

Preparation, Characterization and Liquid Crystalline Properties of some Complexes Schiff base derived from 4-(4-alkoxy benzoyloxy)-2-hydroxy benzaldehyde

Ali Kareem Al-Lami
Department of science
College of essentially education, university of basrah.

Abstract:

Two series of thermotropic liquid crystal dimmers were prepared and characterized, the first series: α, β -bis[4-(4-alkoxy benzoyloxy)-2-hydroxy benzylidene] diamino ethane copper(II)(CuO₂On). In these materials the length terminal alkyl chain is varied from 1 to 7 carbon atoms. The liquid crystalline properties of these materials have been investigated using differential scanning calorimeter and optical microscopy. This study revealed that these materials [nO₂On and CuO₂On] exhibit nematic and smectic A respectively.

الملخص:-

حضرت وشخصت سلسلتين من البلورات السائلة الترموتروبية الدايمرية. السلسلة الاولى هي دايمر: $[\beta, \alpha]$ - بس (٤-٤-الكوكسي بنزويلوكسي)-٢-هيدروكسي بنزلايدين) ثنائي امينو ايثان [nO₂On]. السلسلة الثانية هي معقدات النحاس الثنائية للدايمرات المحضرة: $[\beta, \alpha]$ - بس (٤-٤-الكوكسي بنزويلوكسي)-٢-هيدروكسي بنزلايدين) ثنائي امينو ايثان النحاس [II] Cu(nO₂On).

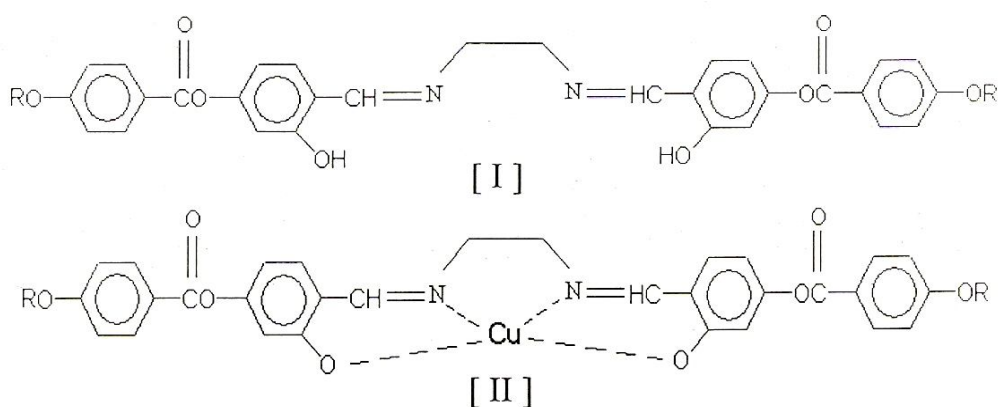
في هذه المركبات يتغير طول السلسلة الطرفية من ١ الى ٧ ذرة كربون. فحصت الصفات البلورية السائلة بواسطة المسح المسعري التفاضلي والجهز دو الضوء المستقطب ،دلت هد الدراسة على امتلاك هذه المركبات اطوار وسطية نيماتية وسمكتية.

Introduction:

The earliest liquid crystal which contained a metal as integral part off the structure was diphenyl mercury (II) compound reported in 1923 by Daniel Vorlander⁽¹⁾. Not much happened then until the late 1970 with the discovery of the metal dithiolenes by Anne-Mare Giroud and Ulrich Mueller- Westerhoff⁽²⁾, but in mid 1980, the field really started to take off. There many reasons why one might want to include a metal in a liquid crystalline structure, quite apart from natural curiosity.

For example, metals are stable radicals, their complexes are colored, there are centers of polarisable electron density and they are centers of reactivity⁽³⁻⁵⁾. If just tow mesogenic units, however, are linked through a flexible spacer, yielding the so called liquid crystal dimmers, then the transition properties are found to be critically dependent on the length and parity of the alkyl spacer in a manner reminiscent of the behavior observed for polymeric systems^(6,7).

