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# Mesomorphic Behavior of Compounds of Low Thermal Phase Stability

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**Abstract**—A number of new Schiff's bases showing nematic mesomorphism of low thermal stability (to below 0°C) were found to also deviate somewhat from known compounds in the relation of transition temperatures to substituent chain variations in their homologous series. Besides a tendency towards rising nematic–isotropic transitions in ascending series, a regular alternation in the solid–nematic and smectic–nematic transitions from even to odd numbered members of the series was observed. This only recently reported alternation was in phase with the corresponding fluctuations in the nematic–isotropic transitions. It was also found that a replacement of methylene groups by oxygen in alkoxy-substituted Schiff's bases resulted in a thermal destabilization of all phases and a reduction in the incidence of mesomorphism.

The effect of structural changes in these simple mesomorphic compounds on thermal phase stabilities showed many analogies to *n*-alkanes and aliphatic ethers implying that the forces which determine the structure of these mesomorphic phases are not very different from those which govern simple crystalline lattices.

## 1. Introduction

Much recent synthesis research on nematic liquid crystalline compounds has been directed towards materials of low nematic thermal stability, as compared to work published prior to 1967. The interest in these low melting phases came about as a consequence of the discovery of dynamic scattering by R. Williams[1] and the increased application of nematic orienting media in studies involving chromatography, NMR, thermotopography, polymerizations, and others.[2–5] In most of these applications low temperature ranges are desirable not only for the sake of convenience but to extend the scale of experimentation and to prevent thermally unstable materials from degradation. Except for C. Weygands[6] 2,4-nona- and 2,4-undecadienoic acids (nematic 23–49° and 32–58°, respectively) and G. W. Gray's[7] sterically hindered 4-*p*-*n*-alkoxybenzylidene-*p*′-

aminobiphenyls the earlier literature shows no record of stable nematic phases below 40°. More recently eutectic mixtures have been reported[5] or offered commercially but apparently, the only additional pure nematic compounds of low thermal stability arose from a study by Keller and Scheurle during 1969[8a] of two homologous series based on N-(*p*-methoxy) and N-(*p*-ethoxybenzylidene)-*p'*-*n*-alkylanilines, three of which developed nematic phases from 20, 36 and 38° on. This was followed in 1970 by the analogous azo- and azoxy compounds with similar low melting points.[8b]

A similar series of azomethines including those based on *p*-*n*-alkyl, *p*-*n*-alkoxy-, and *p*-*n*-acyl-anilines had been started in this laboratory, aimed mostly at studying the effect of displacement of more than one methylene group by oxygen in the substituent of the benzaldehyde portion. However, the emphasis was shifted to *p*-*n*-butyl-aniline derivatives after their very low transition temperatures became known. Moreover, the relationship of transitions to structure in these series was found to differ somewhat from that in higher melting liquid crystalline compounds.

## 2. Experimental

Transition temperatures were determined on a Leitz Ortholux polarizing microscope using a Mettler FP-2 heating stage. Chemicals used were highest purity available. Synthesized intermediates were purified by recrystallization or distillation.

The starting *p*-alkoxybenzaldehydes were prepared from *p*-hydroxybenzaldehyde and potassium hydroxide in a dimethyl formamide-benzene (1 : 1) solvent mixture. This was refluxed (ca. 100 °C) to remove the water of reaction azeotropically. The appropriate alkyl halide was added to this solution and again heated to reflux for 4–6 hours. After the solvents were removed in vacuum, the products were separated from the inorganic residues by a water immiscible solvent followed by fractionation. This method is superior to that of Weygand and Gabler[9] since alkyl chlorides rather than iodides may be used and a much shorter reaction time suffices.

The alkoxyalcohols were chlorinated according to Gilman and Hewlett[10] and combined with *p*-hydroxybenzaldehyde in the same manner.

The carboxylates and carbonates of *p*-hydroxybenzaldehyde were prepared from the latter and the appropriate acid chloride or chloroformate using pyridine as the reaction solvent.

The yields of the substituted aldehydes ranged from 50–70%. There was no attempt to optimize yields in these preparations. The aldehydes are listed in Table 1.

