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Preparation and Thermodynamics of Some Homologous Nitrones, a New Group of Liquid Crystals

Abstract: To investigate the mesomorphic behavior of aldonitrones, a series of 13 homologs of N-(p-alkoxyphenyl)-α-anisylnitrones was prepared and characterized. Although most of these substances exhibit normal nematic or smectic mesophases, the trend in nematic-isotropic transition temperatures to increase as a function of alkoxy chain length is an exceptional occurrence. Comparison of our data with that of analogous compounds previously reported indicates that thermal persistence of the nematic phase of these compounds increases in the following order: 4,4′-dialkoxybenzylideneaniline, 4,4′-dialkoxyazobenzene, N,α-di-(4-alkoxyphenyl)-nitrone, 4,4′-dialkoxyazoxybenzene. In addition, the phase transitions were investigated by means of differential scanning calorimetry. The entropies of the mesophase-isotropic transitions of the nitrones imply that the long alkoxy chains, in contrast to a widely held belief, are not restricted to a single conformation in the mesophase.

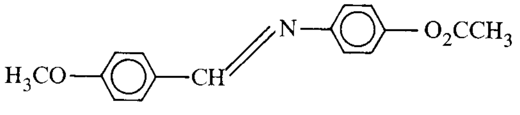
Introduction

The rotational motion of polyatomic molecules in a liquid phase is free or slightly hindered [1], whereas in most solids the three rotational degrees of freedom are replaced by torsional oscillations about an equilibrium position in the lattice. One can easily visualize an intermediate state of matter composed of elongated molecules in which two of the rotational degrees of freedom of a normal liquid are removed, while the third one, as well as at least part of the translational degrees of freedom, is preserved. Materials in this state would be expected to have anisotropic physical properties, and yet might have viscosities in the range of normal liquids. Indeed, within the last century, several thousand materials have been found to exhibit, in some temperature range, such a so-called mesomorphic or liquid crystalline state [2].

Of the substances that display mesomorphic properties, essentially every one can be characterized as a rod-shaped, conformationally rigid, polarizable organic compound. Therefore steric and electronic properties of molecules are of prime importance in effecting a mesophase. In addition, the type of molecular order and accompanying physical properties of the mesomorphic state depend on an intricate and often perplexing balance of these factors [3]. Accordingly, mesophases have been categorized into three general classes, each with its own distinctive molecular arrangement and physical appearance, the latter usually being assessed under a polarizing microscope as well as in ambient light.

The three classes of liquid crystals are smectic, nematic and cholesteric. The smectic mesophase can be represented as having layers of parallel molecules, i.e., one translational and two rotational degrees of freedom have been removed. Molecules in the nematic phase also have their long axes parallel, but unlike the more highly ordered smectic phase, translation of nematic molecules relative to each other is unrestricted in all three directions. Cholestric liquid crystals are similar to the nematic materials in a given plane of molecules, but each successive plane is rotated slightly with respect to the direction of the long molecular axis, the resultant superstructure being helical [4].

Whether a compound will exhibit mesomorphic properties and what type they will be are not easily predicted. Generally, a substance must be optically active as well as rod-shaped and polarizable to display a cholesteric mesophase. Esters of cholesterol and related steroidal alcohols are often cholesteric. Most smectic and nematic compounds, on the other hand, are linear aromatic compounds usually containing polar or polarizable groups.



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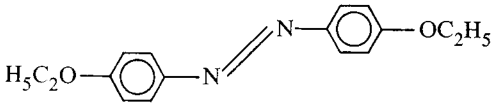

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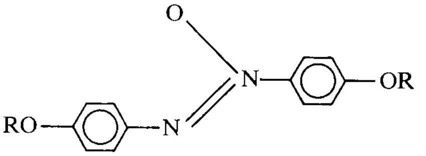


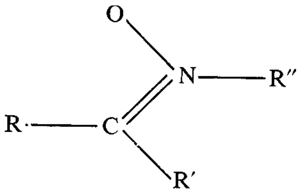
3 R=CH_3

4 R=$C_{12}H_{25}$

The structures *1* through *4* depict some typical liquid crystalline substances. Compound *1*, anisylidene-*p*-aminophenyl acetate (APAPA), is a Schiff base which has an enantiotropic [5] nematic range of 85 to 109°C [6]. Compound *2*, *p*-azophenetole, is a monotropic [5] nematic liquid crystal; this crystal melts to an isotropic liquid at 160°C and the nematic phase reverts to the isotropic liquid at 154°C [7]. Materials *3* and *4* represent two members of the homologous series of *p*-dialkoxyazoxybenzenes prepared and studied thermodynamically by Arnold [8]. The former compound, commonly known as *p*-azoxyanisole (PAA), has a nematic range of 118 to 135°C, while the dodecyl ether *4* exhibits a smectic phase between 82 and 122°C.

These four liquid crystalline substances, which are representative of hundreds of analogous compounds [2], have the following structural feature in common: two *para*-substituted benzene rings joined through an unsaturated polar linkage in the *trans*-configuration. Since azoxy compounds can be envisioned as the N-oxides of corresponding azo substances, we postulated that the N-oxides of Schiff bases might also display mesomorphic properties.

N-oxides of Schiff bases of the general formula *5* are well known in the literature by their common name, nitrones [9]. Here, for example, R, R′ and R″ may be hydrogen or alkyl or aryl groups. Aromatic aldonitrones, such as those depicted by structure *6*, contain the same structural features as outlined in the preceding paragraph, including the *trans*-configuration [9(b), 10]. Yet among the dozens of compounds of this type which have been reported, none was observed to display mesomorphism.