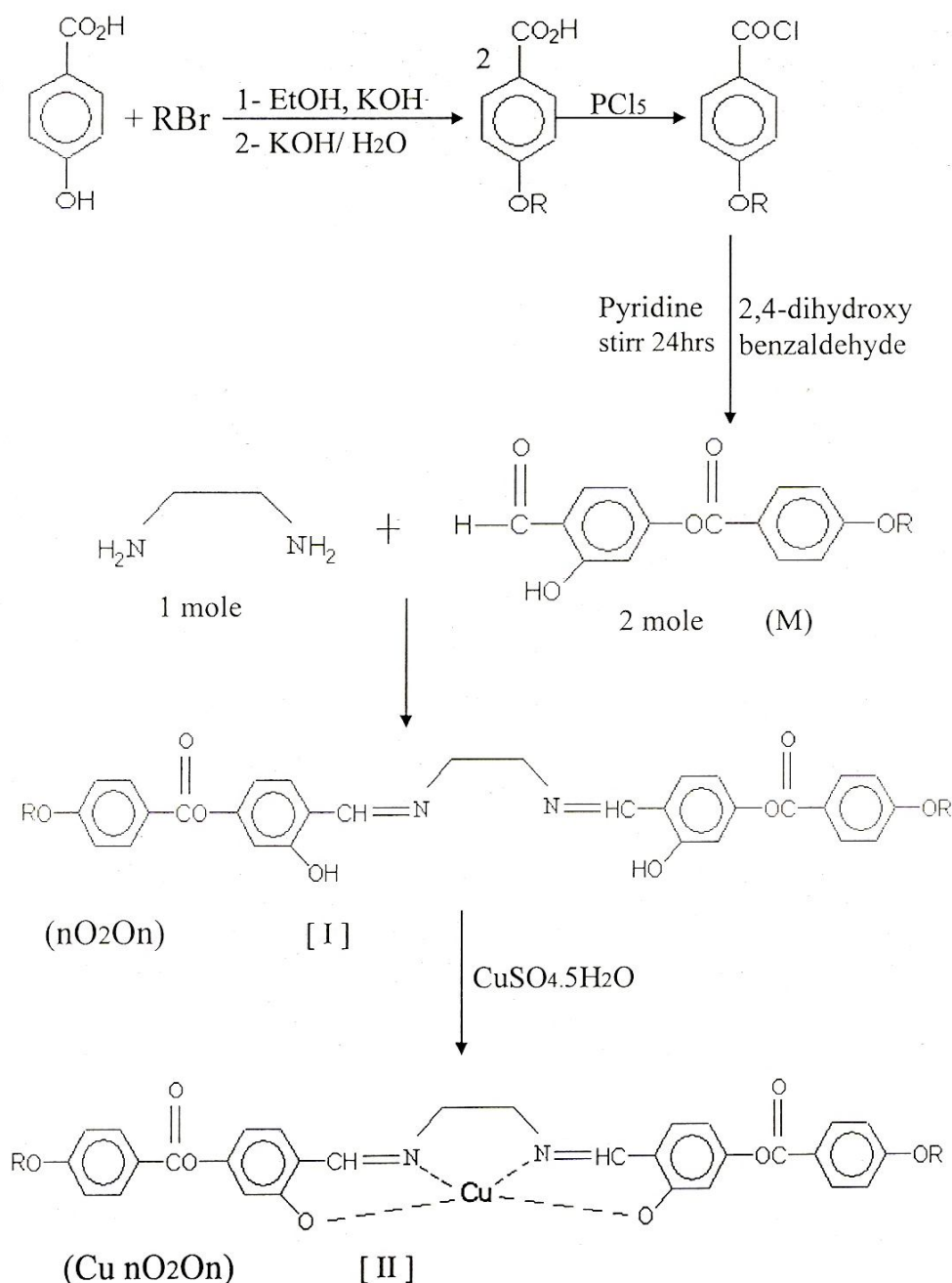
To extend such studies were prepared and studied the transitional behavior of dimeric mesogens the α , β -bis [4-(4-alkoxy benzoyloxy)-2-hydroxyl benzylidene]diamino ethane [I]and dimeric mesogens contained a metal(copper) [II] .



The main in these works is given to investigation of the influence of the structure of the mesogenic groups, conformation of complexes of liquid crystal and the length of the terminal alkyl chain on the nature of the mesomorphic state in dimmer.