TABLE 1 Alkoxybenzaldehydes: *p*-RO—$C_6H_4$—CHO†

| Formula | R | 6p °C/mm Hg | Reference |
|---|---|---|---|
| $C_9H_{10}O_3$ | $CH_3$—O—$CH_2$— | 139/11 | Beil *8* II 67 |
| $C_{10}H_{12}O_3$ | $CH_3$—O—$(CH_2)_2$— | 103/0.3 | 13 |
| $C_{11}H_{14}O_3$ | $CH_3$—O—$(CH_2)_3$— | 101–5/0.06 | 13 |
| $C_{11}H_{14}O_3$ | $C_2H_5$—O—$(CH_2)_2$— | 114–20/0.15 | 13 |
| $C_{13}H_{18}O_3$ | *n*-$C_4H_9$—O—$(CH_2)_2$— | 120/0.05 | 13 |
| $C_{13}H_{18}O_4$ | $C_2H_5$—O—$(CH_2)_2$—O—$(CH_2)_2$— | 146–8/0.43 | 13 |

† Aldehydes R=$C_nH_{2n+1}$ were purchased.

The *p*-substituted aromatic amines used in this work were purchased and used without further purification.

Schiff bases were prepared by refluxing equimolar quantities of the *p*-substituted benzaldehyde and aniline in anhydrous ethanol for 4–6 hours. The solvent and water was removed and the residue recrystallized several times from ethanol until transition temperatures remained constant. The crude yields ranged from 70 to 90%. The IR spectra showed a strong band at 1629 $cm^{-1}$ corresponding to the carbon nitrogen double bond in Schiff base compounds. Other absorptions were compatible with the expected structures. The elemental analyses are listed below.

Elemental Analyses

| No. | Formula | Calculated % C | H | N | Found % C | H | N |
|---|---|---|---|---|---|---|---|
| *1* | $C_{20}H_{25}NO$ | 81.31 | 8.53 | 4.74 | 81.13 | 8.55 | 4.67 |
| *2* | $C_{21}H_{27}NO$ | 81.51 | 8.79 | 4.53 | 81.26 | 8.67 | 4.50 |
| *3* | $C_{22}H_{29}NO$ | 81.69 | 9.04 | 4.33 | 81.42 | 9.05 | 4.32 |
| *4* | $C_{23}H_{31}NO$ | 81.85 | 9.26 | 4.15 | 81.97 | 9.41 | 4.25 |
| *5* | $C_{24}H_{33}NO$ | 82.00 | 9.46 | 3.99 | 81.84 | 9.47 | 4.04 |
| *6* | $C_{25}H_{35}NO$ | 82.14 | 9.65 | 3.83 | 81.84 | 9.67 | 3.77 |

Elemental Analyses (*Contd.*)

| No. | Formula | Calculated % C | H | N | Found % C | H | N |
|---|---|---|---|---|---|---|---|
| *7* | $C_{19}H_{23}NO_2$ | | | Not Analyzed | | | |
| *8* | $C_{20}H_{25}NO_2$ | 77.14 | 8.09 | 4.49 | 76.84 | 8.14 | 3.77 |
| *9* | $C_{21}H_{27}NO_2$ | 77.50 | 8.36 | 4.30 | 77.16 | 8.21 | 4.46 |
| *10* | $C_{21}H_{27}NO_2$ | | | Not Analyzed | | | |
| *11* | $C_{23}H_{31}NO_2$ | | | Not Analyzed | | | |
| *12* | $C_{23}H_{31}NO_3$ | | | Not Analyzed | | | |
| *13* | $C_{19}H_{21}NO_3$ | 73.29 | 6.79 | 4.49 | 73.40 | 6.62 | 4.90 |
| *14* | $C_{18}H_{19}NO_4$ | | | Not Analyzed | | | |
| *15* | $C_{20}H_{25}NO_3$ | | | Not Analyzed | | | |
| *16* | $C_{21}H_{27}NO_3$ | | | Not Analyzed | | | |
| *17* | $C_{23}H_{31}NO_3$ | | | Not Analyzed | | | |
| *18* | $C_{23}H_{31}NO_4$ | | | Not Analyzed | | | |

## 3. Results and Discussion

(A) X—⟨⟩—CH=N—⟨⟩—Y

I: X=*n*-$C_nH_{2n+1}O$
Y=*n*-$C_4H_9$

II[8]: X=$CH_3O$(*a*); $C_4H_9O$(*b*)
Y=*n*-$C_nH_{2n+1}$

III: X=$CH_3O(CH_2)_nO$
Y=*n*-$C_4H_9$

*Part 1*: Figure 1 shows the relationship of transition temperatures to alkyl chain length of N-(*p*-*n*-alkoxybenzylidene)-*p*′-*n*-butylanilines (I) (including data from Ref. 8 for $n = 1$ and 2). The shapes of the curves differ in two interesting aspects from most published ones.

