

**Synthesis, characterization and liquid crystals properties for N, N'-(3,3'-dimethylbiphenyl-4,4'-diyl) dialkanamide****Khaled M. Mohammad¹, Ibtisam K.Jasim² and Abdullah H.Kshash³**1,3. Tikrit University – Education College for Pure Science – **IRAQ**2. Baghdad University – Education College Ibn Al-hytham – **IRAQ**Email: organicchem_1978@yahoo.comAccepted on 10th May 2014**ABSTRACT**

Homologous series of amide compounds were synthesized. Their structures were elucidated using spectroscopic techniques such as FT- IR (Infrared), ¹H-NMR. Mesomorphic properties and phase transitions were studied using polarized hot stage optical microscopy and differential scanning calorimetry (DSC), and are discussed as a function of the number of carbon atoms in the amide chain. It has been found that four compounds in the series are pure nematic mesophase.

Keywords: *O*-Tolidine amide, Nematic, Liquid Crystals, Mesophase.**INTRODUCTION**

The polarized optical microscopy and DSC used to determination the mesophase [1,2]. With development of liquid crystal science and technology more mesogens have been prepared and study. Thermotropic L.C. is one of type of mesogene currently extensively studied [3-6]. Most molecule structure of thermotropic mesogene contain a rigid core compose of two or more aromatic rings connected by connective groups as azomethene CH=N, Azo N=N ester –COOR groups and other to provides a stepped core structure and maintained the molecular linearity in order to exhibit higher stability and form mesophases, The presence of aromatic rings lead to increasing of thermal range of L.C. phases through increasing of molecule Polarizability and Rigidity [7,8]. One or more flexible terminal chain which connected by rigid core by formation of ether, thioether, ester and thioester bond, In general the increasing of chain length accompanied by decreasing of melting point of mesogene [9,10]. Side groups have very important effect on L.C. properties more studies showed that the side groups (as F,Cl,Br,I,CH₃,OCH₃) when presence in the mesogene the ratio width/length of molecule will be increasing this lead to prevent the L.C. properties [11-14]. However, a literature survey indicates that liquid crystalline with amide chain as terminal groups are very rare, so, in the present work, we have prepared series of amide compounds of *O*-Tolidine (Fig.1) in order to establish the effect of introducing amide bond instead of other bonds with the increase in the terminal amide chain on liquid crystalline properties.

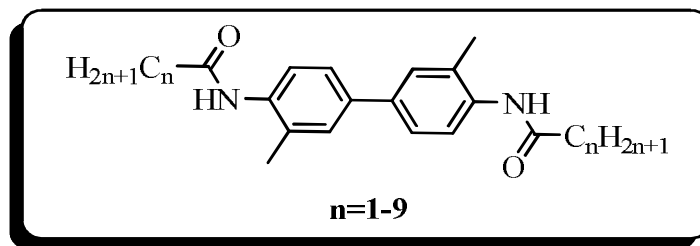


Figure 1. Structure of the studied amides series

MATERIALS AND METHODS

General: Infrared spectra were recorded as KBr pellets on a Bruker-Tensor 27 spectrometer. $^1\text{H-NMR}$ spectra were recorded on Bruker-500 MHz spectrometer using CDCl_3 as a solvent and TMS (Tetramethylsilane $(\text{CH}_3)_4\text{Si}$) as internal standard. The phase transitions were observed with a Leitz Laborlux 12 Pol optical microscope with polarized light in conjunction with a leitz 350 hot stage equipped with a Vario-Orthomat camera of transition temperatures were made using a Shimadzu DSC-60 differential scanning calorimeter with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

Synthesis of amides

Synthesis of acid chloride: Alkanoyl chlorides were prepared as reported method [15].

Synthesis of N,N'-(3,3'-dimethylbiphenyl-4,4'-diyl) dialkanamide (series A): *O*-Tolidine (0.5 g, 2.3×10^{-3} mol) was dissolved in dry pyridine (10.0 mL) in (50 mL) round bottom flask (4.7×10^{-3} mol) acid chloride was added drop wise through separation funnel to the *O*-Tolidine solution in ice bath for 1hr. then allowed to the mixture stirring at room temperature overnight, the mixture acidified with 20 ml of 5% HCl then pour the mixture on crush ice the solid obtained was filtered washed with 5% HCl then successive with distilled water then recrystallized with ethanol.

RESULTS AND DISCUSSION

Acid chloride identified by FT-IR spectrophotometer. The spectrum shows disappearance of stretching vibration for hydroxyl group and increase the wave number for acid chloride carbonyl groups in range ($1789\text{-}1803\text{ cm}^{-1}$). The results are given in table 1 and fig.2.

