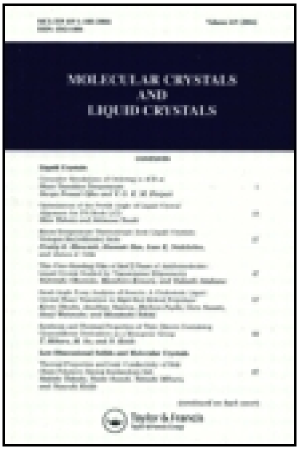

Molecular Crystals and Liquid Crystals

Nitrones: A Novel Class of Liquid Crystals

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Nitrones: A Novel Class of Liquid Crystals

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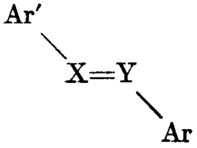
Over the last several years, we have witnessed an upsurge in the quantity of research devoted to mesophase formation and properties.[1] Of particular interest to chemists is the investigation of molecular structure requirements for liquid crystalline substances, and the variation of mesophase physical properties with composition.[2] It has been well established that a large number of compounds which display nematic and/or smectic mesophases possess rod-like shapes and a relatively high degree of polarizability and of conformational rigidity.[3] For example, many liquid crystal materials are based on the general structure I; that is, with appropriate aryl moieties, stilbenes (Ia), anils (Ib), azobenzenes (Ic), and azoxybenzenes (Id)[4] show mesomorphic properties.



I

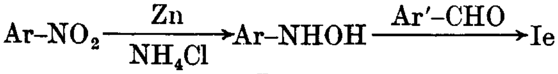
Ia. $X = Y = CH$
b. $X = CH,\ Y = N$
c. $X = Y = N$
d. $X = N,\ Y = N \rightarrow O$
e. $X = CH,\ Y = N \rightarrow O$

Consequently, it appeared somewhat surprising to us that similarly substituted aldonitrones (Ie) have not, to our knowledge, been identified as mesomorphic materials.

Nitrones of this type, which were first prepared and characterized over fifty years ago,[5] are well documented in the literature.[6] In addition, spectral studies[6b,7] have indicated that aldonitrones exist in the stable *trans* configuration shown in structure Ie. These compounds would therefore be structurally analogous[8] as well as isoelectronic with their azoxy counterparts.

Thus the problem arises: can aldonitrones display mesomorphic properties as do the azoxybenzenes, or is there some mechanism operative which precludes this possibility? One such mechanism, as suggested by Gray,[9] is that the intermolecular forces which bind a crystal are so strong that a compound will melt only at a relatively high temperature. Then the thermal motions may be too large to permit the formation of an ordered array of molecules.

We have answered this question by preparing a series of nitrones, whose structures are given in Table I. Each compound was prepared from an aromatic nitro derivative and an aldehyde by the following sequence:[10, 11]



$$\text{Ar–NO}_2 \xrightarrow[\text{NH}_4\text{Cl}]{\text{Zn}} \text{Ar–NHOH} \xrightarrow{\text{Ar}'\text{–CHO}} \text{Ie}$$

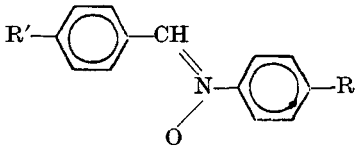
II

The intermediate arylhydroxylamine, II, was not isolated, but was allowed to undergo direct condensation with an aldehyde in alcohol solution.

Of the eleven aldonitrones shown in Table I, three do not display mesomorphism, four are monotropic[2] nematic, three are enantiotropic[2] nematic, and one is enantiotropic smectic. We therefore conclude that nitrones are generally capable of forming mesophases.