Normally, mesomorphic–isotropic transition temperatures of homologous series decrease with increasing chain length, sometimes after having passed a maximum at around $n = 2$–4. Figure 1 shows the opposite trend for all transitions, nematic–isotropic (N–I), smectic–isotropic (S–I), crystalline–nematic (C–N) and crystalline–smectic (C–S). A similar unusual upwards trend in mesomorphic–isotropic transitions for ascending homologous series has been reported previously for only two classes of compounds. The first are molecules where lateral substituents prevent a close packing in their mesomorphic phases, such as N-(*p*-*i*-alkoxybenzylidene)-1′-aminonaphtalene-4′-azobenzenes with branches in the alkyl chains[11] and 2′-substituted N-(*p*-*n*-alkoxybenzylidene)-*p*′-aminobiphenyls.[7] The second is represented by the series of N-(*p*-*n*-alkoxybenzylidene)-

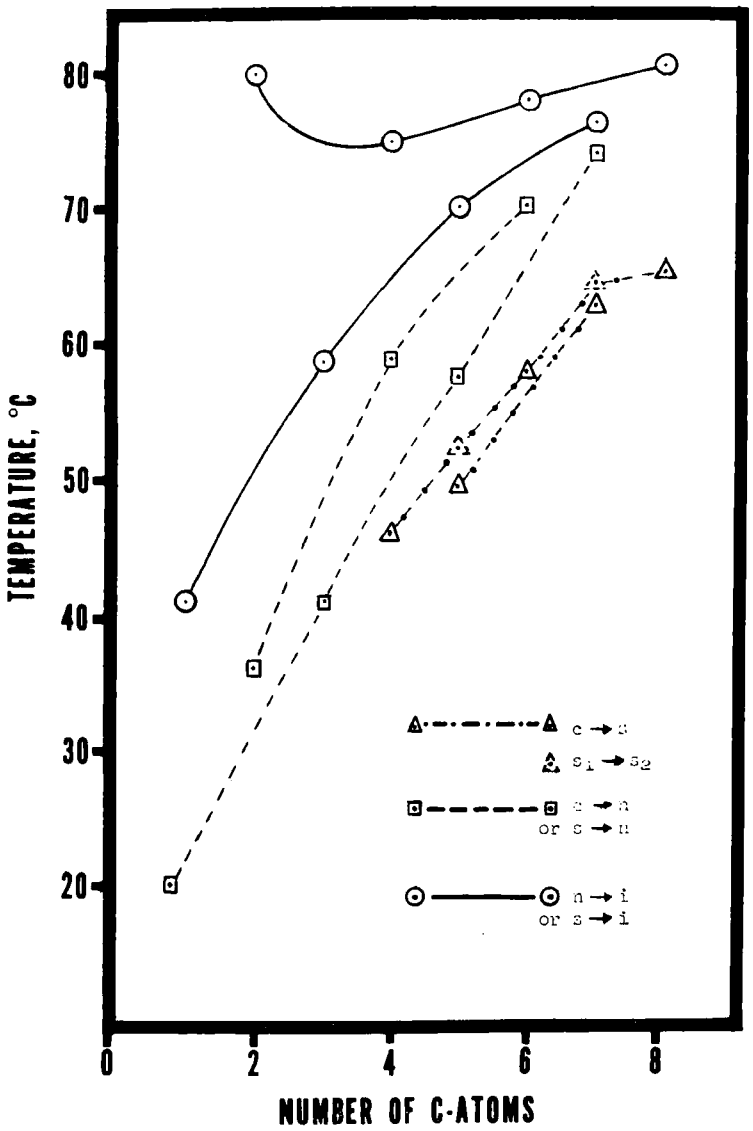



Figure 1. Transitions of N-(*p*-*n*-alkoxybenzylidene)-*p'*-*n*-butylanils (*I*) plotted against the number of C-atoms of the alkyl substituents.

*p'*-aminoacetophenones.[12,13] Gray[7] attributed the phenomenon in the first class to a decrease in the ratio of lateral to terminal interactions because of the broadening of the molecules due to steric hindrance. Thus, in an ascending series of homologues the N–I transitions would initially be governed by terminal forces and only later, the weak lateral attractions are reinforced by the lateral interactions of the growing alkyl chains resulting in a rising gradient of the N–I transition curve. The second class possesses a terminal carbonyl group conjugated with an aromatic system. Castellano *et al.*[12] suggested that the strong terminal attractions originating from the acetyl group would result in a similarly low ratio of lateral to terminal cohesions although at a higher level of total cohesive forces, i.e. higher on the temperature scale. It may be noted that other series with similar strong terminal permanent dipoles show a normal descending trend in their transition–chain length plots, e.g. the butoxy and acetoxy homologues (Table 5). Perhaps in the case of the acetyl group the dipole is forced into a more coaxial orientation with a larger terminal vectorial resultant due to its conjugation with the aromatic system, as compared to acetoxy or other strongly dipolar substituents.

