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Mesomorphism in the 4,4′-Dialkoxy-*trans*-Stilbenes†

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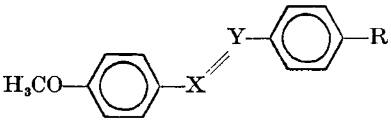
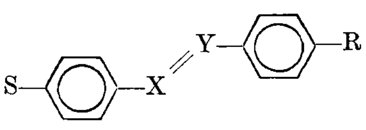
Abstract—In order to ascertain the effect of linkage groups (X=Y) in mesomorphic substances of the general formula



a homologous series of stilbenes has been prepared, where $R = C_nH_{2n+1}O$—, and X = Y = CH. The lower members of the series ($1 \leqslant n \leqslant 10$) are monotropic nematic, while the higher members ($12 \leqslant n \leqslant 16$) are monotropic smectic substances. The mesophase–isotropic transition temperatures are higher than those reported for the related nitrones (X = CH, Y = N → O) and Schiff Bases (X = CH, Y = N). Also the entropies of the nematic–isotropic transitions, as measured by differential scanning calorimetry, are nearly the same in the stilbenes and the nitrones. These results suggest that the permanent dipole associated with the linkage group plays a relatively unimportant role in enhancing the intermolecular attractions which are responsible for mesomorphic alignment.

1. Introduction

Mesomorphic substances possessing the general formula *1*, where two *para*-substituted benzene derivatives are joined by a linkage group *X*=*Y*,



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1a X = Y = CH
1b X = CH, Y = N
1c X = CH, Y = N → O
1d X = Y = N
1e X = N, Y = N → O

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have been the subjects of many chemical investigations.(1) While considerable interest has been displayed regarding the consequence of the terminal substituents R and S upon mesomorphic properties in a given class of materials (e.g. Schiff bases), relatively few reported studies have concerned the role of the linkage group in a series of materials for which R and S are a constant set.(2,3)

A search of the literature reveals that homologous series of Schiff bases (*1b*),(2,4,5) nitrones (*1c*),(3) azobenzenes (*1d*),(2,6,7) and azoxybenzenes (1*e*)(2,6,7) have been reported, in which R and S are confined to *normal* alkoxy groups. It is the purpose of this investigation to prepare an analogous series of dialkoxy-*trans*-stilbenes (*1a*) in order to ascertain their liquid crystalline properties and probe the effect of the linkage groups upon mesomorphic character.

2. Synthesis

The dialkoxy-*trans*-stilbenes prepared for this investigation are listed in Table 1 with their physical properties. Several of the stilbenes were prepared by the Wittig reaction according to the sequence depicted in Fig. 1.(8,9) The remaining stilbenes were synthesized from 4-hydroxy-4′-methoxy-*trans*-stilbene, which, in turn, was made by the classical route outlined in Fig. 2. In all cases, the *trans* isomer was separated from side products, which possibly included some *cis* isomer, by fractional crystallization.

The dimethoxy derivative *2* was identified by comparison of the observed melting point with that reported in the literature (215°).(10) In addition, the infrared and ultraviolet spectra of this substance in solution were consistent with the assigned structure. Also in accord

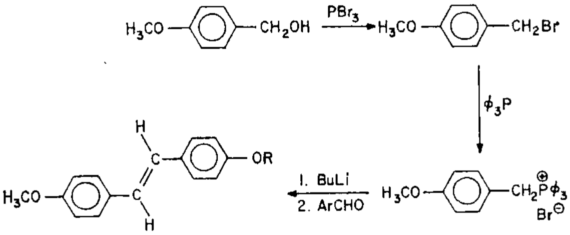
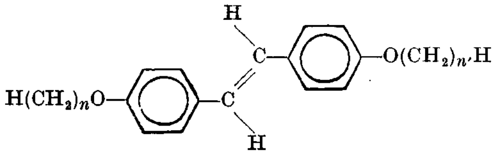


Figure 1. The preparation of some dialkoxy-*trans*-stilbenes employing the Wittig reaction.