Experimental:-

The two series were prepared using the synthetic route shown in scheme(1).



Preparation of 4-alkoxy benzoic acid ⁽⁸⁾:-

A mixture of 4- hydroxyl benzoic acid (0.1mole), alkyl bromide (0.17mole)and potassium hydroxide(0.2mole) in ethanol/H₂O(160/16)ml was refluxed for 24hrs.Then 20%potasium hydroxide (160ml) was added to the same reaction vessel. The mixture was refluxed for 4hrs.After cooling; the solution was neutralized with 10% hydrochloric acid. The crude product was filtered and washed with distilled water and recrystallized from ethanol. (Yield 60-85%).

Preparation of 4- (4-alkoxy benzoyloxy) -2- hydroxy benzaldehyde ⁽⁹⁾ [Nm]:

4-alkoxy benzoyl chloride was synthesis from 4-alkoxy benzoic acid (0.02mole) was mixed with phosphorus pentachloride (0.02mole) and was stirred at 60 C for 25min to give liquid product. Then the POCl₃ [side product] is distilled off by

vacuum distillation 2, 4-dihydroxy benzaldehyde (0.013mole) was dissolved in 10ml dry pyridine. A solution of 4-alkoxy benzoyl chloride(0.01mole)in 10ml pyridine was added dropwise to this solution, after the addition was complete, the reaction mixture was stirring for 24hrs.The crude product was filtered off and washed with 10% hydrochloric acid then several times with distilled water then dried. The crude product was recrystallized from ethanol (yield 60-70%). Typical IR spectrum shown in (Fig.1)

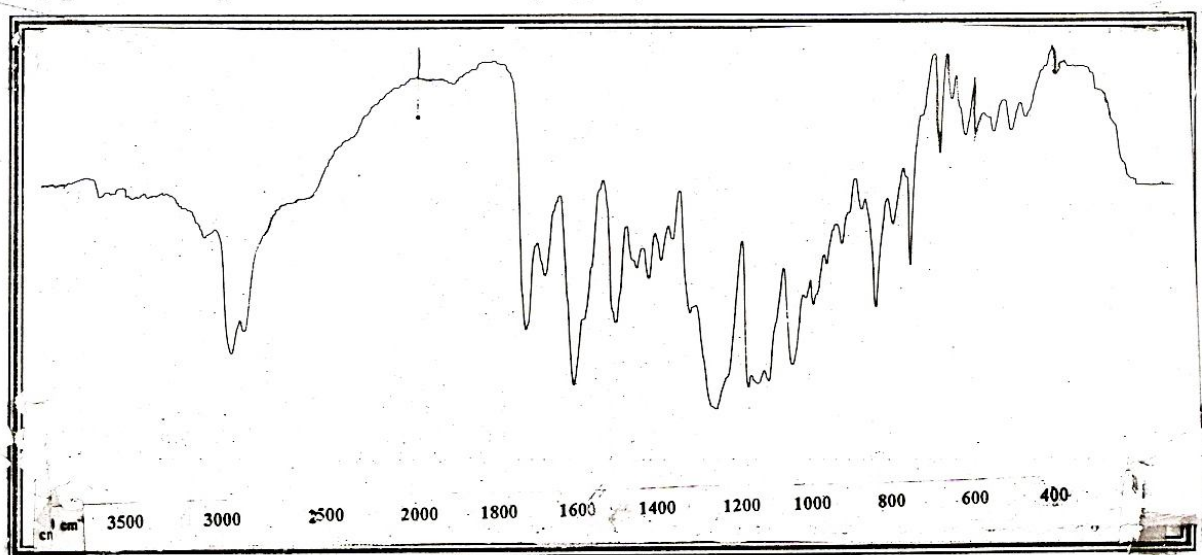


Fig. (1): IR spectrum for 5M.

Preparation of dimmer Schiff bases⁽¹⁰⁾(nO2On):-

1,2-diamino ethane (0.01mole)was added stepwise to a hot solution of 4-(4-alkoxy benzoyloxy)-2-hydroxy benzyldehde (0.02mole) in absolute ethanol (30ml)while cooling to room temperature are the mixture was stirred for 1hr. Yellow precipitate formed which was filtered off and recrystallized from ethanol (yield 90%).