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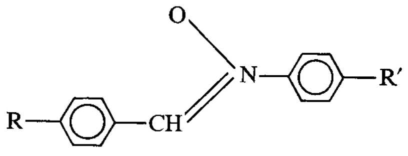

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The usefulness of liquid crystals depends on the fact that the order and the associated optical properties are easily disturbed by small changes in external parameters, due to the small size of the forces responsible for the mesophase order. Differential scanning calorimetry provides a relatively rapid means for measuring the energetics of the mesophase transitions in a large number of compounds. The enthalpy and entropy changes obtained in this way are a measure of the relative stability and order, respectively, of the mesophases. The effect of changes in molecular structure on mesomorphic properties and the ordering forces, then, can be quantitatively assessed.

The purpose of this investigation was to prepare a series of homologous nitrones of the type *6*, where R and R′ are alkoxy groups, and to study the thermodynamic parameters of the pertinent phase transitions by differential scanning calorimetry. These data, in addition to delineating the mesomorphic character of nitrones, would prove valuable in our further understanding of the interactions responsible for mesomorphism in aromatic molecules [11].

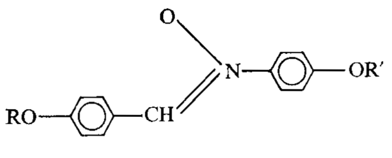
Experimental procedures

All of the new compounds had satisfactory spectral properties and elemental analyses. Infrared spectra were recorded on a Perkin-Elmer 137B Infracord spectrometer. Nuclear magnetic resonance spectra were obtained on a Varian HA-60-IL spectrometer. Ultraviolet spectra were taken on a Cary 14 spectrophotometer.

• *Preparation of* p-*alkoxynitrobenzenes*

The following *p*-alkoxynitrobenzenes were obtained directly from Eastman Organic Chemicals and distilled prior to use: *p*-nitroanisole, *p*-nitrophenetole, *p*-propoxynitrobenzene, *p*-butoxynitrobenzene and *p*-pentoxynitrobenzene. The remaining homologs were prepared as follows: *p*-Nitrophenol was added to a solution of sodium ethoxide in ethanol. To the resulting phenoxide solution was added dropwise over a period of 0.5 h an equivalent amount of

Table 1 Preparation of N-(*p*-alkoxyphenyl)-α-(*p*-alkoxyphenyl)nitrones.



Compound	*R*	*R′*	*Reaction medium*	*Recrystallization solvent*
15	CH_3	CH_3	ethanol/water	benzene
16	CH_3	C_2H_5	ethanol/water	benzene
17	CH_3	n-C_3H_7	ethanol/water	cyclohexane
18	CH_3	n-C_4H_9	ethanol/water	methylcyclohexane
19	CH_3	n-C_5H_{11}	ethanol/water	cyclohexane
20	CH_3	n-C_6H_{13}	ethanol/water	cyclohexane
21	CH_3	n-C_7H_{15}	ethanol/water	carbon tetrachloride
22	CH_3	n-C_8H_{17}	ethanol/water	tetrahydrofuran/ether
23	CH_3	n-$C_{10}H_{21}$	propanol/water	benzene/cyclohexane
24	CH_3	n-$C_{12}H_{25}$	propanol/water	benzene/cyclohexane
25	CH_3	n-$C_{14}H_{29}$	propanol/water	benzene/cyclohexane
26	CH_3	n-$C_{16}H_{33}$	propanol/water	benzene/cyclohexane
27	CH_3	n-$C_{18}H_{37}$	propanol/water	cyclohexane
28	C_2H_5	CH_3	ethanol/water	benzene/methylcyclohexane
29	C_2H_5	C_2H_5	ethanol/water	benzene/chloroform

the appropriate alkyl iodide, which was obtained from either Eastman Organic Chemicals or Columbia Organic Chemicals. The solution was allowed to reflux overnight or until the red color of the phenoxide salt was discharged. After removal of the ethanol in a rotary evaporator, the residue was dissolved in water and extracted with ether. The extract was washed with dilute sodium hydroxide and saturated sodium chloride solutions and dried. The ether was removed at the water pump, and the residual product was purified either by fractional distillation *in vacuo* or by successive recrystallizations from ethanol. The physical properties of the *p*-alkoxynitrobenzenes agreed with those reported in Refs. 12 and 13.

- *Preparation of N-*(p*-alkoxyphenyl*)*-α-anisylnitrones* [*14*]

The following general procedure [15] was used to prepare all of the nitrones listed in Table 1. *p*-Alkoxynitrobenzene (18 mmole) and ammonium chloride (23 mmole) were dissolved or dispersed (depending on solubility) in 25 ml of 60% aqueous ethanol [16]. The solution was cooled to 10°C and zinc powder (65 mmole) was added portionwise with continuous stirring over a period of 1.5 h. During this addition the temperature was maintained below 15°C. The solids were removed by filtration and washed with three 8-ml portions of boiling ethanol. Anisaldehyde (20 mmole) was added to the combined alcoholic filtrates and the mixture was stirred at room temperature for 20 h [17]. The precipitated nitrone was filtered and washed with 25 ml of boiling ether. Several crystallizations of the product from tetrahydrofuran/ether [17] were used to remove the last traces of an accompanying yellow side-product. The white nitrone was repeatedly recrystallized from a suitable solvent until a constant melting point was obtained. The specific reaction conditions and recrystallization solvents are enumerated in Table 1.