TABLE 1 Measured Temperatures and Enthalpies and Derived Entropies of Transitions of the 4,4′-dialkoxy-*trans*-stilbenes[b]



Compound	n,n'	Type of transition	Transition temp. (°C)	ΔH (kcal/mole)	ΔS (cal/°K-mole)	Method of prep.[a]
2	1,1	C→I	216			Wit, FCA
		N→I	176			
3	1,2	C→I	197			Wit
		N→I	179			
4	1,3	C→I	177			FCA
		N→I	161			
5	1,4	C→I	169	9.48	21.5	Wit
		N→I	162	0.181	0.42	
6	1,5	C→I	162	9.84	22.6	FCA
		N→I	154	0.187	0.44	
7	1,6	C→I	157	9.89	23.0	Wit
		N→I	153	0.189	0.44	
8	1,7	C→I	150	10.22	24.2	FCA
		N→I	148	0.159	0.38	
9	1,8	C→I	151	10.02	23.7	Wit
		N→I	146	0.232	0.55	
10	1,9	C→I	149			FCA
		N→I	142.6			
		S→N	142.5			
11	1,10	C→I	146			FCA
		N→I	141			
12	1,12	C→I	142	14.02	33.8	FCA
		S→I	136	5.23	12.8	
13	1,14	C→I	139			FCA
		S→I	134			
14	1,15	C→I	139			FCA
		S→I	132			
15	1,16	C→I	137			FCA
		S→I	131			
16	1,18	C→I	135			Wit, FCA
17	2,2	C→I	209			[c]
		N→I	189			

(a) Wit denotes the scheme shown in Figure 1, while FCA denotes the scheme depicted in Figure 2.

(b) Where no calorimetric data are given, crystallization of the monotropic mesophase was too rapid to allow the measurement to be made.

(c) See Ref. 19.

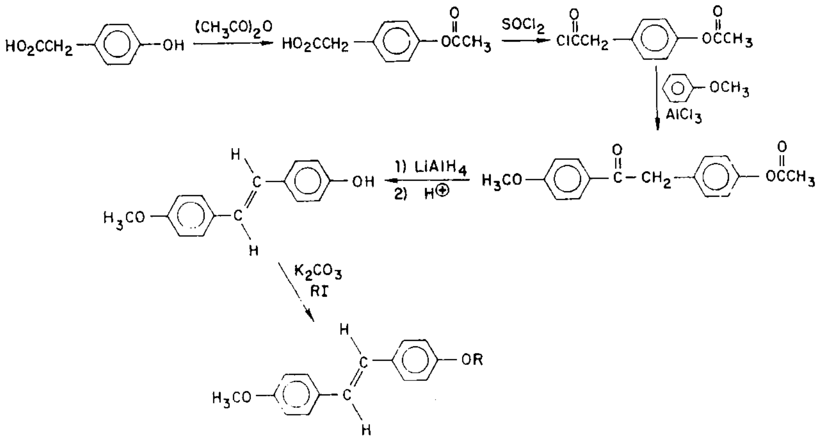


Figure 2. The synthetic route to some dialkoxy-*trans*-stilbenes employing a Friedel–Crafts acylation procedure.

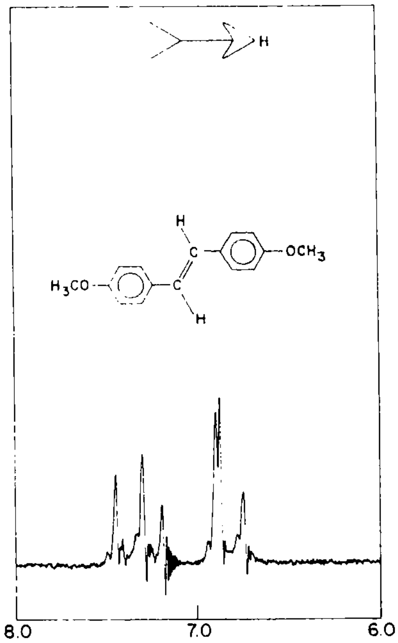


Figure 3. The aromatic/vinylic hydrogen region of the NMR spectrum of stilbene *2* dissolved in $CDCl_3$. The abscissa units are: PPM downfield from TMS.

was the NMR spectrum (Fig. 3) which exhibited a 2-proton singlet resonance (vinylic hydrogens) superimposed upon the 8-proton A_2B_2 resonance of the aromatic hydrogens.