Preparation of complexes Cu nO2On:-

Copper sulfate five hydrates (0.01mole) were added to a hot solution of dimer (0.01mole) in methanol 100ml and the mixture was refluxed for 1hr. After cooling, the mixture was stirred for 1hr. Green precipitate formed which was filtered off and washing several time with hot ethanol (yield 60-85%).

Techniques:-

Melting point was measured on a Gallen Kamp melting point apparatus. Elemental analyses were performed by EA1108 Elemental analyzer. Infrared spectra were recorded on Apye Unicam model sp3-300s spectrophotometer .UV-Visible spectra were measured thermospectronic Helios α -v4.60 (England) . Measurements of transition temperatures were made using a Perkins-Elmer DSC-7 differential scanning calorimeter (DSC). The instrument was calibrated with indium of purity (99.99). Polarizing optical microscopy studies were carried out on alaborlux 12 pols polarizing microscope to gather with a Leitz 350 a hot stage and vario orthomatic. The Grondjean planer texture used in measurement was obtained by shearing the sample between to glass slides

Characterization of compounds:-

The elemental analysis of two series nO_2O_n and $Cu nO_2O_n$ are in a good agreement with the calculated value as shown in table 1 and 2.

Table 1: The elemental analysis of dimmers

Compound	Calculated			Found		
	% C	% H	% N	% C	% H	% N
$2O_1$	67.60	4.92	4.92	67.51	4.83	4.87
$2O_2$	68.04	5.15	4.81	68.01	5.07	4.79
$2O_3$	68.45	5.37	4.69	68.44	5.29	4.61

2O4	68.85	5.57	4.59	68.75	5.56	4.57
2O5	69.23	5.76	4.48	69.20	5.73	4.49
2O6	69.59	5.95	4.38	69.49	5.89	4.41
2O7	69.93	6.13	4.29	69.87	6.06	4.33

I Table 2: The elemental analysis of complexes

Complexes	Calculated			found		
	% C	% H	% N	% C	% H	% N
1O2O1	61.04	4.13	4.45	60.91	4.07	4.22
Cu	61.58	4.35	4.35	61.45	4.39	4.29
2O2O2	62	4.56	4.26	62.31	4.49	4.21
Cu	62	4.76	4.17	62.71	4.80	4.23
3O2O3	62	4.76	4.17	62.71	4.80	4.23
Cu	63	4.96	4.08	63.21	4.89	4.01
4O2O4	63	4.96	4.08	63.21	4.89	4.01
Cu	63	5.15	4.01	63.52	5.05	4.11
5O2O5	63	5.15	4.01	63.52	5.05	4.11
Cu	63	5.32	3.92	63.79	5.29	3.84
6O2O6	63	5.32	3.92	63.79	5.29	3.84
Cu	63	5.32	3.92	63.79	5.29	3.84
7O2O7	63	5.32	3.92	63.79	5.29	3.84

The most important vibration bands observed in the infrared spectra for the dimer and complexes are list in table 3and 4 respectively. Typical IR spectrum for dimer 1O2O1 and Cu 4O2O4 are shown in Fig.2and 3 respectively. The appearance of N=CH stretching vibration of azomethine groups and disappearance of C=O stretching vibration of aldehyde groups in dimeric compound and disappearance of stretching vibration of hydroxyl groups in complexes of dimmer indicated that the preparation of these material is successful.

The UV-Visible spectra for nO2On explain three absorption peaks. The first transition from type $n-\pi^*$ at 314nm related to electronic transition for azomethine groups with alkyl groups. The other transition from type $\pi-\pi^*$ at 332nm related to

electronic transition for azomethine with phenyl groups and at 410nm related to electronic transitions for benzene ring which linking to alkoxy groups .

The UV-Visible spectra for Cu nO2On gave two absorption peaks. The first transition at 485nm related to $eg(xy,yz) \rightarrow b1g(x2-y2)$ and the second transition at 675nm related to $b2g(x,y) \rightarrow big(x2-y2)$. This two peaks related to allowed transition spin in symmetry D4h. Typical UV-Visible spectra for dimeric and complex compound in fig.4 and 5 respectively.