Neither of the above explanations of an abnormally low ratio of lateral to terminal cohesive forces applies to the series of N-(*p*-*n*-alkoxybenzylidene)-*p'*-*n*-alkylanilines *I* and *II*, where in the latter a similar rising trend exists for the ethoxy series but not for the methoxy series.[8] In these homologues the molecules are sterically not restricted and the attractive forces of their " wing " groups seem not particularly imbalanced. However, the sum of their intermolecular cohesive forces must be lower than in other mesomorphic series. This is indicated by their low transition points and expected because of the absence of strong permanent dipoles and the shortness of the alkyl chains with negligible dispersion forces operating between them. Therefore, it can be concluded that ascending mesomorphic transition temperature functions are likely to occur in homologous series of overall low intermolecular cohesiveness. In these series even small changes (e.g. from methoxy to ethoxy in series *IIa*, *IIb*) in the delicate balance of inherently low lateral to terminal interactions will determine whether the transition functions are descending or ascending. In addition, the more subtle effects of chain conformations will

be enlarged. This is reflected in the unusually large amplitude of alternations of transition temperatures from odd to even numbered members of these and other series, discussed below.

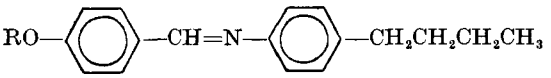
The second distinguishing feature noticeable in Fig. 1 is a regular alternation from even to odd values of $n$ not only in the mesomorphic–isotropic transitions but also for the C–N and S–N transitions, respectively. The smooth lines connecting the transition points of the even numbered lie above those connecting the ones of the odd numbered member of series *I* for both, the N–I and the C–N or S–N transitions. The same trend arises from plotting series *IIa* and *IIb*[8] but pertaining to C–N and N–I transitions only, and it is indicated in the incomplete series *III* where the C–N point for $n = 2$ lies around 37° above the C–N point of the member with $n = 3$. The alternation in mesomorphic–isotropic transition temperatures is quite common and has been explained by Gray[7] and others on grounds of conformational analyses. The terminal force vector of an alkoxy chain with an odd number of carbon atoms in a cog-wheel conformation would deviate from the long axis of the molecule, thus contributing more to lateral cohesions and destabilizing the nematic phase. For the same reason one could predict for the S–N transitions an opposite mode of alternation. The odd numbered members should show the higher temperature range in their transition lines because of the lower stability of the nematic relative to the smectic phases. This is not the case in series *I*. In making this prediction at a time when no such alternations in S–N transitions had been reported, Gray[7] cautioned that " so many arguments may be brought into play that any ideas concerning the absence of alternation of S–N transition temperatures remain purely speculative." Recently, however, Gray and Harrison[14] discovered several series showing in phase as well as out-of-phase alternations in their C–S and S–N temperatures relative to their mesomorphic–isotropic transitions. Since in addition, the shapes of the curves also differed from known types it was stated that " an understanding of the S–N transition may be less easy to achieve than might have been anticipated."

Assuming that the alternations in the C–N and S–N curves of the series *I*, *II* and *III* are not accidental one can conclude that the determining factor for the course of transitions into the nematic phase and from the nematic into the isotropic phase is the same. In

