A Study of Thermal Properties of Some Nematogenic Schiff's Bases

S.H.Ridha
Chemistry Department-College of Education-Ibn-Al-Haitham-University of Baghdad

Abstract

The thermal properties of four nematogenic schiff's bases, n-butyl-to-n-heptyl of bis (4-n-alkyloxybenzylidine)-2,3,5,6-tetramethyl-1, 4-phenylenediamine, have been studied. The transition temperatures and enthalpies of transition were examined by differential scanning calorimeter (DSC). Several correlations were carried out; those included the relations between transition temperatures, enthalpies and entropies of transition with increasing the number of carbon atoms in the terminal alkyl chains. In addition, new regular relations were found between the ratio of the enthalpies and of the entropies, for nematic-isotropic transition and crystal-isotropic transition ($\Delta H_{N-i}/ \Delta H_{C-I}$, $\Delta S_{N-I}/ \Delta S_{C-I}$), with increasing terminal alkyl chain lengths. Many interesting conclusions, concerning the relation between the anisotropic molecular shape and the thermal properties of the above nematogens, have been arrived at.

Introduction

We are all aware that liquid crystal properties of a mesogene are highly related to its molecular structure (1). In an interest in understanding the structure-property relationship, the influences of terminal substitution and of central core substitution on thermotropic liquid crystal behaviour have been systematically evaluated for a great many series (2-4). In this paper ,an attempt is made to investigate the effect of substitution four methyl groups, act as broadening groups in the middle aromatic ring of the central core, on the thermal properties of the homologous series of molecular structure shown below:

$$H_{2n+1}C_nO-\langle O \rangle--CH=N-\langle O \rangle--N=CH--\langle O \rangle--OC_nH_{2n+1}$$

n=4-7
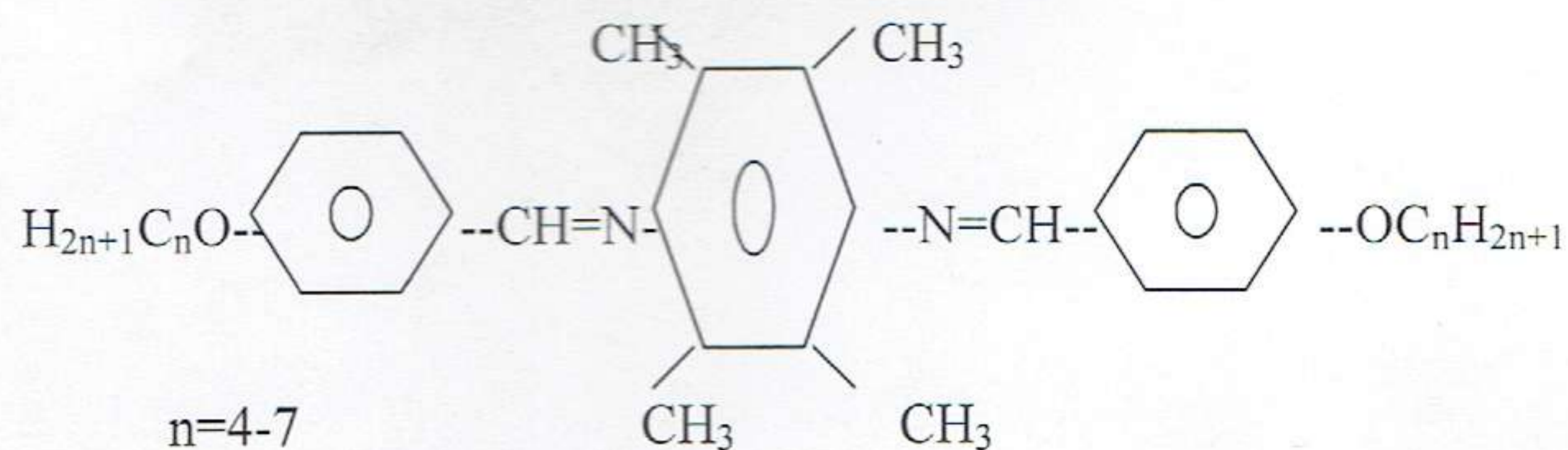
Recently, the previous compounds were synthesized and their liquid –crystalline behaviour was established using polarizing microscopy (5). Each member of the above series only exhibits enantiotropic nematic phase.