- *Microscopy*

The mesophases were identified and the transition temperatures were measured by standard techniques [3] using a Leitz Ortholux POL polarizing microscope equipped with a Koeffler hot stage. The temperatures were calibrated at the melting points of high purity standards, and the thermometric accuracy is estimated to be ±0.5°C.

- *Calorimetric measurements*

The heats of fusion and phase transition were determined by differential scanning calorimetry with a Perkin-Elmer DSC-1B calorimeter. Hermetically sealed aluminum pans

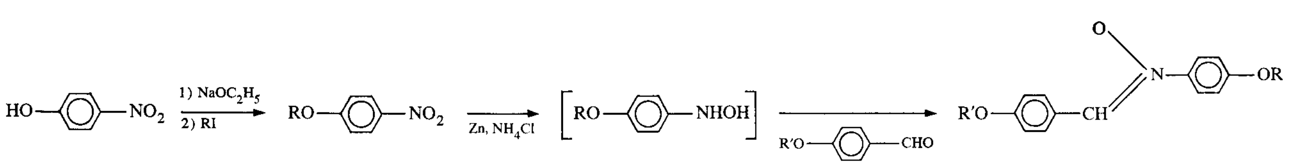
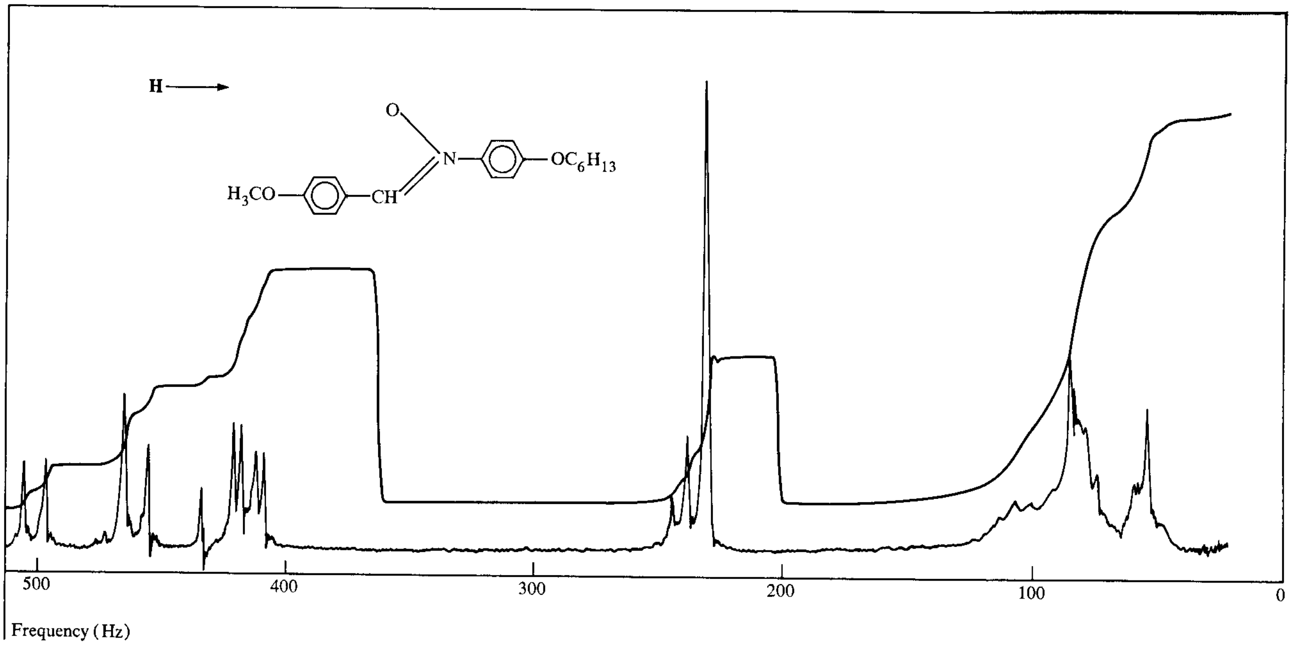


Figure 1 Reaction sequence used to synthesize the aldonitrones.

Figure 2 NMR spectrum of N-(*p*-hexyloxyphenyl)-α-anisylnitrone.



were used as sample containers. The instrument constant was determined by calibration with NBS benzoic acid standard. The heats of transition were obtained by graphic integration, the baseline having been extrapolated to the transition temperature from that region on each side in which the heat capacity varies linearly with temperature. The reported heats and entropies therefore include any caloric effects due to pretransition phenomena. The heats of fusion and phase transition temperatures are believed to be accurate within five percent.

Results and discussion

- *Synthesis*

The homologous nitrones *15* through *29*, listed in Table 1, were synthesized according to the scheme depicted in Fig. 1. The intermediate hydroxylamine derivative, which is enclosed by brackets, was not isolated or purified. Rather, it was allowed to react directly with an aldehyde in an alcohol medium. In every case, the purified nitrone was a white crystalline solid at room temperature. Upon melting, the substances showed some decomposition, as evidenced by a slight yellow color associated with the isotropic liquid. Care was exercised to prevent long exposure of the nitrones to fluorescent light [18].

All of the nitrones exhibited intense infrared absorption at 1255 cm^{-1} (N—O stretch) [9(b), 19] and at 1600 cm^{-1} (C═N stretch) [9(b)]. Strong absorption was also noted at 1500, 1170 and 840 cm^{-1}. The ultraviolet absorption spectra in ethanol of the dimethoxy nitrone *15* was typical and contained two broad bands with λ_{max} at 335 nm ($\log \epsilon = 4.45$, where ϵ is the extinction coefficient) and at 234 nm ($\log \epsilon = 4.02$, ϵ evaluated at the shoulder of the curve). Similar spectra for related materials have been reported previously [20].