Except for stilbene *17*(11) the remaining substances were identified on the basis of synthetic method, elemental analysis, and spectral characterization. The *trans* configurations were assigned for the following reasons: The NMR spectra in the aromatic vinyl region were all superimposeable upon that of the *trans* compound *2*. It would be extremely unlikely that such a circumstance would exist for the *cis* derivative.(12) In addition, it has been well established that a molecule must be rod-shaped in order to exhibit a mesophase.(1,13) The existence of a mesomorphic state for virtually all of the compounds in Table 1 therefore precludes the possibility of *cis* isomers.

3. Experimental

All of the new compounds had satisfactory spectral properties and elemental analyses. Infrared spectra were recorded on a Perkin–Elmer 137B Infracord spectrometer. NMR spectra were obtained on either a Varian HA-60-IL or Jeolco Minimar 60 Spectrometer. Ultraviolet spectra were taken on a Cary 14 spectrophotometer.

p-Methoxybenzyl Bromide

p-Methoxybenzyl bromide was prepared in 85% yield from *p*-methoxybenzyl alcohol and phosphorous tribromide employing the procedure of Beard and coworkers,(8) who prepared the *meta* derivative. The product was purified by distillation, bp 80° (0.1 mm), lit.[14] bp 104° (1.0–1.5 mm).

p-Methoxybenzyltriphenylphosphonium Bromide

Triphenylphosphine (26 g, 0.1 mole) was dissolved in 25 ml of benzene, and 20 g (0.1 mole) of freshly prepared *p*-methoxybenzyl bromide was added. The solution was shaken to induce separation of a crystalline material. The mixture was allowed to stand overnight and was subsequently filtered. The white product, prepared quantitatively, was employed as a reagent in subsequent reactions without additional purification.

p-Alkoxybenzaldehydes

These materials were either obtained commercially or prepared from alkyl iodides and *p*-hydroxybenzaldehyde according to Haller and Cox.(15)

4-Methoxy-4′-Octyloxy-*trans*-Stilbene (*9*)

Fifteen grams of *p*-methoxybenzyltriphenylphosphonium bromide (0.03 mole) was suspended in 450 ml of dimethoxyethane which had been previously dried over calcium hydride. The ylid of the phosphonium salt was generated by the addition of an equivalent amount of *n*-butyl-lithium in hexane (nitrogen atmosphere) followed by a reflux period of 4 hr. *p*-Octyloxybenzaldehyde (7.5 g, 0.03 mole) was added dropwise to the red solution, and the resulting mixture was allowed to stir and reflux for twenty hours. The solvent was removed from the cooled reaction mixture, and water and ether were added to the residue. The insoluble organic material was filtered and subsequently combined with the minority of product which was recovered from the ether layer following layer separation, drying, and removal of solvent. The white solid was further refined by several washings with boiling ethanol and repeated crystallizations from benzene. The final yield of the product, recovered as white plates, was 2.5 g (24%), mp 151°.

Stilbenes *2*, *3*, *5*, *7*, and *16* were prepared by an identical procedure. The physical properties of these substances are enumerated in Table 1.

p-Acetoxyphenylacetic Acid

p-Acetoxyphenylacetic acid was synthesized from *p*-hydroxyphenylacetic acid and freshly distilled acetic anhydride according to Heilbron and Cook.(16)

p-Acetoxyphenylacetyl Chloride

The acid chloride of *p*-acetoxyphenylacetic acid was prepared from the acid by treatment with thionyl chloride in benzene according to a general procedure described elsewhere.(11) The product was purified by distillation, bp 115° (0.2 mm).

p-Acetoxybenzyl *p*-Anisyl Ketone

This ketone was synthesized by Friedel–Crafts acylation of anisole by *p*-acetoxyphenylacetyl chloride in carbon disulfide with aluminum chloride catalyst as reported for related compounds by Young, Aviram, and Cox.(11) The crude white product was recrystallized from methylcyclohexane and from methanol, and was isolated in 42% yield, mp 118 °C.