In this study, the thermal behaviour and phase transition for the nematogenic compound (n=4-7), were performed using differentianal-scanning calorimetry (DSC). The results were discussed on the basis of the thermodynamic data obtained.

For convenience, the above series will be denoted by the acronym nO.4MePh.On, n refers to the number of carbon atoms in the terminal alkyl chains and 4MePh reflected to the substitution of four methyl groups in the middle phenyl ring. The unmethylated analogous known series will be denoted by acronym nO.Ph.On.

Experimental

All compounds of the series (n=4-7) have been synthesized and characterized previously (5). Transition temperatures and enthalpies of transition for these compounds were obtained using a Perkin-Elmer DSC-7 differential scanning calorimeter at a scan speed of 10^0C/min. under a flow of dry nitrogen; Indium was used as enthalpy standard.

ResultsAnd Discussion

Transitional Properties of the nO.4MePh.On Series

As seen from DSC heating traces, there are at least two endotherms. The higher transition is small and broad and corresponded to a transition from a nematic phase to an isotropic

liquid phase (N-I). The lower transition is large and sharp and corresponded to a transition from a crystalline phase to a nematic phase (C-N) (figure1). The member (n=4) shows, in addition, one more endotherm in a lowest temperature corresponded to a transition between two crystalline forms (C-C), one is stable at lower temperature, and the other is stable at higher temperature. The transition temperatures obtained by DSC analysis are comparable with those obtained via polarizing microscopy (5).

In table(1), the transition temperatures and the enthalpies of transition are listed. Entropies of transition, which can be easily obtained from the following relations:

$$\Delta S_t = \Delta H_t / T_t \qquad \text{----------[1]}$$

$$\Delta S_t / R = \ln(N_2 / N_1) \qquad \text{------------[2]}$$

Where t refers to the transition under consideration, R is the gas constant (=8.314Jmol.$^{-1}$.K^{-1}); N_1 and N_2 are the number of states of disorder statistically occupied below and above T_t.

Figure 2 shows the effect of varying the number of carbon atoms in the terminal alkyl chains on the transition temperatures for the nO.4MePh.On. series. We notice that the nematic-isotropic transition temperatures decrease steeply with weak odd-even effect as the series is ascended. This trend demonstrates that the anisotropic interaction between the rigid structures of the molecules, in nematic phase, is strong enough and the additional end flexible chains lower the average of this interaction greatly. While the crystal-nematic transition temperatures (melting points) fall steeply at first then level off with increasing length of the terminal alkyl chain. This indicates that the crystal structure of the compounds especially those of the members (n=5-7) might be similar.

Figures 3 and 4 show enthalpies and entropies of transition, respectively, for the nO.4MePh.On series. Both figures show remarkable similarity indicating a strong coupling between intermolecular force and structural ordering in this system (6). The two figures show that the nematic-isotropic enthalpies and entropies decrease steeply at first then level off at the end of the series (n=7). While the crystal-nematic enthalpies and entropies, in contrast,

increase with odd-even effect as the series is ascended. The trends in figure 3 indicate that the amount of energy needed to breakdown the parallism of the molecules in the nematic phase decreases with the lengthening of terminal alkyl chains, but the amount of energy required to collapse the crystalline lattice of three dimensional order to make a fluid of one dimensional order increases with increasing length of terminal alkyl chain. The trends in figure 4 are attributed to the average number of conformation that the molecules adopt in the nematic phase and in the isotropic phase.

The much reduce temperature range of the nematic phase (ΔT) at the end of the series reflects the fact that the clearing point (T_{N-I}) falls faster than melting point (Table 1).

Conventionally, the ratio of each enthalpies and entropies, for nematic-isotropic transition (N-I) and crystal-isotropic transition (C-I), can be used to compare the relative degrees of molecular interaction forces and of molecular order, respectively, in the phases involved. These thermodynamic parameters, $\Delta H_{N-I}/\Delta H_{C-I}$ and $\Delta S_{N-I}/\Delta S_{C-I}$ for the nO.4MePh.On series are listed in Table 1. The average value of each (5.97%, 5.5%) is larger than that for many series of low molecular weight liquid crystals (3). The values of each ratio in percent were plotted versus the number of carbon atoms in the terminal alkyl chains (figure 5).