Table 3: The locations of the most important absorption bands cm-1 the IR spectra of dimers nO2On.

Group	O-H st.	C-Hst. arom.	C-Hst. aliph.	C=Ost ester	C-H=N	C=Cst.	C-O-C ether
stretching	3	3	2	1	16	1	1170
vibration	250 (W)	3010-3020 (W)	800-2930 (M)	715-1720 (S)	15-1625 (M)	580-1595 (S)	-1180 & 1250 -1260 (S),(S)

S=strong, M=medium, W=weak

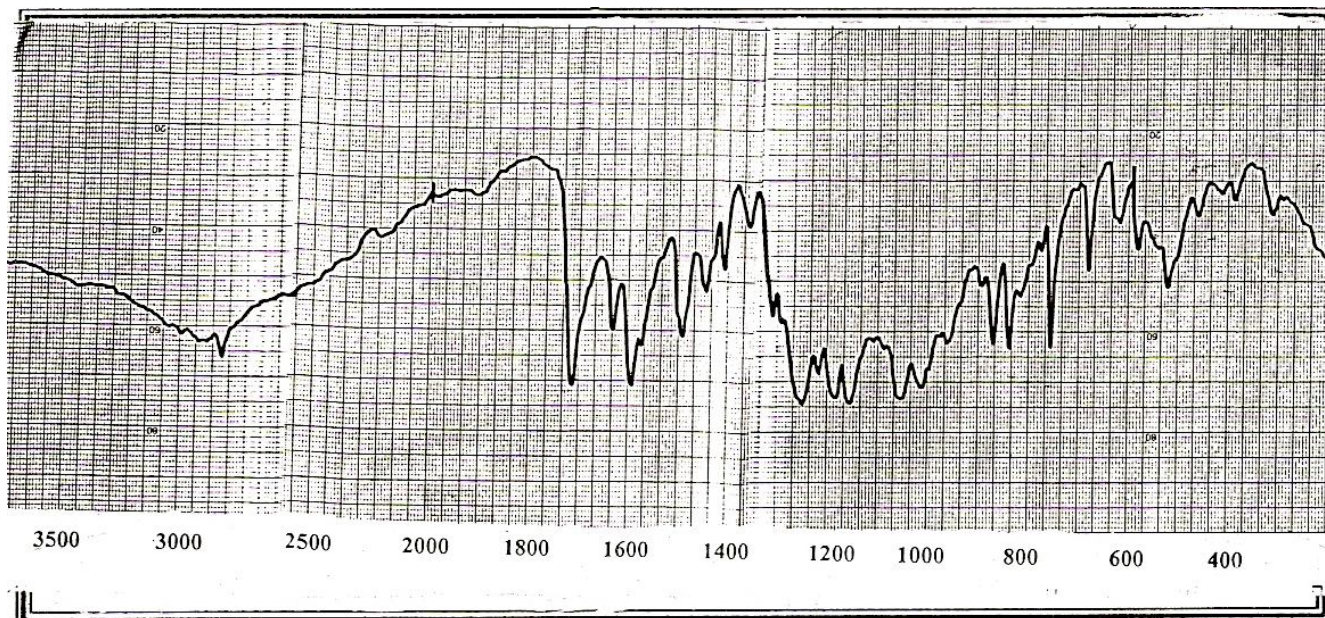


Table 4: The locations of the most important absorption bands cm-1 the IR spectra of complexes Cu nO2On.

Group	C-Hst. arom.	C-Hst. aliph.	C=Ost ester	C-H=N	C=Cst.	C-O-C ether
stretching vibration	3 010-3025 (W)	2 850-2920 (M)	1 710-1715 (S)	1 610-1615 (S)	1 580-1590 (S)	115 0-1160 & 124 0-1260 (S), (S)