The nuclear magnetic resonance (NMR) spectra of the homologous nitrones exhibit many features in common. Figure 2 shows the NMR spectrum of the hexyloxy homolog *20* (henceforth designated the 1,6-nitrone). The region between 410 and 510 Hz, which contains all of the aromatic-proton resonances plus that of the proton associated with the CH═N moiety [21], is virtually the same for the entire series of nitrones under investigation. The benzenoid-proton resonances appear as two A_2B_2 multiplets upon which is superimposed at 467 Hz the singlet due to the benzylic hydrogen. The methoxy group is a sharp singlet at 231 Hz, while the hexyl chain, which includes a triplet at 238 Hz, comprises the remainder of the spectrum.

- *Phase identification and transition temperatures*

Of the 15 homologous nitrones investigated under the microscope, two show no mesophase (*15* and *17*), four were monotropic nematic (*16*, *18*, *28* and *29*), and the remainder were either nematic (*19* through *22*), smectic (*25* through *27*), or both smectic and nematic (*23* and *24*). These data, along with the corresponding transition temperatures, are listed in Table 2.

The texture of the nematic phases on untreated glass surfaces was generally threaded or homeotropic [22]. The smectic phases of the aldonitrones showed a remarkable tendency toward homeotropic textures. The resultant difficulty in identification was overcome by rubbing the microscope slides prior to the melting of the crystals. When not homeotropic, the smectic phases exhibited a focal-conic texture.

Although the 1,1- and 1,3-nitrones (*15* and *17*) exhibited no mesophases under the polarizing microscope, an estimate could be made of their $N \rightarrow I$ (nematic to isotropic) transition temperatures by extrapolating the nematic-isotropic transition line in the phase diagrams of binary mixtures [23].

Figure 3 shows the phase diagram of the 1,1-nitrone with *p*-azoxyanisole, its isoelectronic counterpart. The $N \rightarrow I$ transition temperatures of the mixtures, represented by circles, were obtained by visual observation under the polarizing microscope, where the experimental conditions facilitate supercooling without inducing crystallization in the mixtures rich in the nitrone component. The temperatures of the onset (triangles) and completion (squares) of fusion, on the other hand, were obtained with the differential scanning calorimeter in which the more nearly spherical sample geometry reduces the error due to concentration gradients. The $N \rightarrow I$ line in this system is seen to have a very small curvature. Extrapolation by a linear least-squares fit results in a transition temperature of 120°C for the pure 1,1-nitrone, while a quadratic fit indicates 119°C for the transition temperature.

Extrapolation from a similar phase diagram of the mixture of the 1,3-nitrone with the 2,2-nitrone indicates a nematic-isotropic transition temperature of 109°C for the former substance.

The solid-mesophase or solid-isotropic transition temperatures of the nitrones do not follow a regular pattern as the homologous series is ascended. This is not surprising in view of past results with other homologous series [3, 24]. It should be mentioned, however, that the melting points of the isoelectronic dialkoxyazoxybenzenes are significantly lower than the corresponding nitrone melting points. X-ray diffraction studies currently under way should help to clarify this difference [24].

In considering the homologous series of N-(*p*-alkoxyphenyl)-α-anisylnitrones (*15* through *27*), it is evident that the lower members of the series (C_n, $n \leq 4$) are either nonmesomorphic or monotropic nematic. As the length of the alkoxy group is increased, the aldonitrones become enantiotropic nematic. When the alkoxy group includes ten carbon atoms, a smectic phase is identified as well as a nematic phase. Finally, pure smectic mesomorphism is encountered in the very long members of the series (C_n, $n \geq 14$).

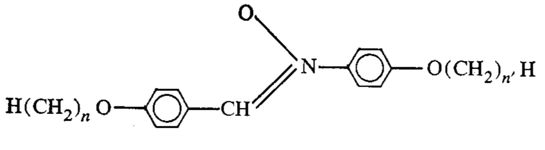
This behavior in mesomorphic character as a function of chain length has been encountered frequently in the past, although the precise demarcations between the groupings are somewhat variable. If one considers the 4,4′-dialkoxy derivatives of benzylideneaniline, azoxybenzene and azobenzene, the total number of carbon atoms in both terminal alkoxy groups varies between 11 and 14 for the onset of the smectic mesophase [2(c), 8, 24, 26]. Our results are consistent with this correlation since the 1,10-nitrone, with 11 carbon atoms in the chains, is the first to exhibit a smectic mesophase.

It has been well established that mesophase-isotropic transition temperature curves for even or odd members of a homologous series are usually smooth functions of the length of the alkyl chain [3, 24]. Figure 4 depicts a similar relation for the homologous aldonitrones under investigation. Smooth curves have been drawn through (a) the nematic-isotropic transition temperatures for odd-membered chains ($n' = 3, 5, 7$); (b) the nematic-isotropic temperatures for even-membered chains ($n' = 4$ through 12); and (c) the smectic-nematic or smectic-isotropic temperatures for even-membered chains ($n' = 10$ through 18). The first two compounds included in Fig. 4, the 1,1- and 1,2-nitrones, did not appear to lie on their respective curves.

In considering the nematic-isotropic temperature trends, it is clearly seen that the odd-membered curve lies below the even-membered curve, and that the distance between the two curves decreases steadily as the number of carbon atoms increases. The merger point is estimated to be at about $n' = 9$ or 10. This behavior is typical of homologous nematogenic substances and has been discussed elsewhere [3].