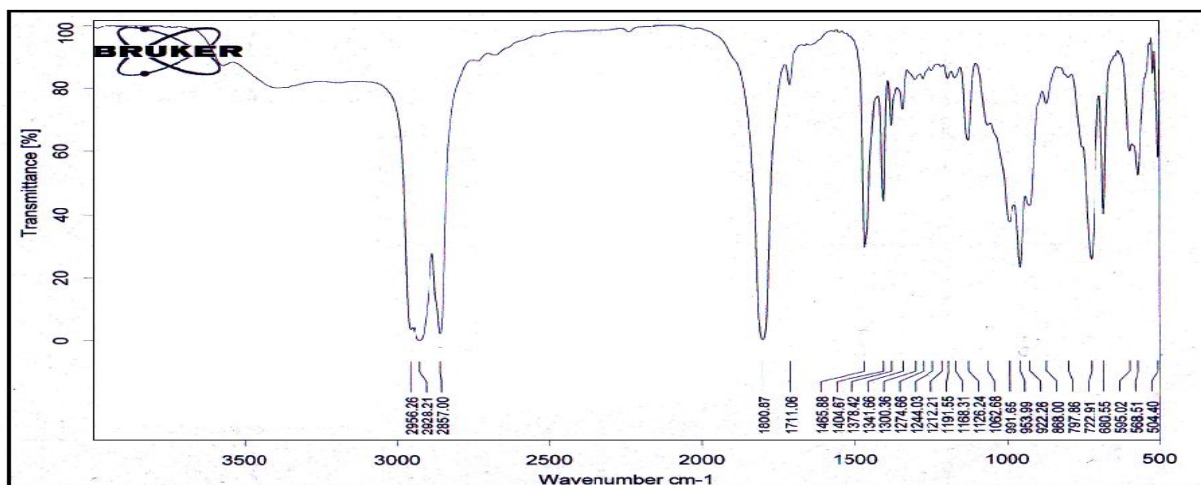


Figure 2. FT-IR Spectrum for Decanoyl Chlorides

Table 1. FT-IR absorption bands for acid chloride series Compounds

n	$C_nH_{2n+1}COCl$										
	$\nu_{as}C-H$		ν_sC-H		$\nu C=O$	$\delta_{as}CH_3$	δCH_2	δ_sCH_3	$\nu CO-C$	γCH_2	$\nu CO-Cl$
	CH_3	CH_2	CH_3	CH_2							
1	3020	-	2936	-	1804	1420	-	1361	954	-	595
2	2993	2947	2883	2868	1789	1457	1406	1337	916	783	609
3	2972	2940	2881	2868	1801	1462	1405	1337	959	723	610
4	2963	2937	2876	2866	1801	1466	1405	1341	946	719	591
5	2960	2934	2874	2864	1803	1466	1404	1341	954	729	593
6	2959	2933	2871	2861	1801	1466	1405	1341	953	726	591
7	2957	2927	2873	2857	1800	1465	1404	1340	950	723	592
8	2957	2928	2874	2857	1801	1465	1406	1344	954	720	591
9	2956	2928	2871	2857	1800	1465	1404	1341	953	722	595

The *O*-Tolidine amide compounds were synthesised in accordance with the following steps as shown in fig.3.