S=strong , M=medium , W=weak

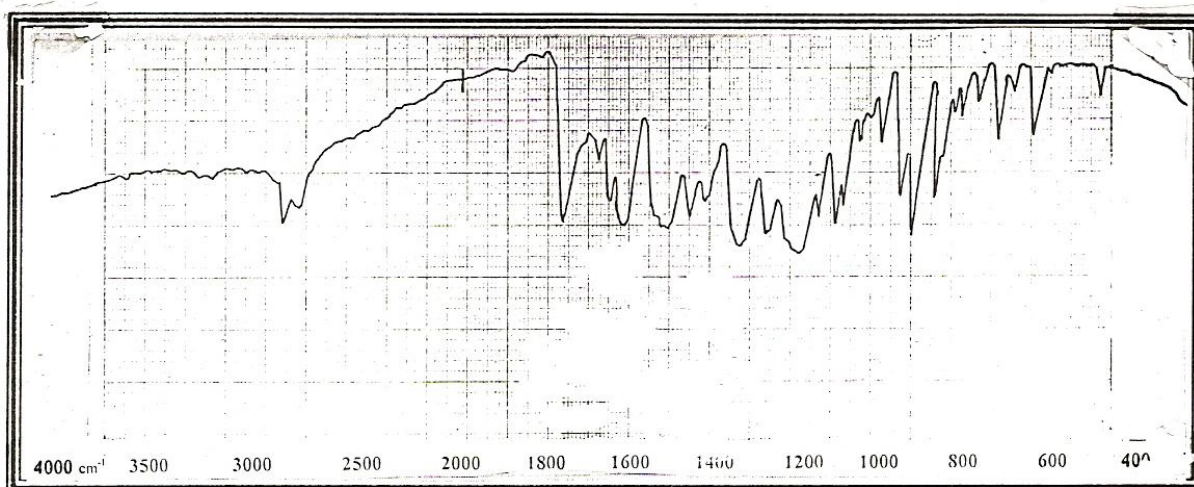


Fig. (3): The IR spectra of Cu 4O2O4



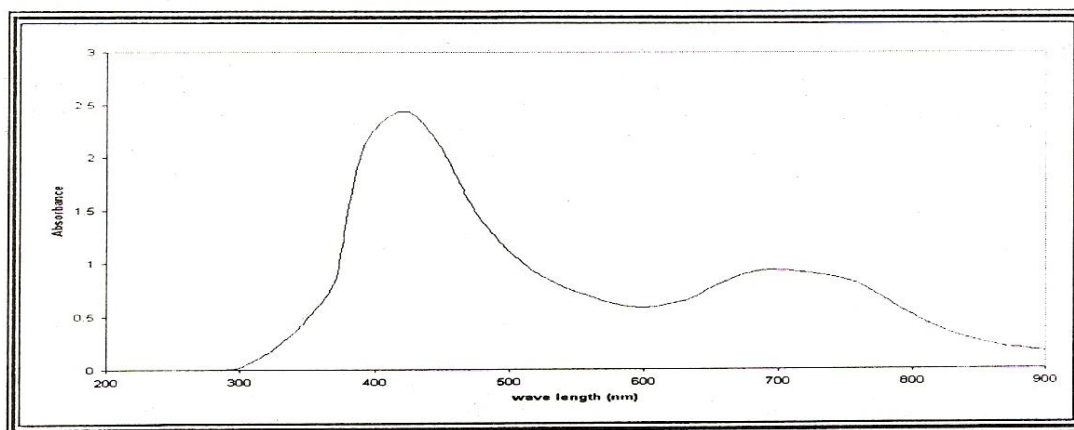


Fig. (5): The UV-visible spectra of compound Cu₃O₂O₃

Mesomorphic behavior:-

Mesogenic properties of dimeric series nO_2O_n and complexes series $Cu nO_2O_n$ were examined by differential scanning calorimetry and optical microscopy. The transition properties of dimmers and complexes are listed in tables 5&6. All members of dimmers series exhibit an enantiotropic nematic phase with typical schielern pattern

[Fig.6]. While the series $\text{Cu nO}_2\text{On}$ exhibit smectic A phase typical small fan shape pattern [Fig.7].

The dependence of the transition temperature on the number of carbon atoms, n , in the alkoxy chain for the series nO_2On and $\text{Cu nO}_2\text{On}$ is shown in Fig.8. It is immediately apparent that the melting points, the nematic – isotropic temperatures, and the smectic-isotropic temperatures are shown a dramatic odd-even effect and it is attenuated on increasing n . The transition temperature which exhibited by the $\text{Cu nO}_2\text{On}$ compounds are generally higher than the temperature which exhibited by the nO_2On compounds because increasing the cohesive energy which result from the hydroxyl groups in 2-position and azomethine groups leads to a strong chelating to copper metal by mean of intrahydrogen bond.