From figure 5 we notice that the points of each ratio lie on one decreasing smooth curve. We also notice that the amount of decrease for each curve is attenuated on ascending the series. It is obvious from figure 5 that the difference between the two ratios $\Delta H_{N-I}/\Delta H_{C-I}$, and $\Delta S_{N-I}/\Delta S_{C-I}$ decreases with increasing chain length. These differences, which assigned by (Δ_{H-S}) listed in the last column of table 1. The values of the later in percent were plotted against the terminal alkyl chain length (figure 6). It is clear that the difference (Δ_{H-S}) decreases rapidly with increasing chain length until approximately diminished. This behaviour gives us the evidence for the principal reason of the steeply decreasing of the nematic-isotropic temperatures (clearing points) as the series is ascended (figure 2). The first fact stems from the results above is: "The more molecular ordered nematic phase with respect to its crystalline parent The more stronger the molecular interaction forces, and consequently, the more energy needed to disturpe it and vise versa". The second fact is: "the more stronger the molecular interaction force (with respect to its crystalline parent), in

nematic phase, relative to its molecular order, the more higher the clearing temperature. This fact is in accord ance with the relation below:

$$T = \Delta H_t / \Delta S_t \qquad\qquad ------------[3]$$

Molecular Shape Anisotropy of the nO.4MePh.On Series

X-ray studies of benzylideneaniline (7) show that the molecules are twisted out of coplanarity on either side central schiff's base linkage, then the structure of the schiff's bases discussed in this paper, assuming the more favorable trans zigzag conformation for the terminal alkyl chains (8), would be as shown below:
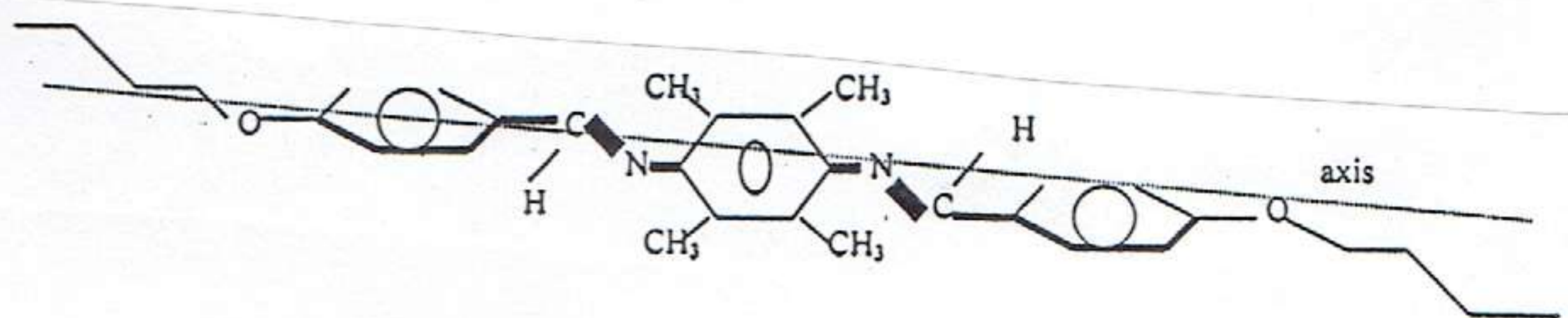
The studies on unsubstituted schiff's bases reveal that the ring linked to the amine part of the imine linkage, is twisted in relation to the central core, the torsion angle being 55.2^0 (7). When four methyl groups are substituted in the diamine ring, the twisting, as expected would be larger around the C_1-N and C_4-N single bonds. This additional twisting, in each side of the diamine ring, causes a decrease in Π-bonding character of C_1-N and C_4-N and therefore the mutual conjugation along the entire molecule would be decreased. As a consequence, the anisotropy of molecular polarizibility, which is the predominant factor for N-I transition (1), would be lowered. This factor is responsible for the reduction in the thermal stabilities of the nematic phases of the nO.4MePh.On series compared with those of their unmethylated analogous nO.Ph.On series (9) (see figure 7).

Since the end terminal groups are free to rotate in either direction with the reference to the central core, the twists about C_1-N and C_4-N in the phenylenediamine ring would be identical. Therefore, the twisting here would be symmetrical as that in the unmethylated nO.Ph.On series. This is true because four methyl groups are

substituted in the diamine ring, if less than four, the twisting would not be symmetrical and the transitional properties would be quite different (3, 10). The evidence for the likeness of the methylated and the unmethylated series in their symmetrical twisting about C_1-N and C_4-N bonds, that I could present is that the trends of the N-I transition temperatures with increasing alkyl chain length, is almost identical (see figure 7).