view of the identical frequency of fluctuations in these transitions it is thought probable that in the case of these two structurally simple series alternation is brought about by changes in packing density, similarly as those responsible for the fluctuations of the melting (C–I) points of homologous *n*-paraffins and their analogues. By comparison with the odd numbered *n*-paraffins it is postulated that the odd numbered alkoxy (counting oxygen as a methylene) group in *I* and *III* and the alkyl Schiff bases in *II* occupy more length for a given mass than the even numbered ones in the crystalline (series *I* and *III*), the smectic (series *II*), and the nematic phases. In the more tightly packed even numbered ones the long axis of the molecules would assume an angular position relative to the crystallographic *c*-axis, as is known for paraffins and their mono- and dicarboxylic acids.[15] Larsson[16] has related the alternation of other non mesomorphic homologous series of long-chain compounds to their packing differences but according to the details of his theory, the transition points of mesomorphic series should not alternate. An interesting discussion of the " odd–even effect " in cholesteric systems has been presented by Ennulat and Brown[17] who, however, considered their information not sufficient for a conclusive explanation of the phenomenon. The assumption that this packing principle applies to mesomorphic phases is based on the parallel rather than reverse mode of alternation of all transition curves in series *I* and *II*. It is hoped that direct evidence will be derived from physical investigations. The assumption appears compatible with the alternation in other properties of homologous series, such as in the dielectric anisotropy of nematic, magnetically oriented melts (Ref. 7, p. 112) or in the entropy differences between the mesomorphic and isotropic states,[18] all of which are related to the tightness of packing of the molecules. As a consequence of the above considerations it appears that the forces determining the structures within different phases are similar and that the division between lateral and terminal interactions as pertaining to phase stability is less sharp than thought previously. If the analogy to *n*-paraffins is correct, it is probable that the substituent chains in series *I–III* exist in a quite rigid zig-zag rather than in a cogwheel conformation in all phases showing alternating transitions, since this has been found to be a requirement for the fluctuation in the melting points of the paraffins.

If true, this also suggests that the driving force in a thermal transition is governed more by the order within the less thermally stable phase and less by the higher entropy of the more stable state. This is supported by the generally accepted fact that the energy absorbed in the S–N transition is expanded in increased translational mobility only. If indeed this transition alternates in an ascending homologous series in phase with its N–I transitions then this alternation should not be caused only by differences in degrees of freedom of motion in the nematic (or respectively, the isotropic) phase. The more contributing cause appears to be the differences in densities of packing, i.e., in cohesiveness of the less stable phase when going from odd to even numbered members of the series, as seems to be the accepted cause for alternation in the melting points of *n*-paraffins.

TABLE 2 N-(*p*-*n*-alkoxy-benzylidene)-*p*-*n*-butylanilines (*I*)




| | R | C–$S_1$ | $S_1$–$S_2$ | S–N | N–I (S–I) |
|---|---|---|---|---|---|
| Ref. 8 | $CH_3$ | | | 20 | 41 |
| Ref. 8 | $C_2H_5$ | | | 36 | 80 |
| *1* | *n*-$C_3H_7$ | | | 41 | 58.9 |
| *2* | *n*-$C_4H_9$ | 46 | | 59 | 75 |
| *3* | *n*-$C_5H_{11}$ | 49.6 | 52.5 | 57.8 | 70.2 |
| *4* | *n*-$C_6H_{13}$ | 58 | | 70.4 | 78 |
| *5* | *n*-$C_7H_{15}$ | 63 | 64.6 | 74.1 | 76.4 |
| *6* | *n*-$C_8H_{17}$ | 65.4 | | | 80.5 |

The reason why most series show regular alternation only in their N–I but not in their S–N or C–N transition curves would then be related to the higher cohesiveness of their molecules due to closer packing for steric and reasons of polarity, when compared to series *I*, *II*, and *III*. In these three series the sum of attractive forces even in the solid and the smectic state would be small enough to permit the configurational factors of the alkyl-chains to become the determining influence on transitional behaviour. This same factor becomes important in other series only after these higher attractive forces have been overruled by thermal vibrations close to their isomorphic transition points.

*Part 2*: The effect on thermal transitions of replacement of methylene groups by an ether oxygen in isomorphic and mesomorphic compounds is complicated by counteracting forces. On one hand, thermal vibrations are facilitated and the polarizability of the molecule is uniformly reduced by around $1.2 \times 10^{-24}$ cm$^3$ (quoted in Ref. 13) resulting in decreased dispersion forces. On the other hand, the group contribution $E$ (298) coh. of an ether oxygen to the cohesive energy of a compound is 1.5 times that of a methylene unit according to recent estimates.[19] These trends are reflected in Fig. 2 where the first order transition temperatures of linear polyethers are plotted against the ratio of methylene groups to oxygen.[17] The cohesive energy densities are increased in polyformaldehyde relative to polyethylene presumably due to permanent and induced dipole interactions thus enforcing a more tightly packed lattice structure. With greater separation of the oxygen atoms, a drastic decrease in melting points is observed, probably because of both decreased dispersion forces within the solid as well as a higher entropy content of the liquid phase, associated with the more flexible ether linkages.