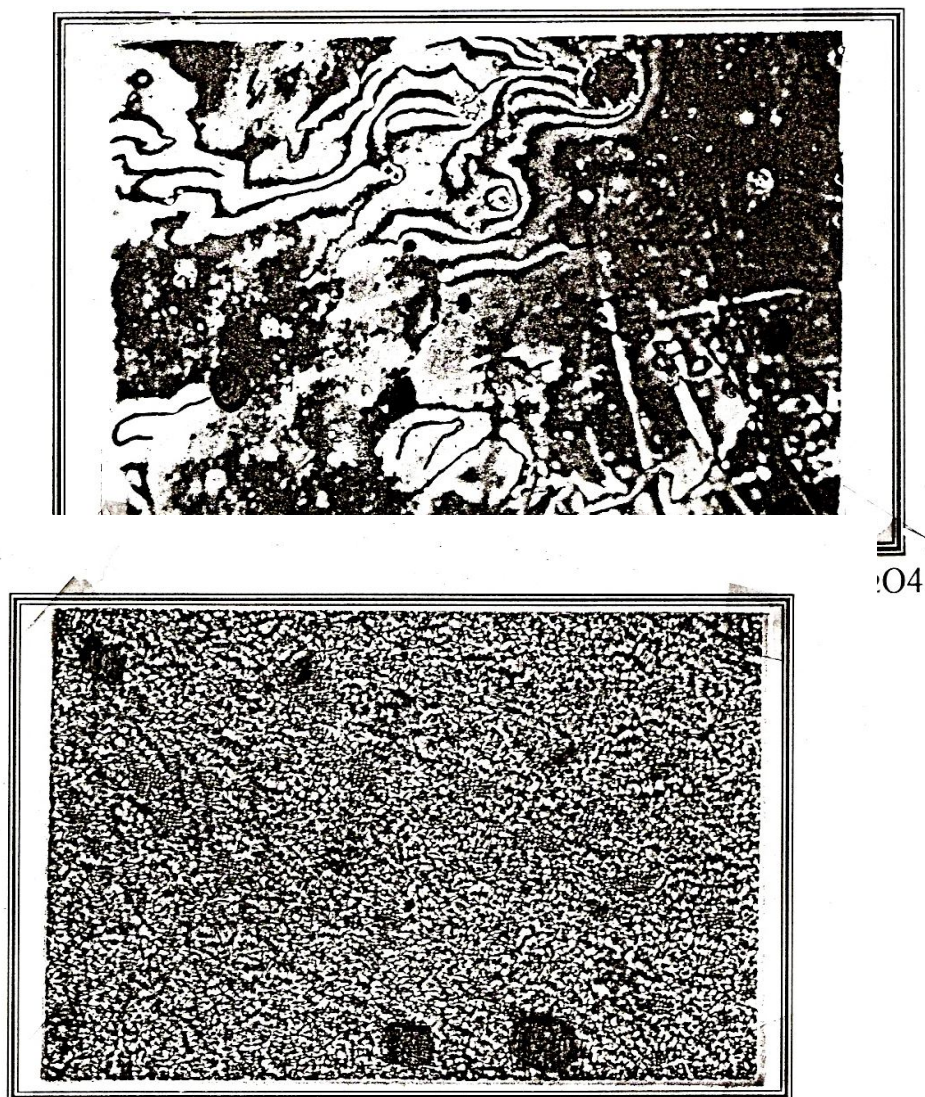


Fig.(7): Texture of Smectic (small fan shape) of compound $\text{Cu 4O}_2\text{O}_4$

Table 5: Phase transition temperature for nO2On series.

n	Nimatic(N)	Isotropic(I)	ΔT
1	175	210	45
2	170	225	55
3	160	203	43
4	165	216	51
5	155	197	42
6	162	209	47
7	153	194	41

Table 6: Phase transition temperature for Cu nO2On series.