In conclusion, it is interesting to note that introducing four methyl groups, in the central ring of aromatic schiff's base, projecting beyond the perimeter of the rest of the molecule, decreases the thermal stability of nematic phase and this is attributed to the molecular biaxility resulting from a decreased length-to-breadth ratio relative to their unmethylated series, which causes not only a decrease in the molecular anisotropy, but also in the lateral interaction responsible for smectic phase stabilization.

References

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Table(1) Thermodynamic data for the nO.4MePh.On series

n	T/°C			ΔH / kJmol⁻¹				ΔS/R			$\frac{\Delta H_{N-I}}{\Delta H_{CI}}$ %	$\frac{\Delta S_{N-I}}{\Delta S_{CI}}$ %	Δ*_H-S %
	C-C	C-N	N-I	C-C	C-N	N-I	C-C	C-N	N-I	ΔT			
4	151.9	188.2	222.3	11.02	15.2	2.32	3.11	3.96	0.56	34.1	8.3	7.4	0.90
5		158.9	194.1		29.63	1.93		8.25	0.497	35.2	6.1	5.7	0.4
6		158.7	183.5		31.75	1.66		8.84	0.44	24.8	4.97	4.7	0.27
7		152.7	169.4		36.26	1.70		10.33	0.46	16.8	4.5	4.3	0.2

$$* \Delta_{H-S} = \frac{\Delta H_{N-I}}{\Delta H_{C-I}} - \frac{\Delta S_{N-I}}{\Delta S_{C-I}}$$

PERKIN-ELMER
7 Series Thermal Analysis System

Fig.(1) DSC heating traces for 7O.4MePh.O7.