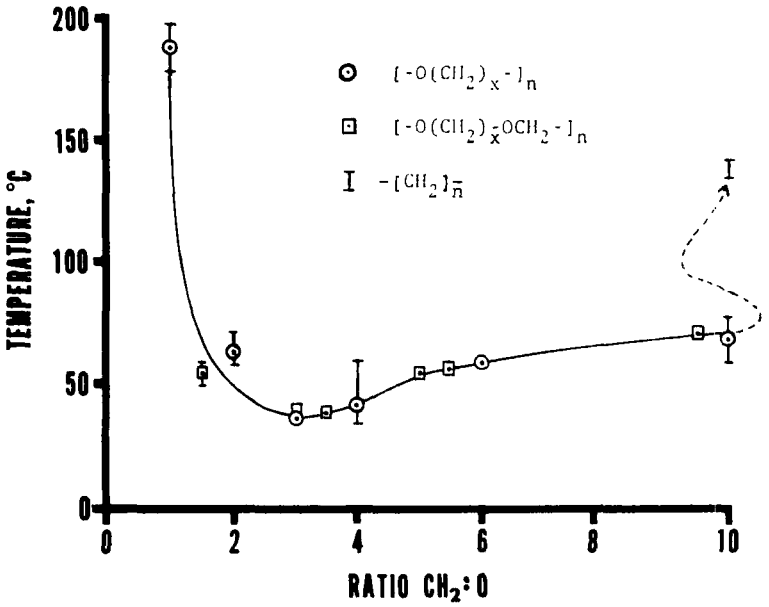



Figure 2. Melting points of polymers of oligo-methylene oxides[17] and of cyclic formals[17] plotted against the ratio of carbon to oxygen atoms.

The magnitude of the latters contribution is indicated by the difference in the barriers to internal rotations of methyl groups around C–C versus C–O bonds. According to calculations from microwave spectra, this energy barrier is 3.55 kcal in propane[24] and only 2.72 kcal in dimethyl ether.[25]

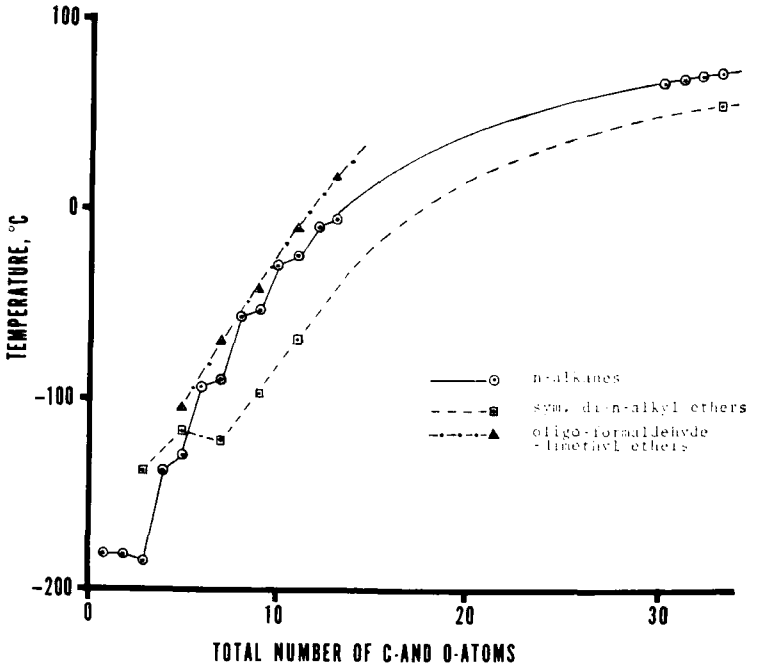



Figure 3. Melting points of *n*-alkanes,[18] ethers,[18] and oligo-formaldehyde ethers[17] plotted against the total number of atoms in chain.

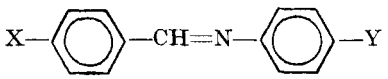
After passing through a minimum the melting points of paraffins and ethers converge towards that of polyethylene. It may be noted that the transitions for polyethers and polyformals are almost identical for a given ratio of $CH_2/O$ regardless of the spacing of the oxygen atoms, demonstrating that the packing density and entropy gain is independent of possible differences in conformations of these linear chain polymers. Similarly, the melting points of homologous oligo-(formaldehyde)-dimethylethers[20] are higher and those of homologous *n*-dialkylethers[21] are lower than those of *n*-paraffins (Fig. 3). Exceptions are the mono- and diethers with a high ratio

of oxygen to methylene groups, reflecting the same trend as found in the polymers, Fig. 2.