A unique feature of our results is the trend of the nematic-isotropic transition temperatures to increase from the propoxy through the decyloxy aldonitrones. A large majority of investigations on homologous ethereal mesomorphic substances reveals that the nematic-isotropic transition temperatures gradually decrease with increasing

Table 2 Measured transition temperatures and derived enthalpies and entropies of the N-(*p*-alkoxyphenyl)-α-(*p*-alkoxyphenyl)-nitrones.



Compound	*n, n'*[a]	*Type of transition*	*Transition temp. (°C)*	*ΔH (kcal/mole)*	*ΔS (cal/°K-mole)*
15	1,1	C → I	149	7.92	19.0
		N → I[b]	120[b]		
16	1,2	C → I	146	9.00	21.5
		N → I[c]	138	0.172	0.42
17	1,3	C → I	155		
		N → I[b]	109[b]		
18	1,4	C → I	123	8.11	20.5
		N → I[c]	123	0.150	0.38
19	1,5	C → N	112	7.47	19.4
		N → I	120	0.168	0.43
20	1,6	C → N	107	6.66	17.5
		N → I	125	0.197	0.50
21	1,7	C → N	120	8.33	21.2
		N → I	125	0.219	0.55
22	1,8	C → N	112	11.80	30.7
		N → I	128	0.268	0.67
23	1,10	C → S	108	11.56	30.3
		S → N	109	[d]	[d]
		N → I	129	0.373	0.93
24	1,12	C → S	110	13.92	36.4
		S → N	121	0.045	0.12
		N → I	127	0.475	1.19
25	1,14	C → S	112	15.52	40.3
		S → I	124	0.927	2.34
26	1,16	C → S	115	15.89	41.0
		S → I	128	1.07	2.66
27	1,18	C → S	119	19.00	48.5
		S → I	127	1.18	2.95
28	2,1	C → I	129	8.04	20.0
		N → I[c]	128	0.239	0.60
29	2,2	C → I	178	10.44	23.1
		N → I[c]	158	0.346	0.80

[a] Here *n* is the number of carbon atoms in the alkoxy chain on the α-phenyl ring and *n'* is the corresponding value for the N-phenyl ring.

[b] Obtained by extrapolation of the N → I transition temperatures from the mixtures, because the supercooled liquid crystallizes prior to the onset of the nematic phase.

[c] Monotropic transition.

[d] Not determined because of the proximity of the C → S and S → N transition temperatures.

chain length [3, 8]. In many of these studies, however, each molecule (or dimer in the case of carboxylic acids) contains two alkoxy groups whose lengths are incremented simultaneously.

For those studies in which the length of a single alkoxy group was varied, the results appear to be quite irregular. Thus in various homologous series, the N → I transition temperature vs chain length curves were observed to exhibit monotonic decrease [27], monotonic increase [28], a maximum followed by a minimum [27], and monotonic increase or monotonic decrease depending on whether the chain length was odd- or even-valued [24]. It is reasonably evident therefore that the nematic-isotropic transition temperatures are a result of a delicate balance of

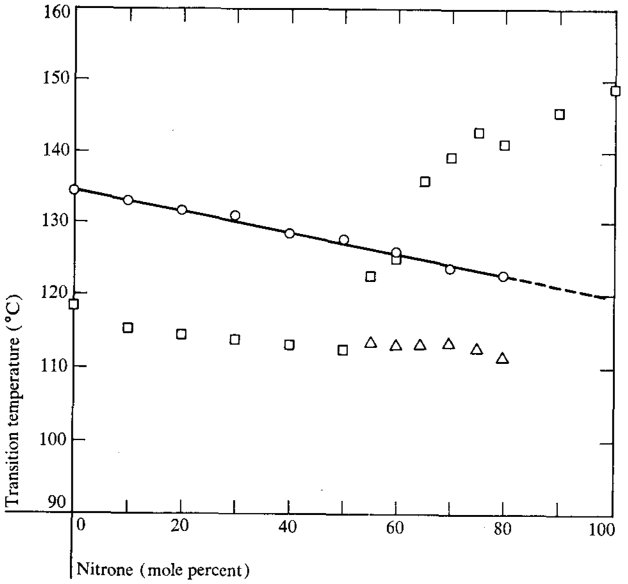
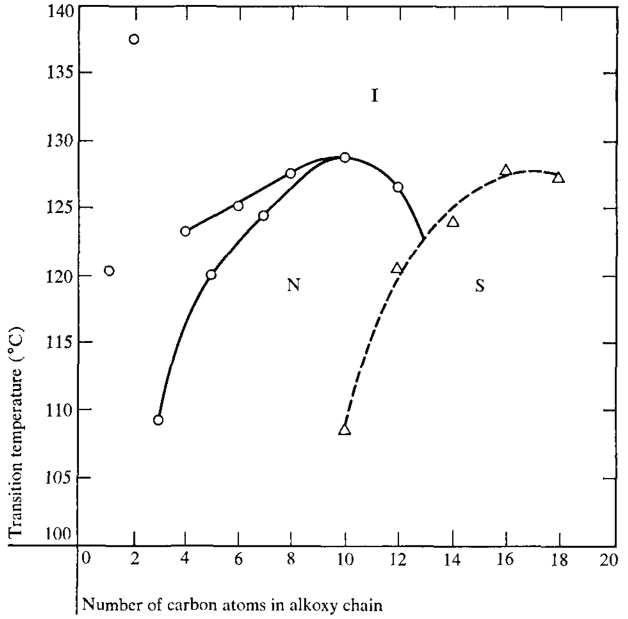


Figure 3 Phase diagram for binary system of nitrone *15* and *p*-azoxyanisole.