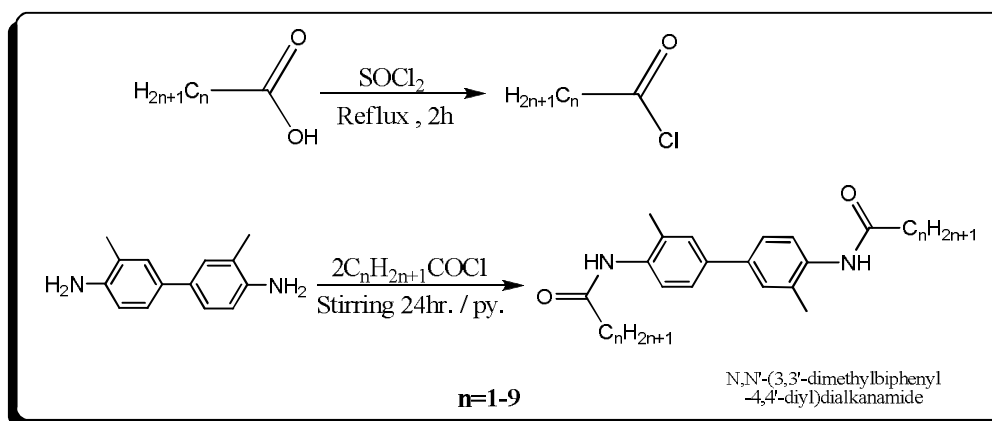


Figure 3. Synthesis step of the prepared amide compounds

The FT-IR spectrums for *O*-Tolidine amide compounds shows the disappearance of the asymmetric and symmetric stretching vibration of amino group and the appearance of stretching vibration of ($\nu N-H$) ($3274-3296\text{ cm}^{-1}$) and ($\nu C=O$) of amide ($1649-1656\text{ cm}^{-1}$), the aliphatic ($\nu C-H$) ($2922-2933\text{ cm}^{-1}$) [16]. The results are given in table 2 and the spectrum is shown in fig.4.

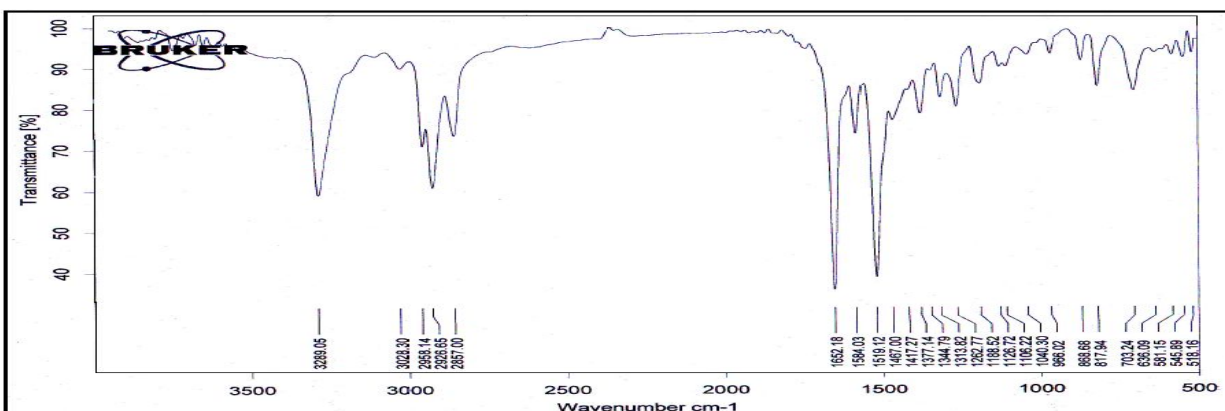
Figure 4. FT-IR Spectrum for Compound A₇

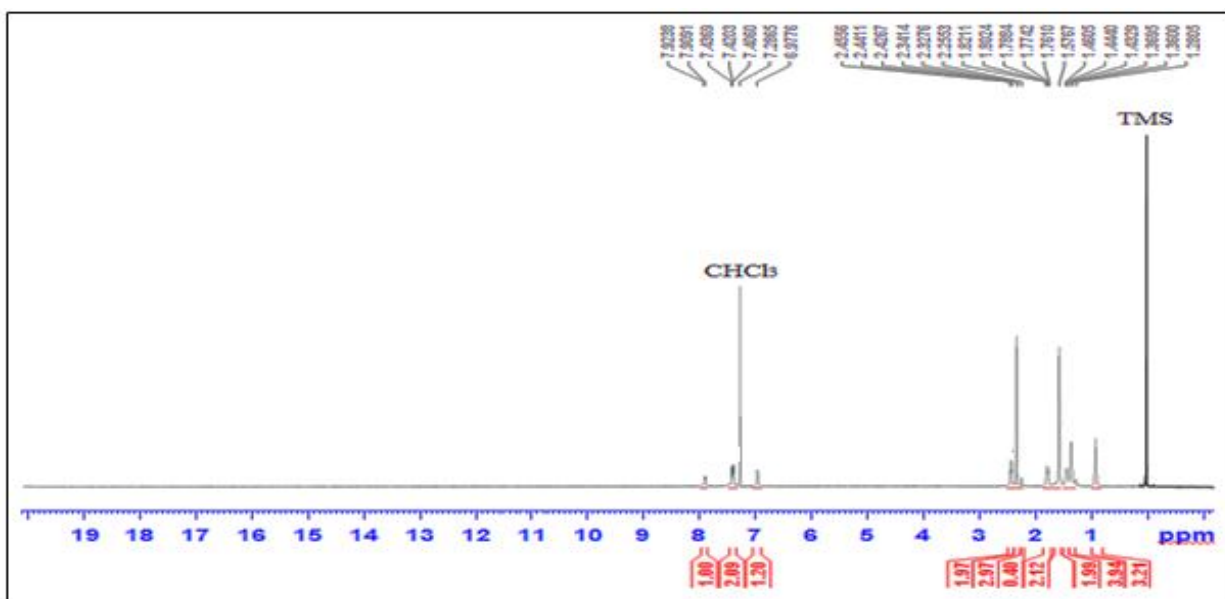
Table 2. FT-IR absorption bands for *O*-Tolidine amide compounds