4-Hydroxy-4′-Methoxy-*trans*-Stilbene

Lithium aluminum hydride (25 g, 0.7 mole) was covered with 50 ml of dry ether in a 3-liter flask equipped with mechanical stirrer, 1-liter addition funnel, and nitrogen purge. Over 4 hr was added dropwise a solution of 25 g (0.09 mole) of *p*-acetoxybenzyl *p*-anisyl ketone in 300 ml of tetrahydrofuran. The mixture was allowed to stir and reflux for three hours, and then cooled. The excess reducing agent was neutralized with 300 ml of ethyl acetate followed by 30 ml of methanol and 120 ml of water. The residual salts were dissolved in 600 ml of 20% sulfuric acid, and 500 ml of ethyl acetate was added. The organic layer was separated, washed with water and saturated sodium chloride solution, and dried over sodium sulfate. After evaporation of the solvent, the crude benzyl alcohol derivative was dehydrated in 200 ml of boiling toluene containing a trace of *p*-toluenesulfonic acid, the water expelled being collected in a Dean Stark trap. The crude stilbene was recovered by evaporation of the toluene and was recrystallized from a large volume of methanol to afford 9.0 g (46%) of the desired white product, mp 202–203°.

4-Dodecyloxy-4′-Methoxy-*trans*-Stilbene (*12*)

A procedure adapted from a report by Zaheer and coworkers(17) was employed in the alkylation of 4-hydroxy-4′-methoxy-*trans*-stilbene. A solution of 0.5 g (0.002 mole) of the hydroxystilbene, 0.6 g (0.004 mole) of potassium carbonate, and 5 ml of 1-iodododecane in 50 ml of acetone was allowed to reflux with stirring for 20 hours. The solvent was evaporated, and the residue was distributed between methylene chloride and water. The organic layer was separated, dried over sodium sulfate, and evaporated to dryness. The white mixture was chromatographed on basic alumina, eluted with chloroform, and crystallized repeatedly from benzene to afford 0.2 g (23%) of the dialkoxystilbene (*12*), mp 142°.

Stilbenes *2*, *4*, *6*, *8*, *10*, *11*, and *13–16* were prepared in a similar manner. Their physical properties are listed in Table 1.

Microscopy

The mesophases were identified and the transition temperatures were determined by standard techniques(1b) using a Leitz Ortholux POL Polarizing microscope equipped with a Mettler FP2-Rev Hot Stage/Controller. The temperatures were calibrated at the melting points of high purity standards, and the thermometric accuracy is estimated to be ± 0.5 °C.

In several cases, isotropic stilbene derivatives could not be supercooled appreciably in a thin film in order to allow the appearance of a monotropic mesophase. To obviate this problem, a fine powder of the crystalline stilbene was thinly distributed across the slide, which was then placed in the hot stage. After melting, the small isotropic droplets could be supercooled to a much larger extent than the thin film, since nucleation occurring in one droplet could no longer induce crystallization throughout the entire sample.

Calorimetry

The heats and entropies of fusion and phase transition were determined by differential scanning calorimetry as described previously.(3)

4. Phase Identification and Transition Temperatures

All of the dialkoxy stilbenes in this investigation, with the exception of the 1,18 derivative *16*, exhibit a monotropic nematic or a monotropic smectic mesophase. The pertinent phase transition temperatures, enumerated in Table 1, are plotted in Fig. 4.

Melting Points

Although it is well known that mesophase–isotropic transition temperatures often decrease monotonically as one ascends a homologous series,(1b) such an occurrence in the case of melting points is rare indeed. Except for a very minor deviation (~ 1°) at the melting point of the 1,7 derivative, the methoxy-alkoxy stilbenes exhibit lower melting points as the molecular weight increases. No evidence of even/odd alternation can be detected.

Nematic Phases and Clearing Points

Nematic phases were observed in the decyloxy and lower homologs.

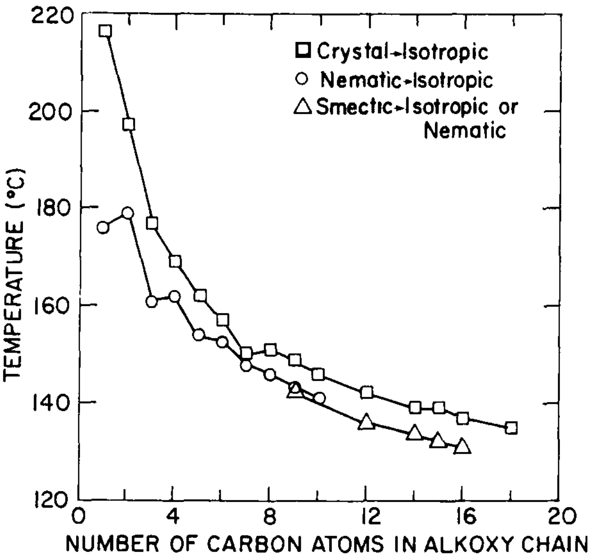


Figure 4. Phase transition temperatures for 4-methoxy-4′-*n*-alkoxy-*trans*-stilbenes.