Figure 4 Transition temperatures for the homologous aldonitrones *15* through *27*; ○ nematic → isotropic; △ smectic → nematic or isotropic.



several factors such as molecular shape, conjugation and resonance, size and position of dipoles, polarizability, and conformational preference of the alkoxy chains.

One important structural feature of the aldonitrones that is shared by some of the other substances that exhibit a trend of the N → I transition temperature to increase is the transverse dipole at the end of the molecule due to the methoxy group present in compounds *15* through *27*. We speculate, in accordance with some earlier suggestions, that dipoles of this type help to preserve the parallel molecular orientation that is found in nematic materials. As one increases the length of the alkoxy group at the opposite end of the molecule, say from butoxy to hexyloxy, the dipole associated with the methoxy group remains unchanged while the overall polarizability and length of the molecule are increased slightly. The net result is a relative stabilization of the nematic phase, or a higher transition temperature.

Conversely, when two alkoxy groups are incremented at the same time, such as in the 4,4′-dialkoxyazoxybenzenes [8], a dipole at the end of the molecule is no longer maintained. Then the added polarizability may be insufficient to stabilize the nematic order because destabilizing factors, such as increased values of ΔS, where ΔS is the transition entropy increment, become more important. Hence the nematic-isotropic transition temperature may decrease. A similar mechanism may be operative in some of the methoxy nitrones under investigation. That is, for nitrones with large alkoxy groups such as the 1,10- and 1,12-nitrones, the relative increase in length and polarizability between the two substances is small, and therefore the destabilizing factors may be causing a reversal in the rising N → I curve, as seen in Fig. 4.

The shape of the smectic-isotropic transition temperature curve as a function of alkoxy chain length is shown in Fig. 4. It is very similar to the curves reported elsewhere [3, 24, 28], and hence additional discussion on this matter is unwarranted. It is necessary to remark, however, that the solid curve of N → I temperatures in Fig. 4 appears to intersect the S → I curve, rather than merge with it as is usually found [3]. It is possible, although not likely, that slight traces of impurities were present in the 1,12- and 1,14-nitrones, thereby lowering the N → I transition temperatures and causing this anomalous behavior. In considering, however, that the quantitative difference between "intersection" and "merger" is only a few degrees centigrade, perhaps this result is not so anomalous as it initially appears.

Weygand and Gabler [29] have found that liquid crystal N → I transition temperatures for 4,4′-dialkoxyazoxybenzenes (*3*), 4,4′-dialkoxyazobenzenes (*2*) and 4,4′-dialkoxybenzylideneanilines (similar to structure *1*) tend to vary similarly for at least the first five alkoxy groups that have been investigated. Of the nitrones under investigation, only the dimethoxy (*15*) and diethoxy (*29*) compounds are suitable for comparison with Weygand and Gabler's results because of the symmetrical nature of the pendant groups. Table 3 contains the nematic clearing point values for the pertinent substances. The regularity in the temperature differentials among the several classes

Table 3 Effect of the linkage group on the nematic clearing point of some aromatic liquid crystals.

	Substituent			
	4,4'-dimethoxy-		*4,4'-diethoxy-*	
Substrate	$T_{NI}(°C)$	$\Delta T(°C)$	$T_{NI}(°C)$	$\Delta T(°C)$
Azoxybenzene[a]	134	+14	168	+10
N,α-diphenylnitrone	120[b]	(0)	158	(0)
Azobenzene[a]	110[b]	−10	150	−8
Benzylideneaniline[a]	99	−21	143	−15

[a] From Ref. 29.

[b] Extrapolated from data obtained with mixtures.

of compounds suggests that the alkoxynitrones may exhibit nematic mesophases that become isotropic at temperatures between those of the corresponding azo and azoxy compounds; also, the similar Schiff base materials would have the least persistent mesophases as functions of temperature.

A further test of this hypothesis is shown in Fig. 5, where the squares represent the N → I transition temperatures for nitrones *15* through *19* and the circles represent the corresponding temperatures of *p*-methoxybenzylidene-*p*-alkoxyanilines [7, 24]. Once again the nitrone mesophase persists to a higher temperature in each case, although the temperature differential drops somewhat for the propoxy derivatives.

The proposed order of nematic mesophase stability, viz., azoxy, nitrone, azo and Schiff base, can be partially rationalized on the basis that the strong transverse dipole associated with the dative N—O bond, which is located in the rigid central part of the molecule, dominates the intermolecular interactions of the type that help stabilize molecular alignment. Compatible with this view is the observation that with increasing pendant group length, the difference in stability tends to diminish between the azoxy and the azo as well as between the nitrone and the Schiff base clearing points, as seen in Table 3 and in Ref. 29. The longer alkoxy chain, by increasing the contribution of the polarizability, reduces the dominance of the strong transverse dipole moment among the intermolecular attractive forces. It is noteworthy that in the isoelectronic pairs of azoxy and nitrone substances, or azo and Schiff base materials, the compounds with the carbon-containing linkage group invariably have the thermally less persistent nematic phase. An unambiguous interpretation of this fact is not easily forthcoming.

- *Calorimetric determinations*

The measured heats and the derived entropies of transition are listed in Table 2.