Fig2 The influence of the number of carbon atoms,n, in the terminal alkyl chains, on the transition temperatures for the nO.4MePh.On series, C-C (□), C-N (Δ), N-1 (O)
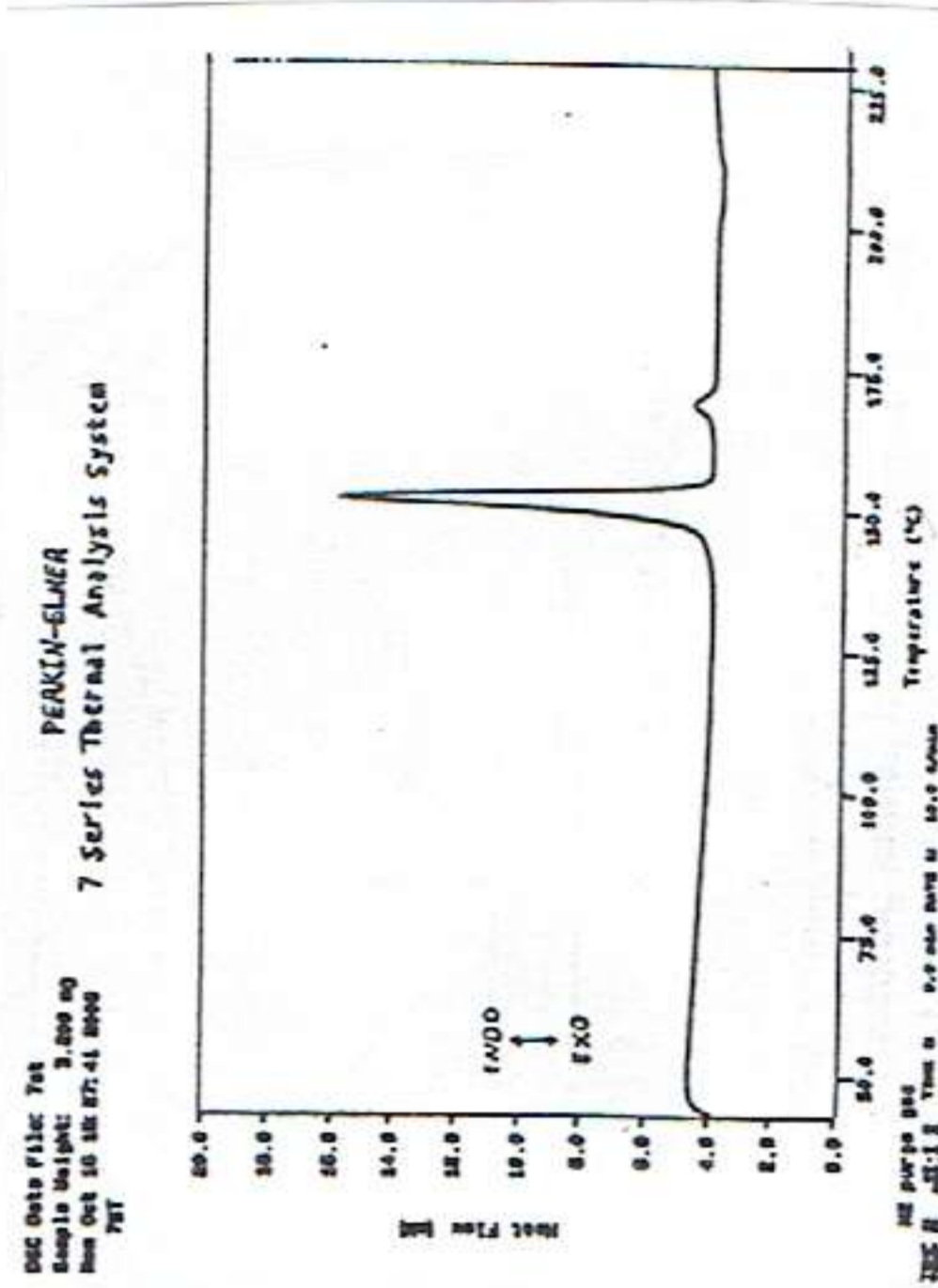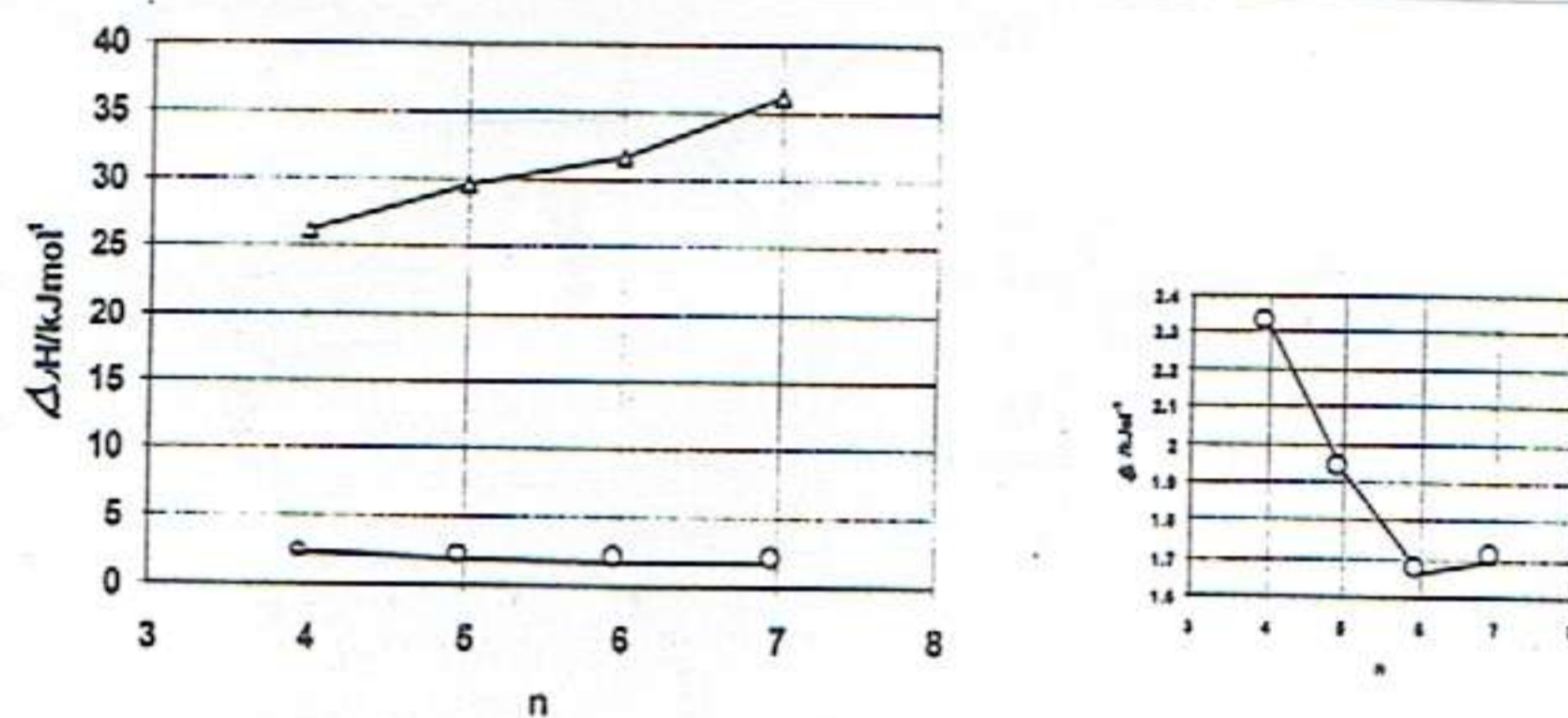
Fig.(3) The influence of the number of carbon atoms in the terminal alkyl chains on clearing enthalpies of transition (o) and melting enthalpies of transition (Δ) for nO.4MePh.On series.
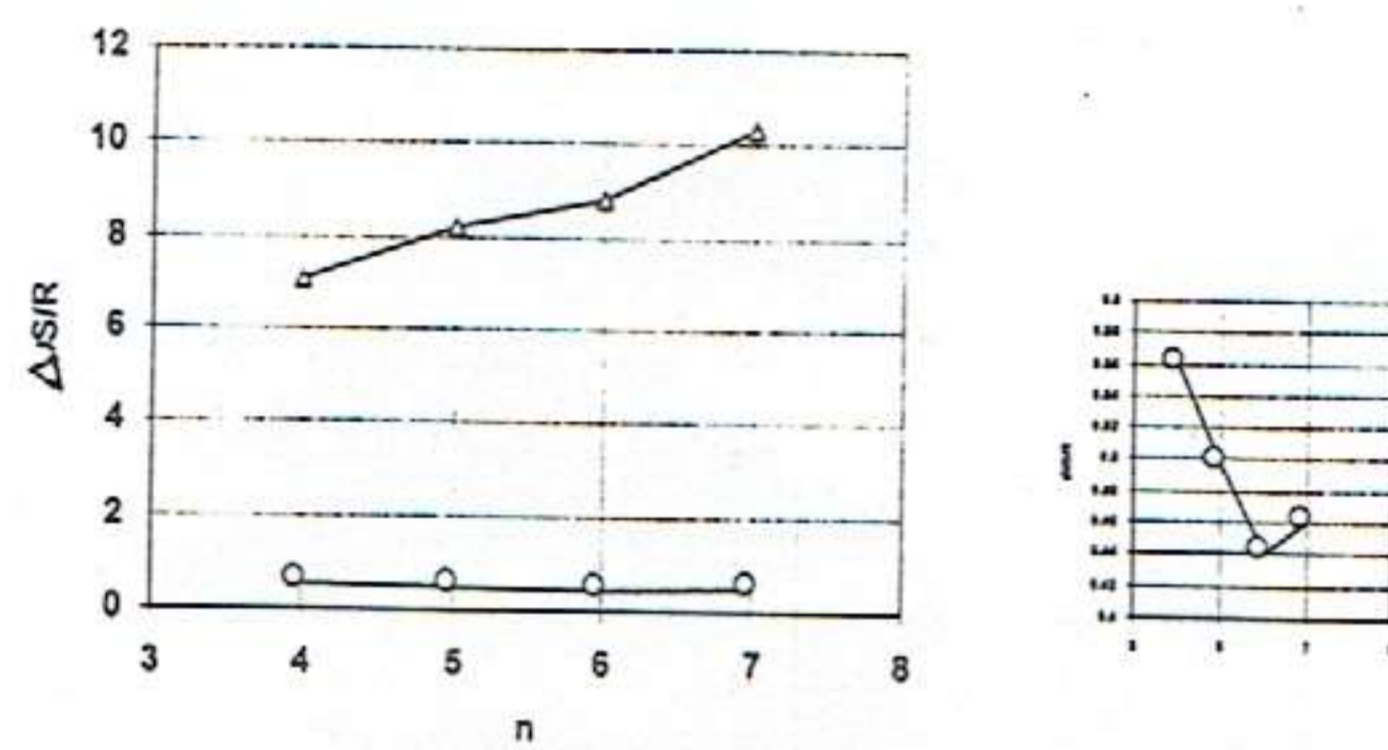