Comp.	n	νN-H	νC-H		νC=O amide	νC=C		δN-H		νC-N	δC-H		γ CH ₂
			Arom.	Aliph.		In plane	Out of plane	In plane	Out of plane				
A ₂	1	3280	3030	2924	1652	1583	1515	1368	612	1282	1128	865	-
A ₃	2	3285	3027	2933	1655	1583	1518	1370	618	1263	1126	863	706
A ₄	3	3277	3029	2930	1651	1584	1520	1374	609	1263	1127	866	748
A ₅	4	3274	3028	2927	1649	1584	1520	1376	615	1266	1124	864	704
A ₆	5	3288	3034	2923	1650	1588	1504	1373	619	1249	1128	880	718
A ₇	6	3289	3028	2926	1652	1584	1519	1377	636	1262	1126	868	703
A ₈	7	3287	3028	2922	1651	1599	1502	1377	613	1273	1118	845	723
A ₉	8	3296	3027	2923	1656	1584	1512	1376	615	1264	1118	866	703
A ₁₀	9	3290	3028	2922	1652	1583	1519	1376	613	1265	1118	867	703

Two compounds (A₇, A₁₀) of *O*-Tolidine amide identified by ¹H-NMR spectroscopy, ¹H-NMR spectrum for A₇ shows triplet signal at δ=0.92 assigned for methyl groups for aliphatic chain, multi signal at δ=1.3-1.6 ppm assigned for methylene groups in aliphatic chain, multi signal at δ=1.78 ppm assigned for β methyl group in aliphatic chain triplet signal at δ=2.44 ppm assigned for α methyl groups for aliphatic chain, while methyl group attached to aromatic rings observed as single signal at δ=2.34 ppm the aromatic hydrogen observed as multi signal at δ=7.4-7.92 ppm the N-H single signal at δ=6.9 ppm [16], (Table 3). The chemical shift for two compounds shown in fig. 5. and fig.6.

Table 3. Chemical shift for A₇, A₁₀ Compounds

Comp.	n	CH ₃	CH ₂	βCH ₂	αCH ₂	N-H	Ar-CH ₃	Ar-H
A ₇	6	0.92 t	1.3-1.6 m	1.78 m	2.44 t	6.97 s	2.34 s	7.40-7.92 m
A ₁₀	9	0.90 t	1.3-1.55 m	1.80 m	2.45 t	6.97 s	2.34 s	7.40-7.95 m

Figure 5. ¹H-NMR Spectrum for Compound A₇

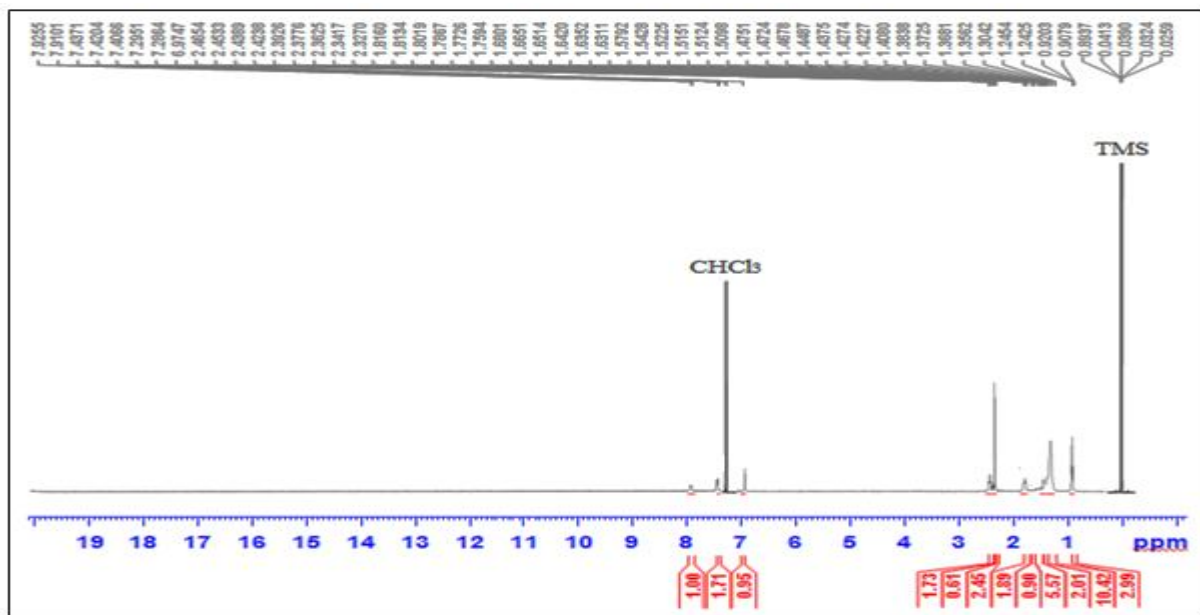
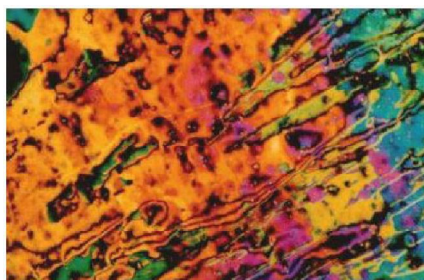