n	Smectic(S)	Isotropic(I)	ΔT
1	195	221	26
2	203	241	38
3	187	218	31
4	195	230	35
5	184	209	25
6	187	219	32
7	181	201	20

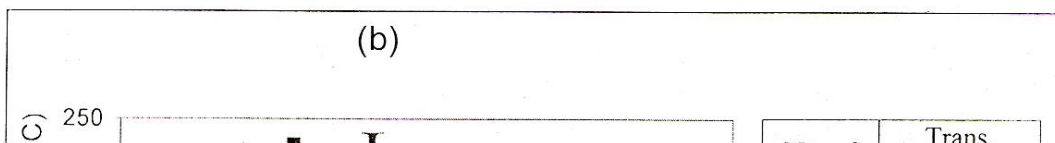
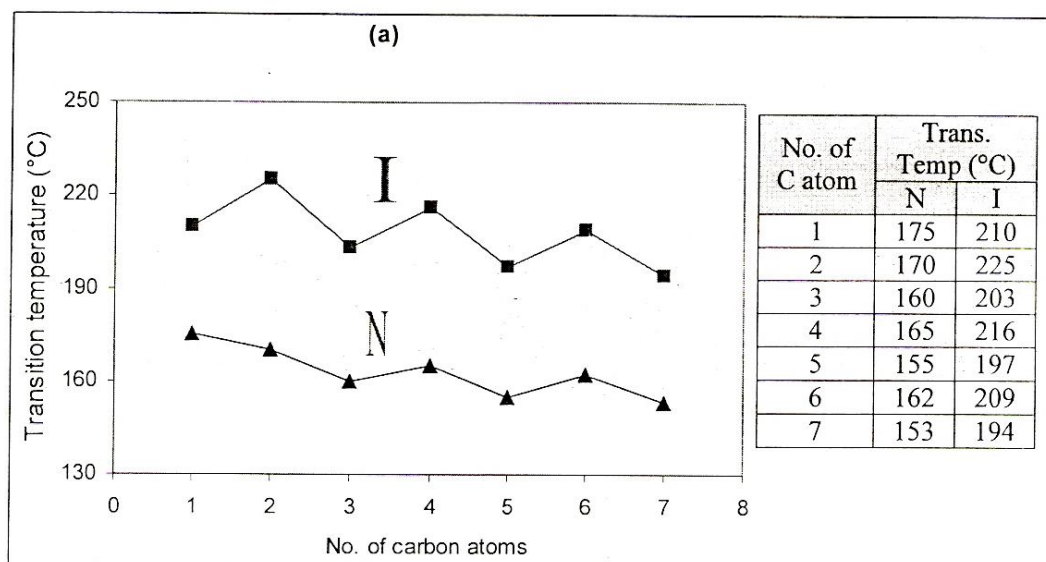


Fig.8: Represented the relation ship between the number of carbon atoms and:

A - The transition temperature for the dimmers nO_2O_n

B –Transition temperature for the complexes $Cu nO_2O_n$

References:-

ISSN-1994-697X

- 1-D.Bruce, K.Heyns and V.Vill, *Liq. Cryst.* 813, 23, 1997
- 2-A.Girroud and V.Mueller-Westeroff, *Mol. Cryst. Lett.* 11,41, 1977.
- 3-B.Donnin and D.Bruce, "**Structure and Bonding**", Ed.D.M.P.Minger, Springer-Verlag, P193, chapter 5, 1999.
- 4-K.Binnemans and C.Gorller -Waland, *Chem.Rev.* 2303, 102, 2002.
- 5-L.Oriol, M.Pinol and L.Serrano, *Prog.Polym.Sci*, 873,22,1997
- 6- L.T.Imire and G.R.Luckhurst, *J. Mater.Chem.*, 121, 5, 2002
- 7-A.Hameed, N.Saleh and A.Al-Dujaili, National *J.Chem.* 121, 5, 2002.
- 8-J.Dave and R.Vora, "**Liquid Crystals and Ordered Fluids**", Press, New York, 477, 1970.
- 9-M.Marcose ,P.Romero and J..Serrano .*Chem. Commun.*,1641,21,1989.
- 10-P.Lemasurier and G.Luckhurst, *J.Chem.Soc. Trans.*, 1593,94,1998.