An application of these relations between C–I transitions to sterically uncomplicated mesomorphic compounds of low overall cohesiveness rests on the assumption that the same forces will determine their behaviour. This assumption is supported by the following two examples:

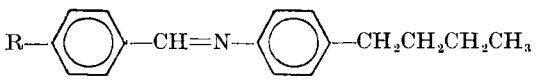
Firstly, the substitution of one methylene group adjacent to a phenyl ring results in a thermal stabilization of all phases. This is apparent from a considerable number of examples, some of which are listed in Table 3. It is suggested that the dipole–dipole interaction

TABLE 3 Transitions of Alkylaryl Ethers and Hydrocarbon Analogues

| Ether | | $T_{tr}$ | Hydrocarbon | | $T_{tr}$ |
|---|---|---|---|---|---|
| $C_2H_5OC_6H_5$[20] | | —30(C–I) | $n$-$C_3H_7$—$C_6H_5$[20] | | —99.5(C–I) |
| $n$-$C_4H_9OC_6H_5$[20] | | —19(C–I) | $n$-$C_5H_{11}$—$C_6H_5$[20] | | —78 (C–I) |
|  | | | | | |
| *X* | *Y* | | *X* | *Y* | |
| $CH_3O$ | $CH_3O$[23] | 142(C–I) | $CH_3O$ | $C_2H_5$[8] | 28 (C–N) |
| | | | | | 57 (N—I) |
| $CH_3O$ | $n$-$C_4H_9O$[12] | 108.5(C–N) | $CH_3O$ | $n$-$C_5H_{11}$[8] | 20 (C–N) |
| | | 115(N–I) | | | 41 (N–I) |
| $n$-$C_3H_7O$ | $n$-$C_3H_7O$[22] | 107(C–N) | $n$-$C_3H_7O$ | $n$-$C_4H_9$(*l*) | 41 (C–N) |
| | | 133(N–I) | | | 59 (N–I) |

of the ether oxygen with the neighbouring benzene ring affects the transitions similarly as a high ratio of oxygen to methylene groups does in aliphatic ethers (see Figs. 2 and 3). Secondly, the substitution of a second or third methylene group belonging to an alkoxy chain causes a thermal destabilization of all phases in addition to a decrease in the incidence of mesomorphism, especially of the smectic type. These findings are based on data from two previous studies,[13,22] in addition to the present one (Tables 4 and 5). The decrease in transition points and in the incidence of mesomorphism of these compounds has been attributed to conformational factors.[7,22] In later work[13] a reduction in the dispersion forces between the alkoxy–alkoxy

TABLE 4 N-(*p*-*n*-polyalkoxy-benzylidene)-*p*-*n*-butyl-anilines

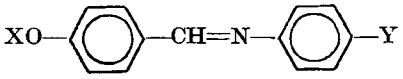


| | R | C–N | N–I (C–I) |
|---|---|---|---|
| *7* | $CH_3OCH_2O$— | | 12.5 |
| *8* | $CH_3OCH_2CH_2O$— | 34.5 | 56.6 |
| *9* | $CH_3OCH_2CH_2CH_2O$— | —2.5 | 4.4 |
| *10* | $C_2H_5OCH_2CH_2O$— | | 36.2 |
| *11* | *n*-$C_4H_9OCH_2CH_2O$— | | 38.8 |
| *12* | $C_2H_5O(CH_2CH_2O)_2$— | | 20.3 |

chains was considered a more probable cause since the chain conformation should depend strongly on the position of the oxygen, which was not the case. This left the higher thermal phase stability of alkoxyl-versus alkyl-substituted Schiff bases unexplained. It is apparent from Tables 4 and 5 that the methoxy–methoxy compounds *7* and in Ref. 13 already show a decrease in their transition points compared to the propoxy-analogues. This is unexpected in view of the behavior of the aliphatic ethers, Fig. 3 where the oligo-formaldehydes show the highest transition points. However, the analogy to the aliphatic poly-ethers persists as the two oxygen atoms become separated by additional methylene groups. Thus, with a decreasing ratio of oxygen to methylene groups the transition temperatures decrease further while their difference $\Delta$ to the alkoxy analogue increases (Table 5).

