DNN0_2$

The ONAc have higher Smectic thermal stability than the another Schiff bases because of the acetyl group in position 4 of anilinic ring with a strong dipolar moment a cross the long axes of molecule favors lateral

intermolecular interactions which give rise to more ordered smectic phase[6,12].

The Iodo and nitro groups have less Smectic thermal stability than the another groups because in most eases these substituent will substantially broden the molecules and decrease the lateral attractive forces[13].

The Cu $(DNAc)_2$ complex melt at higher temperature than the ligand (DNAc) and the clearing temperature are also higher and exhibited smectic phase only, However the Smectic phase (Sc) ranges are wider in the complexe than the ligand because of the Cu (II) complexes in the mesomorphic state have a square planar geometry allows a better molecular packing arrangement, favoring the appearance of more ordered mesophase .

The Nematic phase in the DNH_3 and $DNOCH_3$ are identified by the appearance marbaled texture on heating and Schlieren in cooling. The smectic phase (Sc) Schiff bases was identified by Schlieren texture in heating and focal conic in cooling, but the Sc in $(DNAc)_2$, was identified by the Schlieren texture in heating and cooling from the isotropic liquid (fig.5.a.b . c . d)

Table 2 : Phase transition temperatures (^0C)for DNX series and Cu (II)

Compound	C – Se	C – N	Se – 1	N – 1	ΔT_s	ΔT_N
DNMO[a]	-	84	-	130	-	25
DNM[b]	-	79.38	-	99.01	-	19.7
DNBr[a]	120	-	148	-	28	-
DNCl[a]	98	-	120	-	22	-
DNF[a]	80	-	95	-	15	-
DNI[a]	105	-	124	-	19	-
$DNNO_2$[a]	123	-	132	-	9	-
DNAc[b]	100.6	-	137.1	-	36.4	-
$Cu(DNAc)_2$[b]	172.8	-	226.6	-	53.8	-

a = polarized microscope data

b = differential scanning calorimeter

C : Solid N : Nematic S : Smeetic I: Isotropic

ΔTs : Smectic thermal range. ΔTN : Nematic thermal range

III) Charge transfer complexes

The UV visible spectral for ligand (fig.6) in CH_2CI_2 exhibited an intense two absorption bands at 280 nm (€ = 1500) and 327 nm (€ = 3800) for π- π^* transitions, but the spectral for the complex (acceptor) show also two bands at 307 and at 355 nm as well as broad band at 680 nm (€ = 100).

Addition of increasing amounts of donor to acceptor in benzene results an increase in the absorbance values of the acceptor bands, this observation indicates the formation of molecular complexes between the donors and acceptor.

The curve was characterized by clear isopiestic point (fig.7) at 680nm indicating the presence of only two absorbing species in solution, the free and complexed chelate.

The absorbance values around 680 nm in a 1.00 cm cell were monitored for the calculation of association constant. Preliminary analysis was carried out by using the plots of Rose - Drago. The plots (fig.8) of [A] / A - Ao and l/D where [A] [D] the concentration of acceptor and doner respectively and A , Ao the absorbance of mixture and acceptor respectively at 680 nm band linear indicating that the predominate species that exists in solution is the 1: 1 complex.

a) Donor effect

As can be seen from the order of increasing strength of the complexes with

different donors follows the increasing donor ability of the base, as measured by their association constant.

The adduct association constant increase in the order:

Butyl amine> 4 - methyl pyridine> N,N - dimethyl aniline

The ability of butyl amine to be much stronger base towards acceptor because

of the free lone pair of electron on the nitrogen atom.

The lower stability of 4 - methyl pyridine adducts relative to butyl amine reflects the decrease donor property of the nitrogen atom due to the conjugation with the phenyl ring reduces the charge on the nitrogen of the imino group.

The still lower stability for the adduct of N , N – dimethyl aniline is reasonable due to the sterric effect of two methyl groups of imino group [14]

Table (3) show that the changes of K, ΔG and ΔS are in the same sense. The negative values of ΔHAD and ΔSAD suggest that the complexes are very stable and undergo strong steric restraint.

b) solvent effect

The effect of solvent variation is to decrease the stabilities the value of Keq to butyl amine at 298 K in different solvent in the sequence:

Solvent	Benzene	>	Cyclohexanon	>	Dichloroethane
Keq	5.10		2.50		2.08

This may be attributed to decreasing attraction between solvent molecules. and the copper atom or decreasing solvation energy of the bases.