Upon examining the transitions and corresponding temperatures for the series of homologs III–IX, it is easily seen that the lower members of the series, III–VI, either show no mesophase

TABLE 1. Transition Temperatures of Some Aldonitrones[a]



No.	R′	R	Transition[b]	T[c]
III	CH_3O-	CH_3O-	C → I	149
IV	CH_3O-	C_2H_5O-	C → I	146
			N → I	138[d]
V	CH_3O-	n-C_3H_7O-	C → I	155
VI	CH_3O-	n-C_4H_9O-	C → I	123
			N → I	123[d]
VII	CH_3O-	n-$C_6H_{13}O$-	C → N	107
			N → I	125
VIII	CH_3O-	n-$C_8H_{17}O$-	C → N	112
			N → I	127
IX	CH_3O-	n-$C_{16}H_{33}O$-	C → S	115
			S → I	127
X	C_2H_5O-	CH_3O-	C → I	129
			N → I	128[d]
XI	CH_3O-	CH_3CO_2-	C → I	166 (dec)
XII	CH_3CO_2-	CH_3O-	C_1 → I	146
			C_2 → I	154
			N → I	134[d]
XIII	C_2H_5O-	p-$CH_3OC_6H_4$-	C → N	180
			N → I	289 (dec)

[a] All compounds were characterized by IR, UV and NMR. Satisfactory elemental analyses were obtained in every case.

[b] C = crystal, N = nematic, S = smectic, I = isotropic liquid.

[c] In °C.

[d] Monotropic liquid crystal.

or are monotropic nematic. The middle members, VII and VIII, are enantiotropic nematic, and the long-chain homolog, IX, is enantiotropic smectic. This type of behavior is very common[12] as evidenced, for example, by the mesomorphic properties of *p*-alkoxybenzoic acid dimers[13] and *p*-alkoxybenzylidene-*p*-aminoacetophenones.[14] Gray has postulated that the lower members of a series might not show mesomorphism because the melting point may be higher than the predicted nematic-isotropic transition temperature[15]; also, Gray points out that smectic tendencies increase with the length of the alkoxy chain, since the lateral intermolecular attractions increase at the expense of terminal interactions.[16] These explanations appear to be quite satisfactory.

The nematic-isotropic transition temperatures for the ethoxy, butoxy, hexoxy, and octyloxy homologs, IV, VI, VII and VIII, when plotted against the number of carbons in the alkoxy chain, do not lie on a smooth, monotonic curve.[17] This is somewhat unusual, although precedent for this result can be found in the *p*-alkoxybenzylidene-*p*-aminoacetophenones.[14] We feel that the explanation offered by Castellano and McCaffrey[14b] is insufficient, since it is based on the assumption that the ratio of lateral to terminal interactions is very low. This is certainly not the case for the aldonitrones, which contain a strong N–O dipole, nor should it be true for the acetophenone derivatives, since *p*-*n*-propoxybenzylidene-*p*-aminoacetophenone exhibits a monotropic smectic phase.[14a] An alternative explanation must await additional physical measurements upon the homologous nitrones.

p-Azoxyanisole, one of the most well-known liquid crystals, has a nematic range of 118–136°.[18] This is in sharp contrast to the isoelectronic aldonitrone, III, which melts at 149° and shows no mesomorphism. The relatively high melting point of the nitrone may be masking its liquid crystal phase,[9] and this possibility is currently under investigation in our laboratories. Similarly, the azoxy analog of nitrone XII is reported to have an enantiotropic nematic range of 116–132°.[19] Compound XII, as seen in Table I, melts 30–40° higher but has a monotropic phase which turns isotropic at 134°. It would be attractive to attach significance to the proximity of these N → I transition temperatures, but this would be premature.

Acknowledgements

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8. Structural analogies are based on studies carried out in solution. Dr. A. Bednowitz is currently investigating the crystal structures of nitrones and azoxy compounds.
9. See Ref. 2, p. 159.
10. This synthesis is based on the preparation of N-anisyl-α-phenyl nitrone by Dr. H. K. Ono of Brandeis University. We are grateful to Dr. Ono for communicating his procedures prior to publication.
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