Their morphology showed a great diversity; under identical conditions of observation, the mesophases of various homologs appeared in threaded, centered, or homogeneous textures.

Among the stilbenes which exhibit nematic mesophases, only two materials (*2* and *17*) have been reported in the literature.(18,19) Of these two substances, a mesophase (nematic) has been attributed only to the dimethoxy compound *2*,(18,20) although the original reference and the nematic–isotropic transition temperature have eluded our detection. We have found, however, that the isotropic liquid from *2* must be supercooled 40°, by the powder technique described above, before a nematic phase becomes apparent at 176°. Within seconds after the appearance of this mesophase, the material reverts to the stable crystalline form. It is not surprising, therefore, that other chemists(21) have not reported a nematic phase for this compound, since considerable supercooling is required and the phase is fleeting. In the same light, it is very surprising that Williams has reported a device which employs compound *2* in its nematic phase.(20)

Several features of the plot of N—I transition temperatures *vs* chain length (Fig. 4) are characteristic of other homologous series which have been previously studied. Among these features are (a) the appearance of a nematic mesophase only for the lower members of the series, the higher members tending to exhibit the smectic phase;(1,3) (b) even/odd alternation in transition temperatures, whereby the compounds bearing alkoxy groups with an odd number of carbon atoms delineate the lower branch of the plot;(1,3) (c) a general decline in the transition temperatures as the homologous series is ascended.(1)

Although features (a) and (b), as described in the preceding paragraph, are quite regular occurrences, the appearance of feature (c) is quite variable in studies of homologous series.(3) This variability has been discussed elsewhere,(1,3) but it is noteworthy that the N-(*p*-alkoxyphenyl)-α-anisylnitrones, which are structurally similar to the stilbenes *2* to *17* except for an *N* → O moiety replacing a C—H moiety in the linkage group, exhibit nematic clearing points which rise and subsequently fall as the chain length is increased. This large behavior discrepancy may be ascribable to the variation in (1) dipolar character, (2) steric requirements of the N → O *vs* the C—H groups, or (3) overall molecular geometry between the diverse classes of compounds. However, a simple explanation based on these factors is not easily conceived.

Smectic Phases and Clearing Points

Microscopic observation of the smectic phases of compounds *10*, *12*, *13*, *14*, and *15* proved possible in small droplet form only. The appearance of the droplets allowed a clear-cut distinction from nematic textures, but we had to rely on additional evidence to establish that the observed phases were not metastable solids. We identified these phases as smectic on the basis of the absence of supercooling when formed from the isotropic phase; isotropic to crystalline transitions generally supercool, while isotropic to smectic ones generally do not. In addition, flow-motion could be observed in some droplets during their conversion to crystalline solids.

5. Heats and Entropies of Transitions

Six of the monotropic mesophases crystallized slowly enough to permit the determination of the heat of the mesomorphic–isotropic transition. These heats and the corresponding entropies of transition are listed in Table 1.

The entropies of the nematic–isotropic transitions of compounds *5* through *8* lie in the neighborhood of 0.4 e.u., which is close to the average for nematic compounds with two *p*-phenylene rings and short alkoxy wing groups.(3) While the ΔS_{NI} of the 1,8 stilbene is substantially above those of the shorter chain length homologs, the trend toward higher entropies of transitions with increasing chain length is less pronounced in this series than in the series of homologous nitrones.(3)

Rapid crystallization prevented the measurement of the smectic–isotropic heats of transition in all compounds except one. In that instance, compound *12*, the observed heat of the smectic–isotropic transition is remarkably high for a substance with a dodecyloxy wing group. Also, ΔS_{SI} accounts for 38% of the total entropy change between the solid and isotropic phases for this material. As a comparison, the sum of the transition entropies between the smectic B and isotropic phases amount to 32% of the sum between the solid and isotropic phases in *n*-amyl dodecyloxybenzylideneaminocinnamate.(22) This implies that the order in the smectic phase of compound *12* is in the vicinity of that in the smectic B phase.