These trends appear less pronounced for compounds with strong permanent dipoles at the opposite end of the molecule. Thus, the differences $\Delta$ in the transitions of alkoxy-versus alkoxy–alkoxy benzylidene analogues differ less for anilines having acetoxy, alkoxy or acetyl para-substituents (Table 5). This may indicate that the lateral attractions between the aromatic groups are relatively less important than the interactions between the " wing " groups in determining the stabilities of *all* phases. Thus, the transition points appear to be governed by the sum of steric repulsions and cohesive attractions between the linear, rigid " wing " groups, similarly as in purely aliphatic compounds. The ratio of lateral to terminal forces within these groups would then be responsible for the incidence

TABLE 5 Alkoxy and Polyalkoxy-benzylidene-anils with Different Substituents



| | X | Y | C–$S_1$ | $S_1$–$S_2$ | S–N<br>C–N | N–I<br>S–I<br>C–I | Δ |
|---|---|---|---|---|---|---|---|
| *13* | $n$-$C_4H_9$— | —$OCOCH_3$ | 73.6 | 84.9 | | 114.2 | |
| *14* | $CH_3OCH_2CH_2$— | —$OCOCH_3$ | | | | 105 | 9.2(SI–CI) |
| Ref. 18 | $n$-$C_4H_9$— | —O-$n$-$C_4H_9$ | | | 122 | 125 | |
| *15* | $CH_3OCH_2CH_2$— | —O-$n$-$C_4H_9$ | | | | 113 | 8(NI–CI) |
| Ref. 18 | $n$-$C_5H_{11}$— | —O-$n$-$C_4H_9$ | | | 115 | 116.5 | |
| *16* | $C_2H_5OCH_2CH_2$— | —O-$n$-$C_4H_9$ | | | | 103.4 | 13.1(NI–CI) |
| Ref. 18 | $n$-$C_7H_{15}$— | —O-$n$-$C_4H_9$ | | | 100.5 | 115.5 | |
| *17* | $n$-$C_4H_9OCH_2CH_2$— | —O-$n$-$C_4H_9$ | | | | 83.9 | 31.6(NI–CI) |
| Ref. 23 | $n$-$C_8H_{17}$— | —O-$n$-$C_4H_9$ | 98.5 | | 105 | 115 | |
| *18* | $C_2H_5(OCH_2CH_2)_2$— | —O-$n$-$C_4H_9$ | | | | 77.9 | 45.1(NI–CI) |
| Ref. 13 | $n$-$C_3H_7$— | —$COCH_3$ | | 67.2 | 90.9 | 101.7 | |
| Ref. 13 | $CH_3OCH_2$— | —$COCH_3$ | 82.4 | | | 94 | 7.7(NI–SI) |
| Ref. 13 | $n$-$C_4H_9$— | —$COCH_3$ | | | 96.4 | 108.8 | |
| Ref. 13 | $CH_3OCH_2CH_2$— | —$COCH_3$ | | 70.7 | 83.1 | 90.2 | 19(NI–NI) |
| Ref. 13 | $n$-$C_5H_9$— | —$COCH_3$ | 80.2 | | 104.4 | 106.3 | |
| Ref. 13 | $C_2H_5OCH_2CH_2$— | —$COCH_3$ | 73.1 | | | 76.6 | 29.7(NI–SI) |
| Ref. 13 | $CH_3OCH_2CH_2CH_2$— | —$COCH_3$ | 71.6 | | | 73.5 | 32.8(NI–SI) |
| *1* | $n$-$C_3H_7$— | $n$-$C_4H_9$ | | | 41 | 58.9 | |
| *7* | $CH_3OCH_2$— | $n$-$C_4H_9$ | | | | 12.5 | 46.4(NI–CI) |
| *2* | $n$-$C_4H_9$— | $n$-$C_4H_9$ | 46 | | 59 | 75 | |
| *8* | $CH_3OCH_2CH_2$— | $n$-$C_4H_9$ | | | 34.5 | 56.6 | 18.4(NI–NI) |
| *3* | $n$-$C_5H_{11}$— | $n$-$C_4H_9$ | 49.6 | 52.5 | 57.8 | 70.2 | |
| *10* | $C_2H_5OCH_2CH_2$— | $n$-$C_4H_9$ | | | | 36.2 | 34(NI–CI) |
| *9* | $CH_3OCH_2CH_2CH_2$— | $n$-$C_4H_9$ | | | −2.5 | 4.4 | 65.8(NI–NI) |

and nature of mesomorphism. This is compatible with the observation that methylene substitution by an atom which possesses a permanent dipole while causing a reduction in dispersion forces results in a destabilization of all phases (unless adjacent to phenylene), but less so for nematic phases.

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