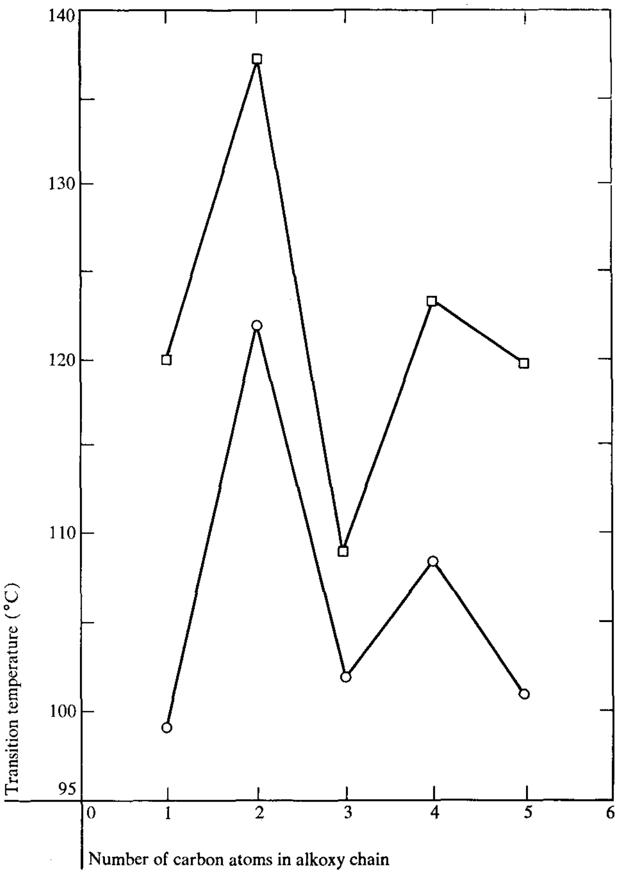


Figure 5 Nematic → isotropic transition temperatures for N-(*p*-alkoxyphenyl)-α-anisylnitrones (□) and anisylidene-*p*-alkoxyanilines (○).

Figure 6 Transition entropies for N-(*p*-alkoxyphenyl)-α-anisylnitrones.

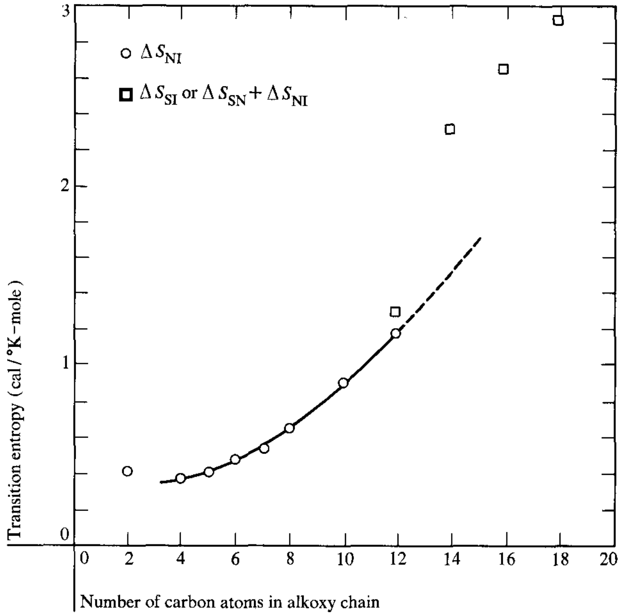
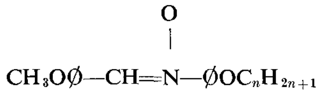
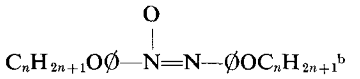
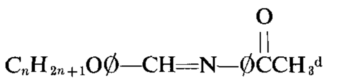


Table 4 Entropies of mesomorphic transitions for an homologous series of liquid crystals.

Homolog[a]	*Average* ΔS_{NI} *for* $n \leq 5$ *(eu)*	*Increment in* ΔS_{NI} *per chain carbon atom for* $n \geq 8$ *(eu)*	*Increment in* ΔS_{SI} *per chain carbon atom (eu)*
 $\mathrm{CH_3O\emptyset{-}CH{=}\overset{\overset{O}{\vert}}{N}{-}\emptyset OC_nH_{2n+1}}$	0.41	0.13	0.15
 $\mathrm{C_nH_{2n+1}O\emptyset{-}\overset{\overset{O}{\vert}}{N}{=}N{-}\emptyset OC_nH_{2n+1}}$[b]	0.62	0.32	0.54
Cholesteryl—$\mathrm{O_2C{-}C_nH_{2n+1}}$[c]	0.30[f]	0.073[f]	0.20
 $\mathrm{C_nH_{2n+1}O\emptyset{-}CH{=}N{-}\emptyset\overset{\overset{O}{\Vert}}{C}CH_3}$[d]	0.34		0.23
$\mathrm{(C_nH_{2n+1}O\emptyset{-}CO_2H)_{dimer}}$[e]	2.8		0.48

[a] Here ∅ denotes a benzene ring with substitutions in positions 1 and 4.
[b] From Ref. 8.
[c] From Ref. 31.
[d] From Ref. 28(c).
[e] From Ref. 30.
[f] These data refer to cholesteric-isotropic transitions.

In fusion, as is usual for molecules of high complexity, little regularity is observed in the thermal data. A trend of increasing entropy of fusion with increasing alkoxy chain length is observed only for the compounds with long chains.