6. Linkage Group Effects

The mesomorphic transition temperatures for the several classes of compounds *1a–1e* are depicted graphically in Fig. 5. With the exception of the stilbene clearing points, all of these data have been previously reported.(1a,3,5) To facilitate comparison of the different types of compounds, the choice of wing groups was limited to *n*-alkoxy homologs.

It can be seen in Fig. 5 that irrespective of the linkage group, the 2,2 derivatives (i.e. diethoxy) consistently exhibit the highest nematic clearing points in comparison with materials of the same class with wing groups of varying lengths. This agreement, which is present in spite of significant electronic variations among the several linkage groups, suggests that the alkoxy wing groups provide a reproducible effect upon the mesomorphic–isotropic transitions.

Such substituent regularity, which has been noted previously,(1b,2,3)

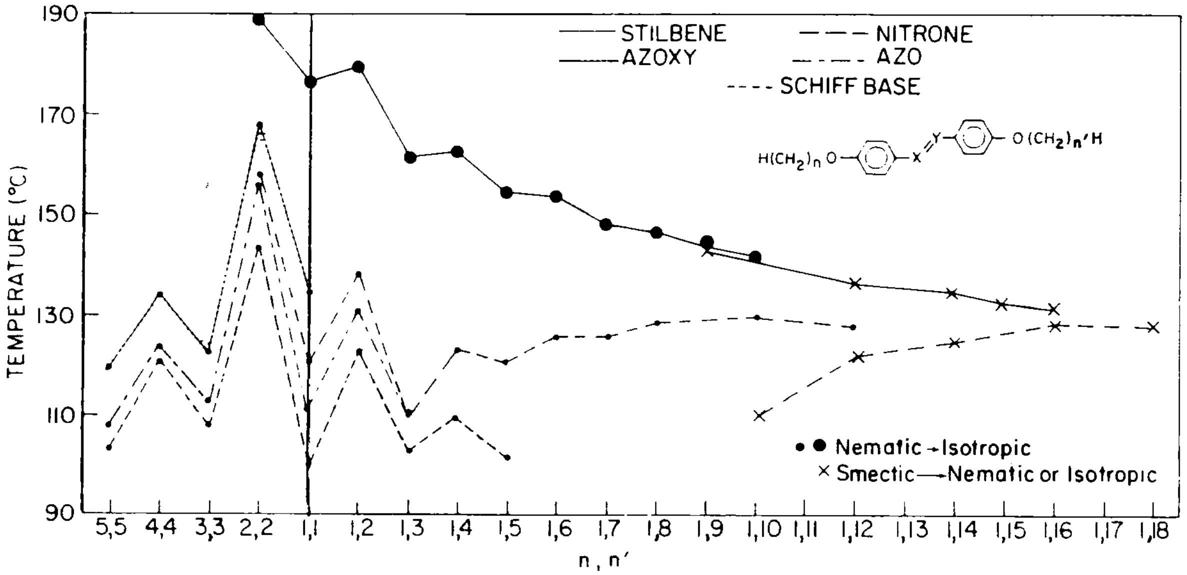


Figure 5. Mesomorphic clearing points as a function of chain length for several classes of dialkoxy liquid crystals. Two separate homologous series, each originating at $n,n' = 1,1$, are plotted on the abscissa. In the cases of the Schiff bases and nitrones, X = CH.

is further substantiated by the striking parallel nature of the different families of curves in Fig. 5. It is therefore assumed that the wing group effects are approximately constant for a given set of values of *n,n'*, and that *differences in mesomorphic character are strongly correlated with the nature of the linkage group.* In the following, we examine which of the structural properties associated with the linkage group may be responsible for this correlation.

Role of Permanent Dipoles

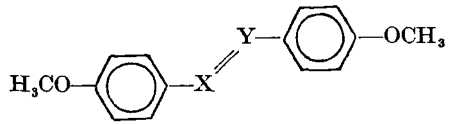
Table 2 lists some physical properties of structurally related nematic derivatives in order of decreasing nematic thermal stabilities. Since all of the linkage groups under consideration should be represented in Table 2, the dimethoxy substances are a convenient choice; however, virtually any set of *n,n'* dialkoxy derivatives could have been selected without affecting the following conclusions.