Table (3) : Thermodynamic constants for 1:1 adduct of complex with nitrogen donors in Benzene at 298K.

Donor	K L. mol^{-1}	-ΔG Kj. Mol^{-1}	-ΔH Kj. Mol^{-1}	-ΔS j. Mol^{-1}. K^{-1}
Butyl amine	5.10	4.03	27.2	77.7
4 – methyl pyridine	1.63	1.21	12.3	37.3
N , N– dimethyl aniline	1.03	0.07	9.4	31.2

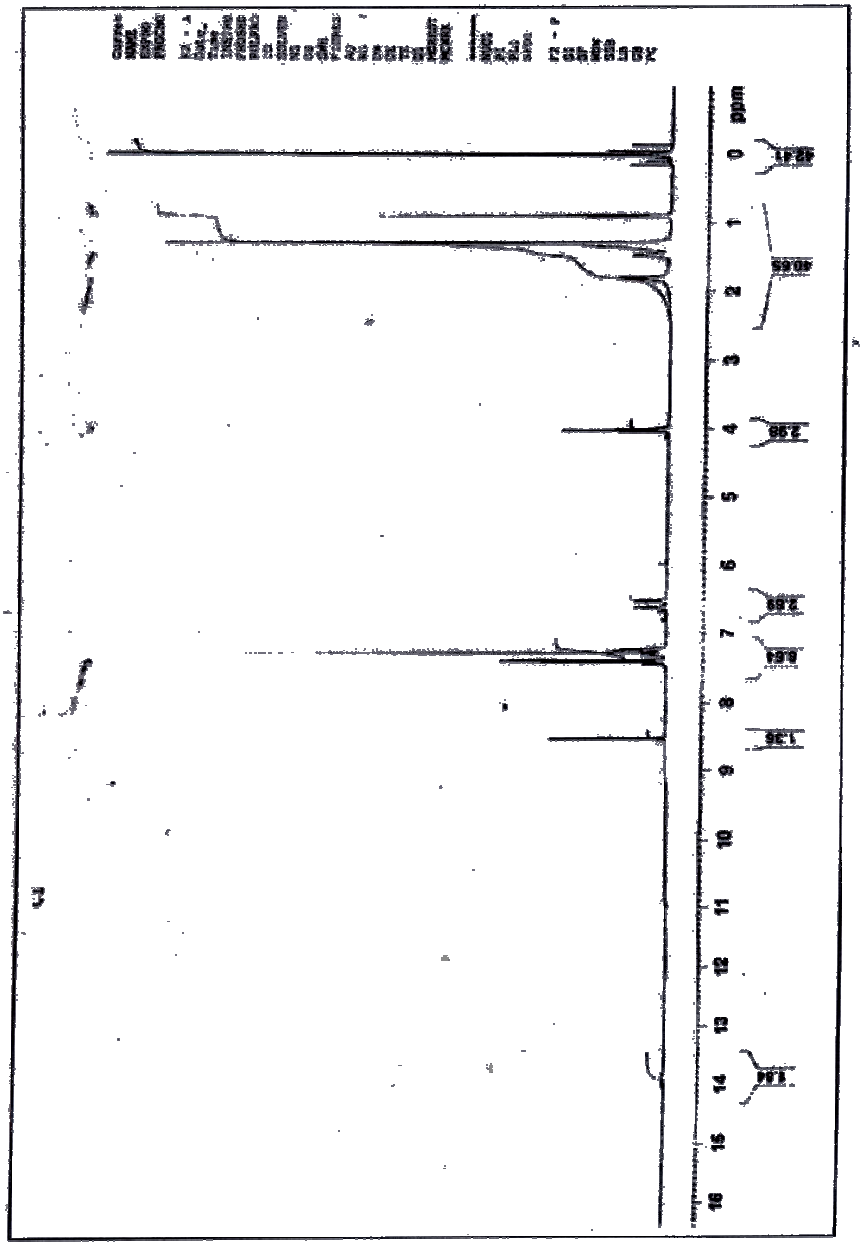


Fig.(1) : The ^{1}HNMR Spectral for DNC]