The changes in entropy between the mesomorphic and the isotropic states of the N-(*p*-alkoxyphenyl)-*α*-(*p*-methoxyphenyl) nitrones are plotted as functions of chain length in Fig. 6. A single smooth curve satisfactorily represents the trend in the entropy of the nematic-isotropic transitions, with the even-odd alternation falling within the experimental error. For the substances with short alkoxy substituents, the data points level out at about 0.4 eu (cal/°K-mole). This entropy change is of the order of magnitude expected for the replacement of two torsional oscillations in the nematic phase by two nearly free over-all rotations in the isotropic phase. Furthermore, the relative constancy of the observed entropy changes, as the chain length varies from two to six carbon atoms, indicates that both the energy difference between conformational isomers and the potential barrier to internal rotation change very little between the nematic and the isotropic states for short pendant groups.

For large alkoxy chains, on the other hand, the steady although not quite linear rise in ΔS_{NI} with increasing number of carbon atoms above seven indicates that the probability of certain conformations is decreased or the barrier to internal rotation about each carbon atom is increased in the nematic phase relative to the isotropic liquid phase. It is safe to assume that in the isotropic liquid, a large number of conformations are almost equally probable. Since the increment in transition entropy per additional carbon atom in the chain is only about 0.13 eu, and in view of the discussion in the following paragraph, we conclude that the pendant groups in the nematic phase cannot be restricted to a single (elongated) conformation.

With regard to the overall behavior of the entropy of the nematic-isotropic transitions with increasing chain length, the nitrones under study show a similarity to the homologous series of dialkoxyazoxybenzenes investigated by Arnold [8], as well as to some less closely related series of nematic compounds [28(c), 30]. Even more remarkable is the similarity of the entropy changes in the cholesteric-isotropic transitions of the cholesteryl alkanoates discussed by Barrall, Johnson and Porter [31]. The numerical values of ΔS_{NI} at the flat portion of the curve (the short-chain section) and of the increments of ΔS_{NI} at the long-chain part vary from series to series and are compared in Table 4. While the variations themselves are not easily interpreted, the transition entropy increments per carbon atom are far below $R \ln 3$ in all cases. This latter value is the increment expected for transitions that involve the change from a single conformation of an alkyl chain to a set of equally probable conformations, as observed for example, in the melting of *normal* paraffins [32]. Thus, despite widely held views to the contrary (see Ref. 3 and other references therein), alkyl pendant groups in nematic liquid crystals cannot exist in a single elongated conformation [33].

The entropy difference between the smectic and the isotropic phases as a function of chain length is also shown in Fig. 6. Although the point plotted for the 1,12-nitrone represents the sum of the smectic-nematic and nematic-isotropic entropies of transition, it appears anomalously low. Similar breaks in the ΔS_{SI} curve can be observed, however, in the cholesteryl alkanoates [31], the dialkoxyazoxybenzenes [8] and the *p*-alkoxybenzoic acid dimers [30]. In all instances the break appears at that chain length beyond which no intermediate mesophase exists between the smectic and the isotropic phases.

The increment in the smectic-isotropic transition entropy per carbon atom in the chain is 0.15 eu. This value is somewhat smaller than the typical ΔS_{SI} increment in other homologous series, as shown in the last column of Table 4. Furthermore, in the nitrone series this increment is barely larger than the increment in ΔS_{NI}, which indicates the unusual situation that alkoxy pendant groups in nitrones are only slightly more conformationally restricted in the smectic than in the nematic phase.

Finally we examine the calorimetric data for the two nitrones that are not, strictly speaking, members of the homologous series. The 2,2-nitrone *29* is of interest because it is isoelectronic with 4,4′-diethoxyazoxybenzene. The geometries, polarizabilities, charge distributions and conformational rigidities of the two compounds are expected to be closely similar. This is indeed reflected in the remarkably close agreement in the nematic-isotropic transition entropies of the two substances, 0.80 and 0.814 eu, respectively [8].

Compound *28* differs from compound *16* only in the interchange of the methoxy and ethoxy pendant groups. While it is well known from the literature [3] that minor structural changes of this kind influence the nematic-isotropic transition temperature, it is somewhat surprising that the transition entropies differ by nearly 50 percent. This fact points out the need for a great deal of caution in the detailed interpretation of the thermodynamic data of liquid crystalline phase transitions in terms of structural and electronic changes between related molecules. Measurements on numerous mesomorphic compounds are still required before generalizations of acceptable predictive power can be obtained.

Summary

A novel series of liquid crystalline compounds, N-(*p*-alkoxyphenyl)-α-(*p*-alkoxyphenyl)-nitrones, was synthesized and investigated. Comparison of the thermal properties of these mesophases with those of some structurally related substances indicates the following:

1) The trend of the nematic-isotropic transition temperatures to increase in the homologous series of N-(*p*-alkoxyphenyl)-α-anisylnitrones persists to the decyloxy compound. This unique occurrence may be related to the dipolar character of the methoxy group at the end of the molecule.

2) Nematic mesophase stability, as measured by the nematic-isotropic transition temperatures of related dialkoxy-substituted substances, increases in the order azomethine, azo, nitrone and azoxy compounds, which suggests a dominant role for the strong centrally located transverse dipole moment of the dative N—O bond.

3) The incidence of smectic mesomorphism in the nitrones and the associated transition temperature trend are similar to those of other homologous series. The measured smectic-isotropic transition entropies, on the other hand, are lower in nitrones.

4) The increment in the entropy of the nematic-isotropic transition, per methylene of the pendant group, is low in the nitrones as well as in other homologous series of liquid crystals. This observation leads to the conclusion that the assumption of a single elongated conformation of the pendant alkoxy chains in nematic phases is incorrect.

Acknowledgment

We are pleased to acknowledge the technical assistance of H. A. Huggins, who performed the microscopy and calorimetry.

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Received April 17, 1970

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