It has been postulated numerous times that dipole–dipole and dipole-induced dipole interactions enhance mesomorphic character and thermal stability. Yet, there appears to be *no correlation between nematic clearing points and the presence of a permanent dipole in the linkage groups.* That is, the nematic phase of stilbene *2* exists at a temperature which is over 40° higher than the analogous PAA (*18*) and almost 80° higher than the isoelectronic Schiff Base *21*. Indeed among these three substances, only the stilbene lacks a permanent dipole moment in the center of the molecule. Interestingly, *p*-azoanisole (*20*), which also bears no central dipole, exhibits a nematic clearing point which is intermediate between the clearing points of *18* and *21*.

It could be argued that the permanent dipoles in compounds *18* and *19* associated with the N → O bond are increasing the mesomorphic thermal stability, but that this effect is masked by the increased steric requirements associated with the protruding oxygen atom. This is certainly a possibility, but, we feel, a remote one, since space-filling molecular models do not indicate any increase in molecular breadth when comparing azobenzene and azoxybenzene.

With regard to smectic mesophases, it has been suggested by many investigators that relatively large lateral interactions become increasingly important when considering the thermal stabilities of this type of mesophase. One would expect a centrally-located dipole to

TABLE 2 Physical Properties of Some Structurally Related Nematic Liquid Crystals



No.	X	Y	C—I Temp. (°C)	N—I Temp. (°C)	Linkage Group Permanent Dipole	Molecular Planarity
2	CH	CH	216	176	none	planar(a)
18	N	N → O	117(b)	134(b)	~perpendicular to uniaxial direction	nonplanar(c)
19	CH	N → O	149(d)	120(d)	~perpendicular to uniaxial direction	?
20	N	N	165(b)	110(b)	none	planar(e)
21	CH	N	146(b)	99(b)	~parallel to uniaxial direction	nonplanar(f)

(a) Assumed, based on study of *trans*-stilbene.(23)
(b) From Ref. 2.
(c) From Ref. 24.
(d) From Ref. 3.
(e) Assumed, based on study of azobenzene and azotoluene.(25)
(f) Assumed, based on study of several Schiff Bases.(26)

increase the ratio of lateral to terminal interactions, and, as a consequence, enhance the appearance and clearing point of the smectic phase. Our results, as shown in Fig. 5, contradict these expectations; that is, the smectic mesophases of stilbenes are more thermally stable than those of the nitrones in spite of an additional site of lateral dipole moment in the latter class of compounds. In addition, the thermochemical data for the smectic isotropic transition of stilbene *12* indicate a more highly ordered smectic phase for the stilbene relative to the analogous nitrone.(3)

The lack of significance of the central permanent dipole moment complements other results obtained in earlier investigations. Specifically, it has been shown that permanent dipoles located either in the wing groups(15) or in the aromatic rings(27) do not enhance nematic thermal stability. Hence other factors are playing more dominant roles in the appearance of mesomorphic character.

Role of Symmetry

It is a well known phenomenon that molecules characterized by a high degree of molecular symmetry tend to exhibit relatively high melting points. Since *trans*-stilbene is virtually a planar, centrosymmetric molecule,(23) the high melting point of stilbene *2*, relative to the other compounds in Table 2, could be rationalized on the basis of its high symmetry. It might then be attractive to attach the same significance to the high nematic clearing temperature of stilbene *2*, i.e., symmetrical molecules may exhibit stronger intermolecular interactions (and associated higher clearing points) in the nematic phase as well as in the solid phase, relative to less symmetric molecules.

Of the flaws inherent in this empirical suggestion, the most vexing problem concerns the azo derivative *20*. *p*-Azoanisole should contain the same symmetry elements as its isoelectronic counterpart, stilbene *2*, since the related substances *trans*-azo-benzene and -toluene are both nearly planar, centrosymmetric molecules.(25) Yet azoanisole exhibits a nematic clearing point which is among the lowest listed in Table 2.

Clearly, many definitive experiments remain to be carried out in order for the chemist to unravel and understand the complex combination of factors which are responsible for the physical properties of liquid crystals. Among the other factors to be considered, molecular polarizability and intermolecular separation are two which certainly deserve more quantitative attention. Accurate determinations of refractive indices of nematogenic compounds in their nematic or isotropic states would be most helpful in assessing molecular polarizability. In addition, volume expansions in the phase transitions, and density measurements, performed in one of the mobile states, would be indicative of average intermolecular separation.

Acknowledgements

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