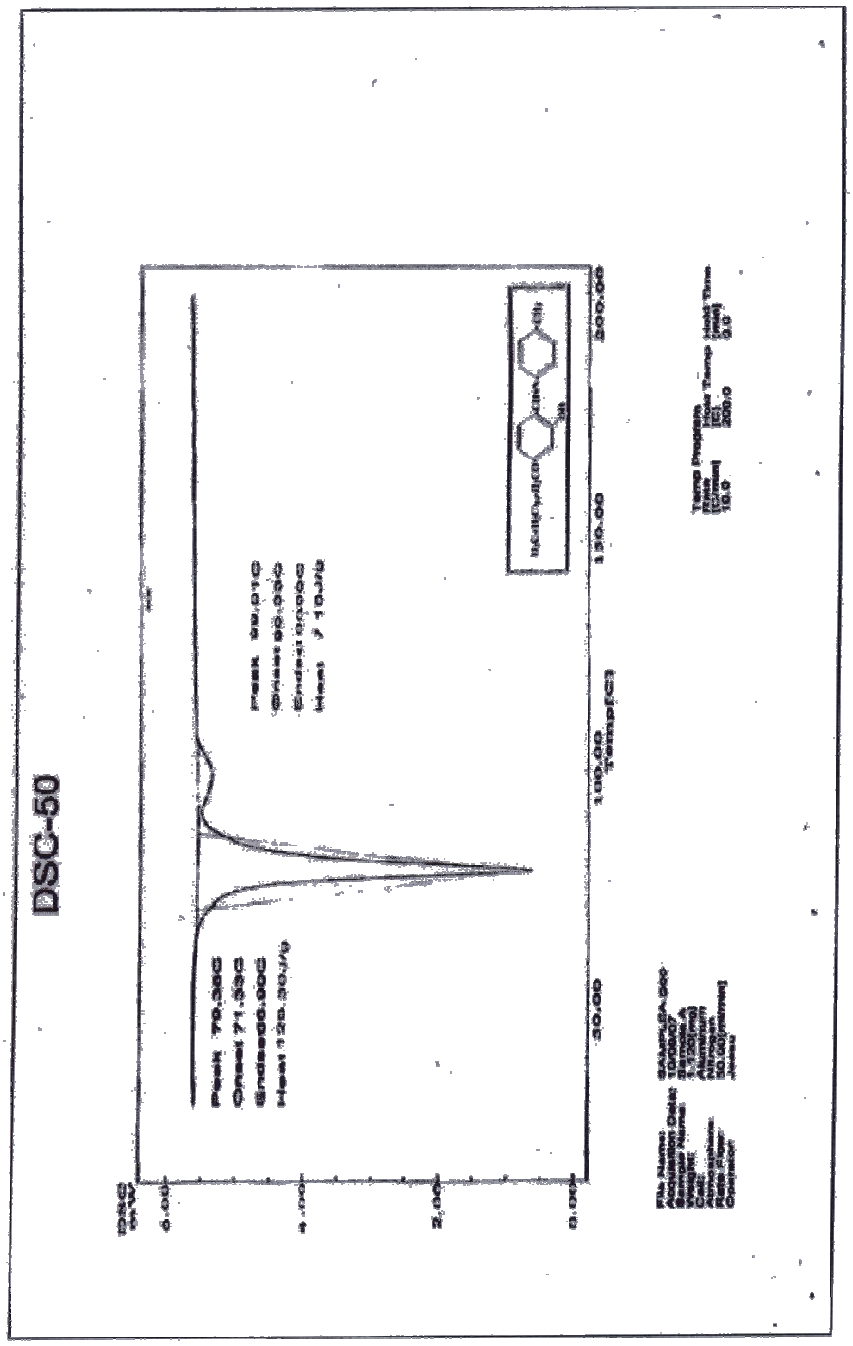


Fig.(2) : The DSC Curve for DNM