Fig.(4) The influence of the number of carbon atoms ,n, in the terminal alkyl chains on clearing entropies of transition (O) and melting entropies of transition for nO.4 MePh.On series.
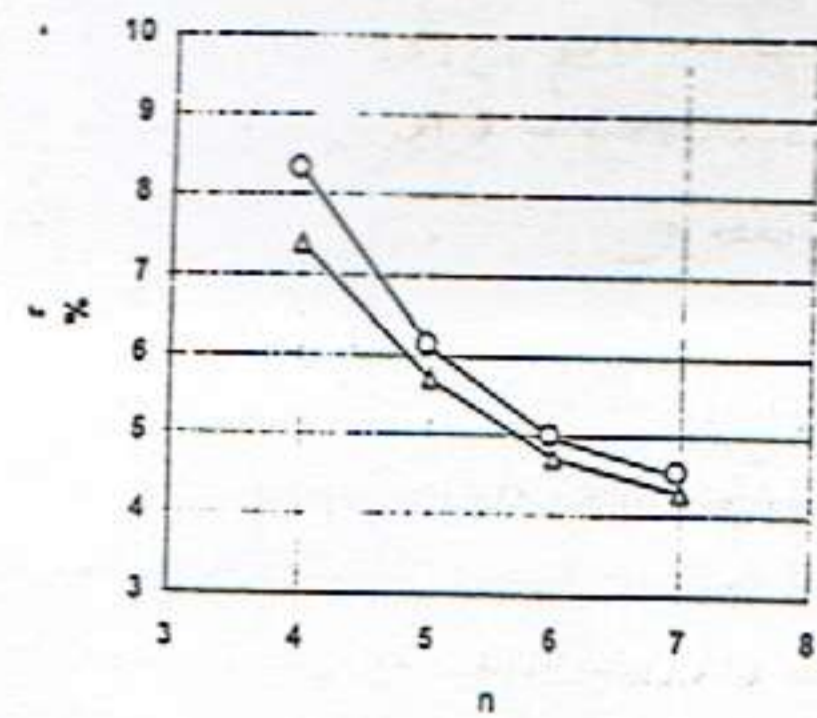
Fig. (5) The influence of the number of carbon atoms, n, in the terminal alkyl chains, on the degree of molecular interaction forces (O) and on the degree of molecular order (Δ), in nematic phase with respect to its crystalline parent (ΔH_{N-I} / ΔH_{C-I}), (ΔS_{N-I} / ΔS_{C-I}).
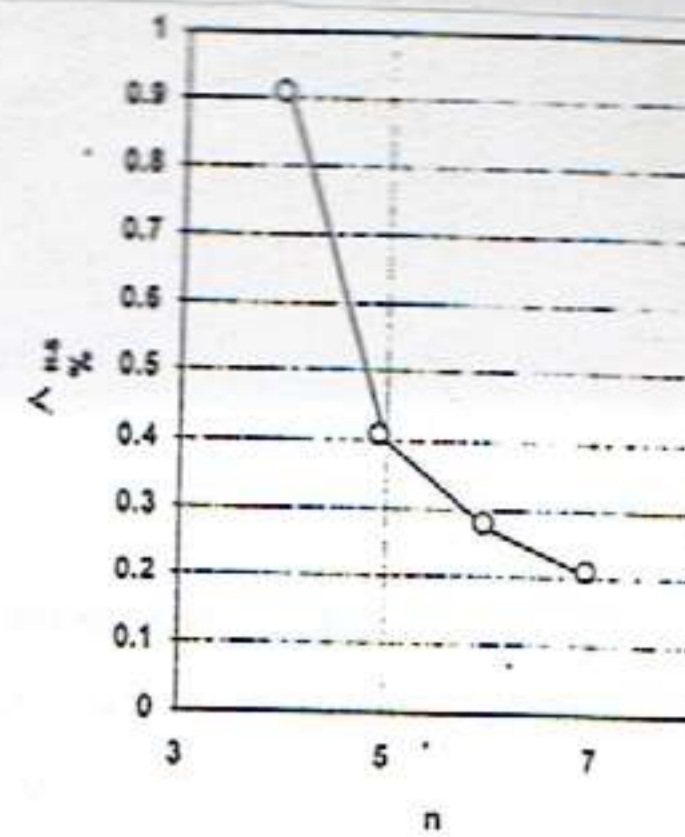