Figure 6. $^1\text{H-NMR}$ Spectrum for Compound A_{10}

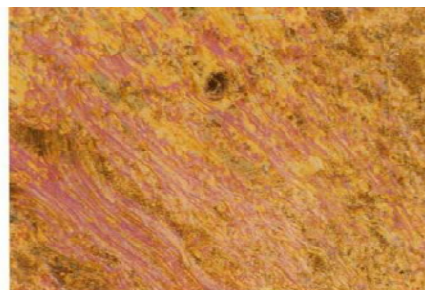
The DSC scans carried out on these compounds show transitions at temperatures which are in agreement with those obtained by optical microscopy. The phase transition temperatures of all compounds are given in table 4. Four compounds exhibit monotropic mesogenic behavior and show Nematic phase (N) only. Figure 7 reflects the marbled texture.

Table 4. The phase transitions of compounds ($^{\circ}\text{C}$).

Comp. ymb.	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}
n	1	2	3	4	5	6	7	8	9
Cr \rightarrow N	-	-	-	242.6	214.3	-	221.4	150.6	-
N \rightarrow I	-	-	-	248.9	239.2	-	304.6	349.5	-
ΔT_N	-	-	-	6.2	24.9	-	83.1	198.9	-



(A)



(B)

Figure 7. A. Marble texture for Nematic phase in heating at 242.6°C for A_5 , B. Marble texture for Nematic phase in heating at 150.6°C for A_9

APPLICATIONS

This study is useful for knowing the effect of amide bond on the L.C. properties as a terminal group and the texture of the prepared amide compounds.

CONCLUSIONS

The DSC thermogram expressed the dependence of the transition temperature on the number of carbon at the alkanamide chain. Therefore the nematic phase range increase with the increasing of aliphatic chain but the melting point decrease with the increasing of aliphatic chain (Fig. 8). A plot of the transition temperature and melting point against the number of carbon atoms in alkanamide chain.

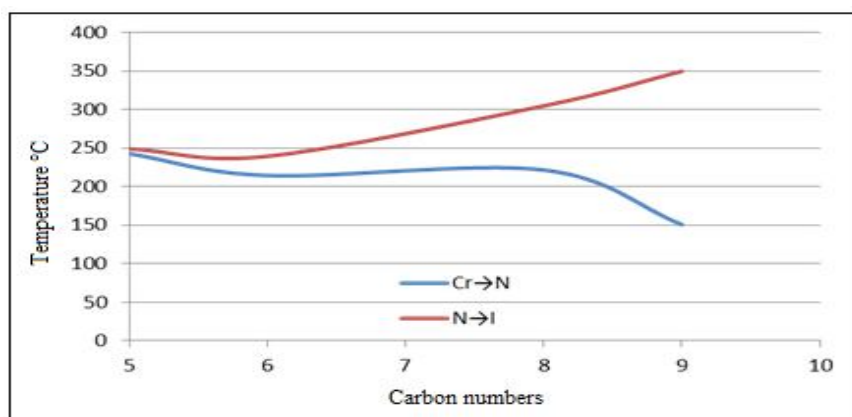


Figure 8. A plot of the transition temperature against the number of carbon atoms

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