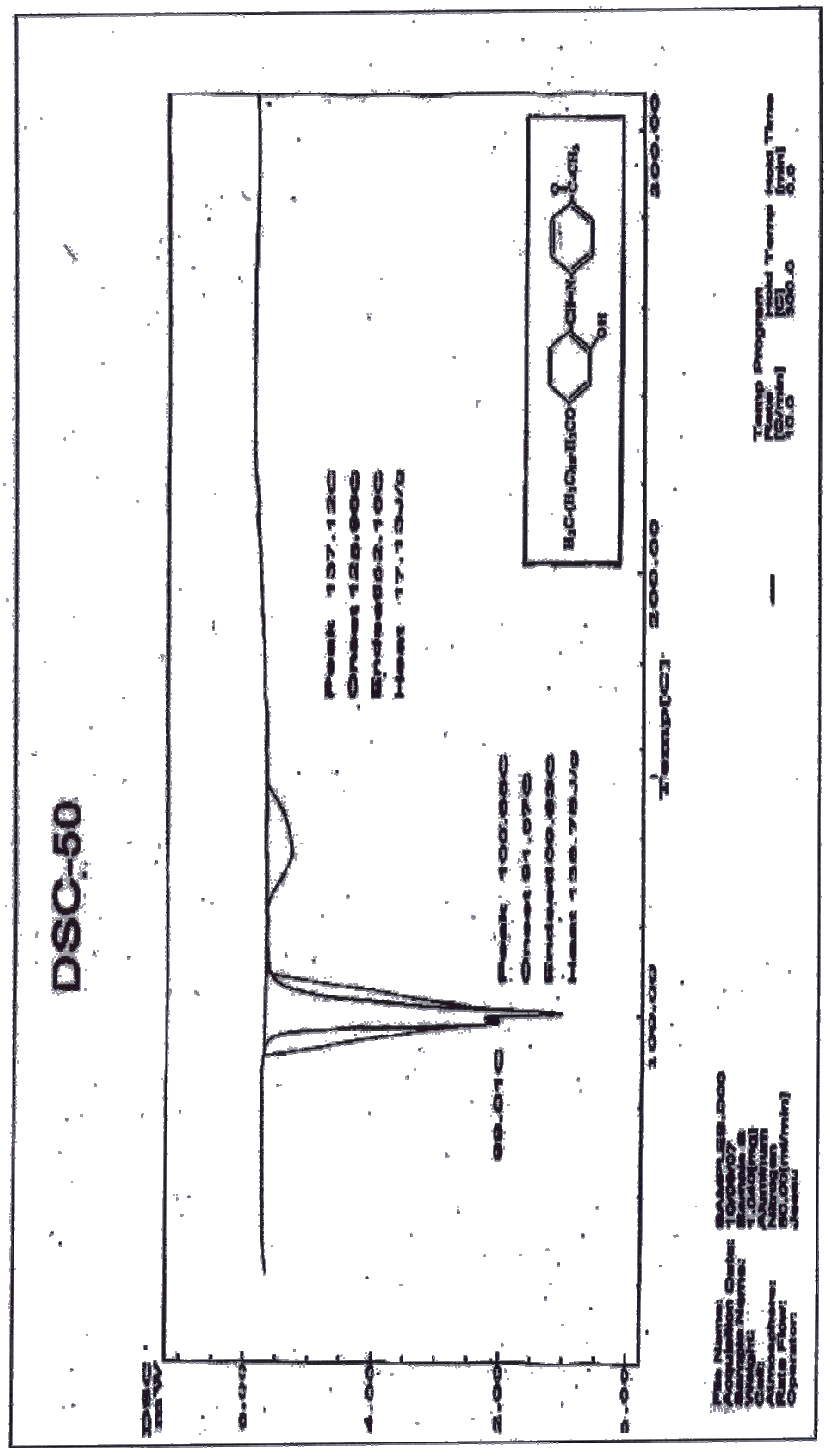


Fig.(3) : The DSC Curve for DNAc