Fig. (6) The influence of the number of carbon atoms, n, in the terminal alkyl chains, on the magnitude of the difference between the degree of molecular interaction forces and the dgree of molecular order, in nematic phase with respect to its crystalline parent (ΔH_{N-I} / ΔH_{C-I}), (ΔS_{N-I} / ΔS_{C-I}).
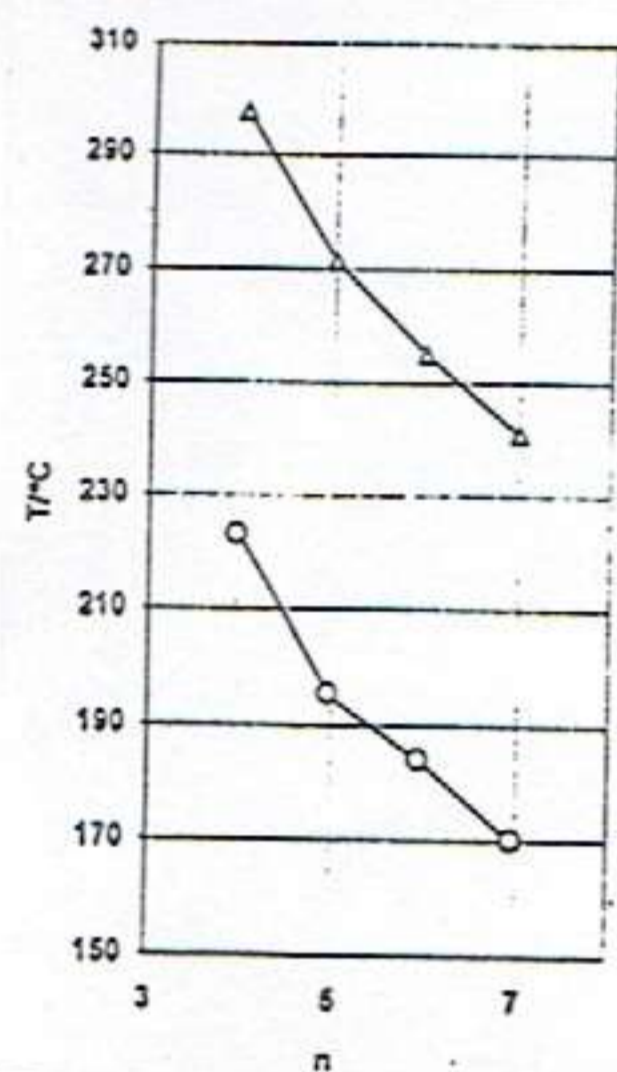