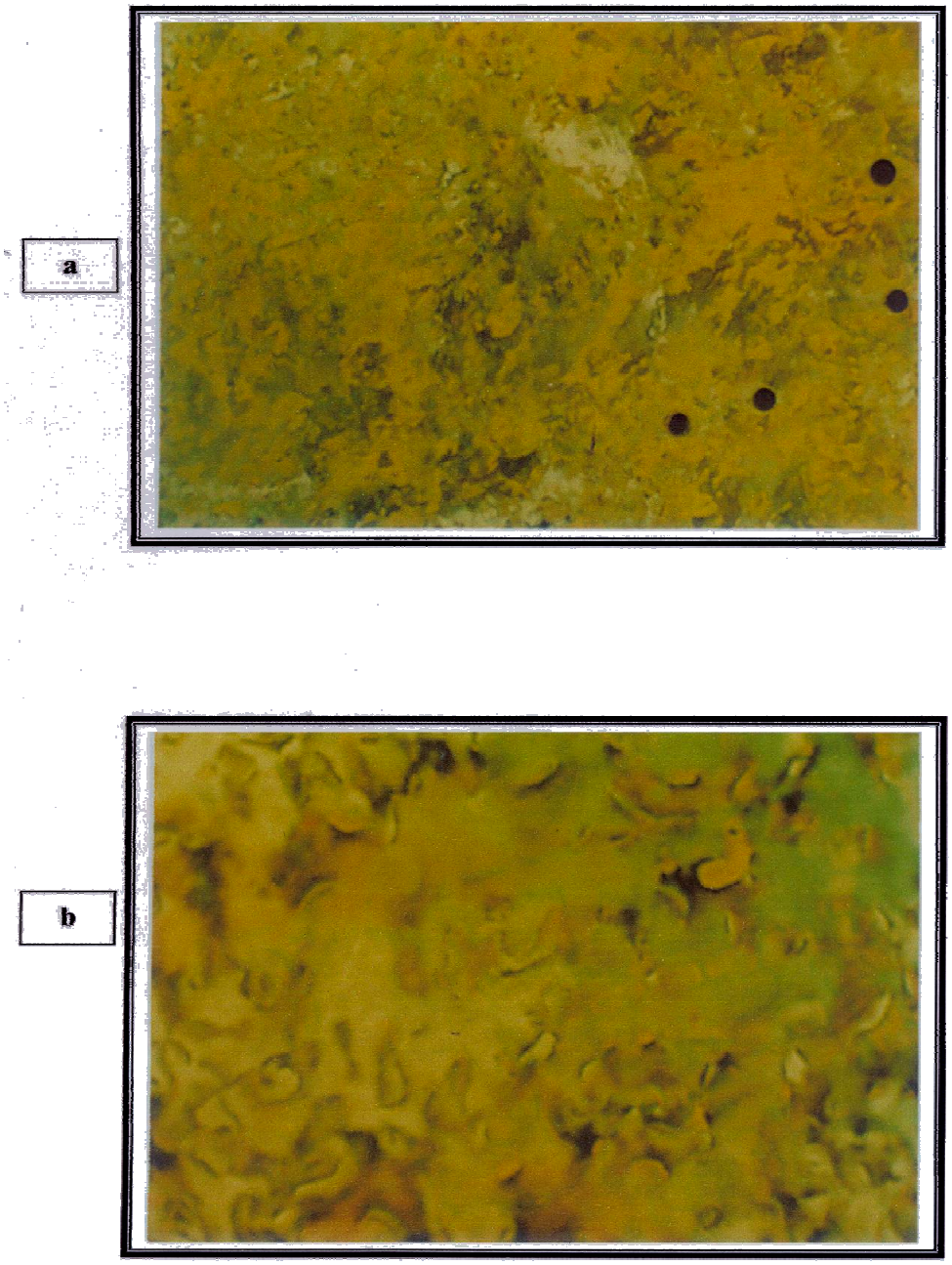
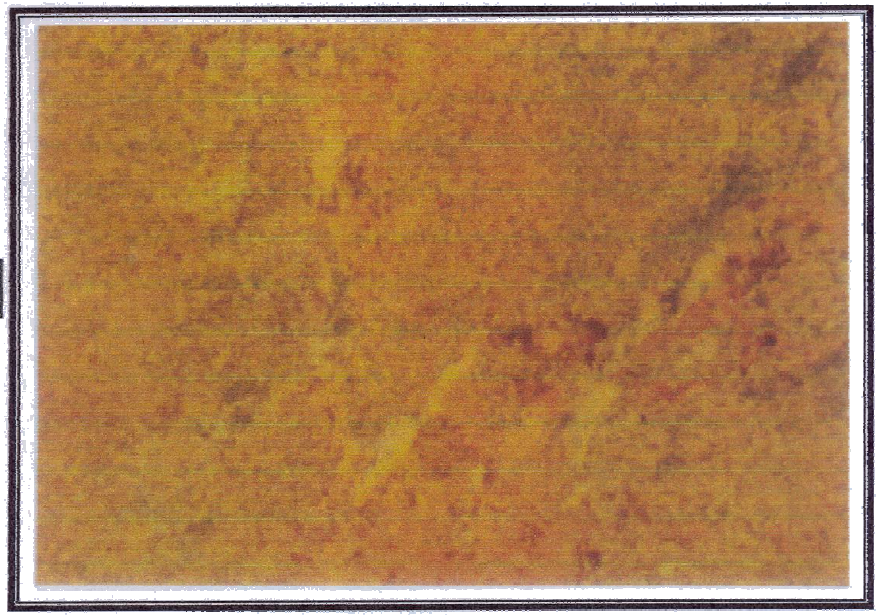


Fig.(5): Polarized optical micro-graphs of:
(a) Marbled texture of Nematic phase for DNM
(b) Schlieren texture of Nematic phase for DNM
(c) Focal-Conics texture for Smectic phase for DNM
(d) Schlieren texture for Smectic phase in $Cu(DNAc)_2$

c

d



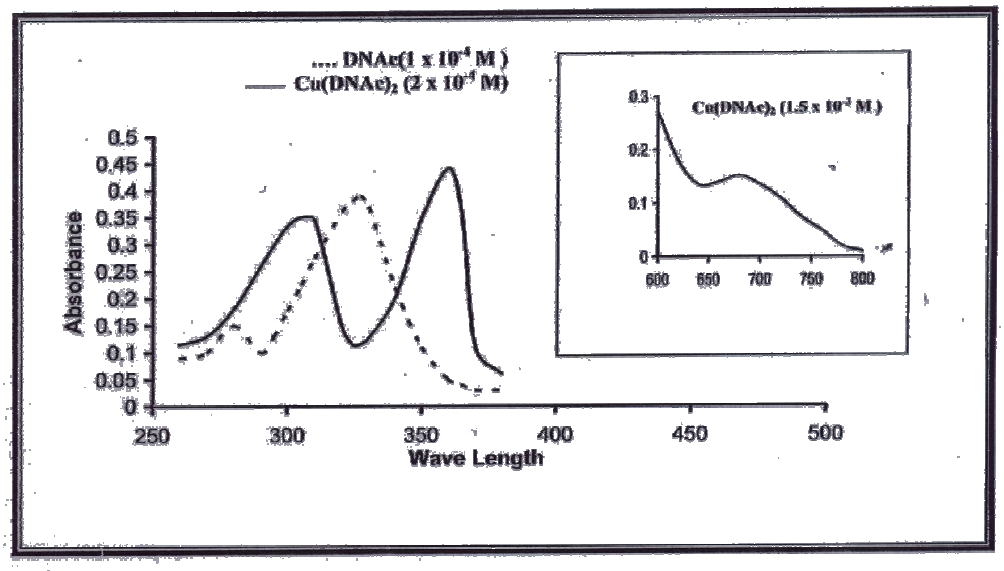


Fig.(6): The UV-Visible spectra for ligand (DNAc) and complex $(Cu(DNAc)_2$ in dichloromethane