Fig.(7)The influence of the number of carbon atoms,n, in the terminal alkyl chains, on the N-I transition temperatures for (a) nO.4MePh. On series (O) and (b) nO.Ph.On series (▲)

دراسة الخواص الحرارية لبعض قواعد شف النيماتوجينية

ساجدة هادي رضا
قسم الكيمياء ، كلية التربية- ابن الهيثم، جامعة بغداد

الخلاصة

درست في هذا البحث الخواص الحرارية لاربعة مركبات قواعد شف نيماتوجينية ،
n-butyl – to – n- heptyl of bis (4-n- alkyloxybenzylidene)- 2-3-5-6-
tetramethyl-1,4-phenyenediamine.

قيست درجات الحرارة الانتقالية وانثالبيات الانتقال بوساطة جهاز مسح المسعربةالتفاضلي
وضعت عدة علاقات متبادلة بين درجات الحرارة الانتقالية، انثالبيات و انتروبيات الانتقال
مع زيادة عدد ذرات الكاربون في السلاسل الالكيلية الطرفية فضلا عن ذلك، كشف عن
وجود علاقات جديدة منتظمة بين تناسب الانثالبيات وتناسب الانتروبيات للانتقال نيماتي –
ايزوتروبي الى تلك للانتقال بلوري – ايزوتروبي($\Delta H_{N-1}/\Delta S_{C-1}$)($\Delta H_{N-1}/\Delta H_{C-1}$)
مع زيادة طول السلاسل الالكيلية الطرفية . من خلال هذه الدراسة أمكن التوصل الى
استنتاجات مهمة حول علاقة الشكل الانزوتروبي الجزيئي والخواص الحرارية
للنيماتوجينات أعلاه.