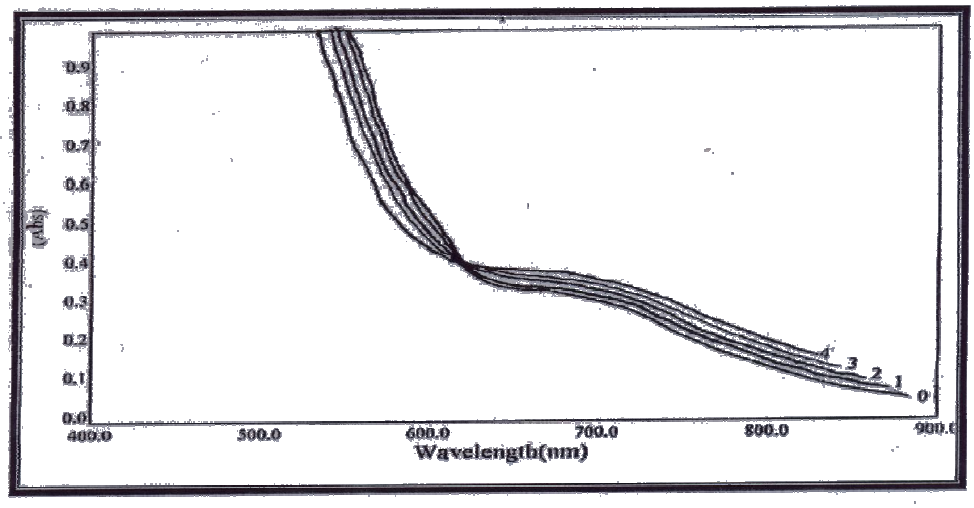


Fig (7): Electronic absorption spectra of acceptor – butyl amine in benzene . The concentration of acceptor is 3 X 10 $^{-3}$ M while the concentration of the donor is : (1) 0.119M (2) 0.206M (3) 3.00M (4)0.425 M

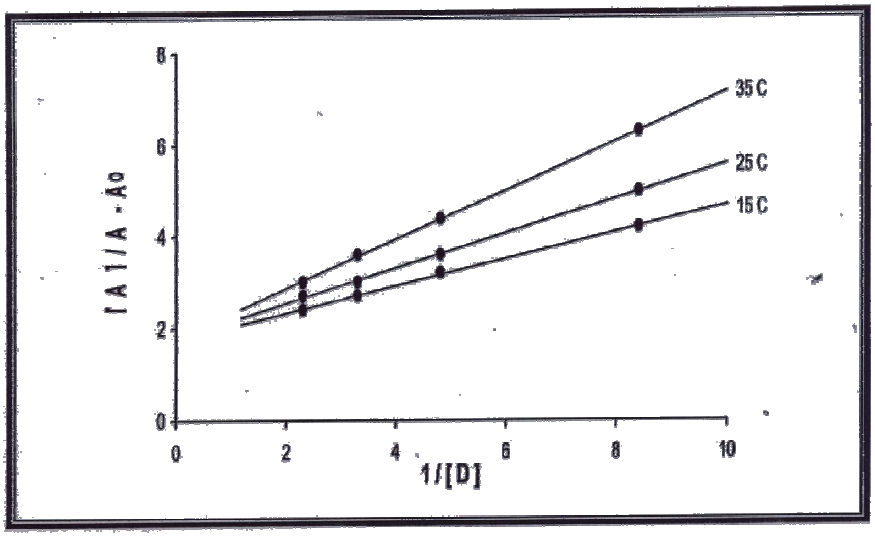


Fig.(8): The Rose-Drago relation ship of (Butyl amine-accepter) system in benzene

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تحضير بلورات سائلة معوضة بمجاميع قطبية طرفية ودراسة صفاتها البلورية السائلة والطيفية

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الخلاصة :-

حضرت قواعد شف جديدة معوضة بمجاميع قطبية في المواقع بـــــــــــــــــــارا ($COCH_3$, OCH_3, CH_3 , NO_2, I, BR, F , Cl) وأشتق من القاعدة المعوضة بمجمـــــوعة ($COCH_3$) معقد للنحاس الثنائي وأظهرت قواعد شف المعوضة بجموعة مثيل وميثوكسي- الطور النيماتي ولكن قواعد شف الأخرى ومعقد النحاس الثنائي وأظهرت الطور السمكتي (Sc).

استخدم المعقد المحضر في دراسة ظاهرة انتقال الشحنة حيث استخدم كمستقبل للألكترونات مع قواعد نتروجينية مختلفة كمانحات في البنزين في درجات حرارية مختلفة وكان ارتباط جميع المانحات مع المعقد بنسبة 1: 1 وكانت قوة المنح للقواعد النتروجينية بالشكل التالي :-

Buty1 amine > 4 – methyl pyridine > N,N – dimethyl aniline