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# Liquid Crystals VII.† The Mesomorphic Behavior of Homologous *p*-Alkoxy-*p*′-Acyloxyazoxybenzenes

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**Abstract**—In a continued effort to synthesize compounds which exhibit nematic mesomorphism at room temperature, homologous *p*-alkoxy-*p*′-acyloxyazobenzenes and *p*-alkoxy-*p*′-acyloxyazoxybenzenes were prepared. The *p*-substituted groups were normal alkyl chains containing from one to seven carbon atoms. Of the 98 compounds which were prepared in both the azo and azoxy series, 87 exhibited enantiotropic and 3 monotropic nematic properties while only 8 showed smectic behavior. The azoxy " compounds " were generally lower melting than the azo compounds. This is presumably due to the fact that the former are mixtures of isomers (oxygen may be on nitrogen attached to the alkoxyphenyl group or on nitrogen attached to the acyloxyphenyl group). The higher nematic thermal stability of the azoxy materials compared to the azo compounds and to analogous Schiff base compounds may be attributed to broadening of the molecule as a result of the presence of a lateral oxygen atom. This would have the effect of increasing the terminal to lateral interactions.

## 1. Introduction

This paper$^{(1)}$ is the seventh in a series devoted to the preparation of nematic compounds which exhibit their properties at or below room temperature. The discovery of several unusual electro–optic effects in certain classes of nematic compounds$^{(2,3)}$ prompted this investigation. Much of our effort during the past several years has been directed toward the synthesis of Schiff base materials in order to accomplish this objective.$^{(1,4-7)}$ In the present study, however, the related compounds were not Schiff bases but were unsymmetrical, para-substituted azobenzene and azoxybenzene derivatives containing both alkoxy and ester groups.

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† This paper was presented at the 162nd National American Chemical Society Meeting in Washington, D.C., September 1971.

## 2. Experimental(8)

### *p*-ALKOXY-*p*′-ACYLOXYAZOBENZENES

The coupling of para-substituted alkoxyanilines (obtained from Aero Chemical Co., Newark, N.J.) with phenol was carried out by the conventional procedure of Vogel(9) to yield the corresponding *p*-alkoxy-*p*′-hydroxyazobenzene compounds. Esterification of the hydroxy group was accomplished by stirring 0.01 M of the phenolic azo compound with 0.011 M of the appropriate acyl anhydride in 50 ml of pyridine for a 12-hour period at room temperature. At the end of this time the mixture was poured over 200 ml of ice. The orange crystals which separated were washed with water, dried *in vacuo* and recrystallized from 2-propanol. Recrystallization from 2-propanol was repeated until the nematic–isotropic transitions were constant and reversible. The transition temperatures of the compounds in this series are presented in Table 1.

### *p*-ALKOXY-*p*′-ACYLOXYAZOXYBENZENES

The oxidation of the azo compounds was accomplished by a modified procedure previously described.(10) The resulting yellow azoxy compounds which were obtained in 50–70% overall yield were recrystallized from 2-propanol until the nematic–isotropic transitions were constant and reversible. The transition temperatures and thermodynamic data of the compounds in this series are presented in Table 2.

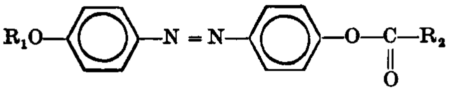
### *p*-ALKOXYBENZYLIDENE-*p*′-ACYLOXYANILINES

The preparation and purification of these compounds was accomplished by previously reported procedures.(4,5)

### DETERMINATION OF TRANSITION TEMPERATURES

Transition temperatures were determined with both a Thomas–Hoover melting point apparatus and a differential scanning calorimeter (DuPont Model 900 Thermal Analyzer). In the latter case, sample sizes were between 5 and 15 mg while the heating rate was 10° per minute. The materials were contained in hermetically sealed aluminum cups. The transition temperatures were reproducible within 1°. The transition enthalpies were obtained by

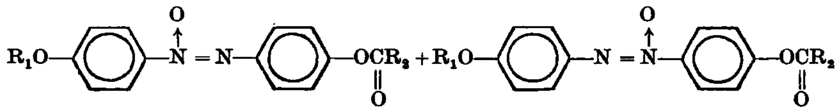
TABLE 1 *p*-Alkoxy-*p*′-Acyloxyazobenzenes



| No. | $R_1$ | $R_2$ | Crystal–Nematic Transition °C | Nematic–Isotropic Transition °C |
|---|---|---|---|---|
| 1 | $CH_3$ | $CH_3$ | — | 122 (112)[(a)] |
| 2 | $CH_3$ | $C_2H_5$ | 92 | 117 |
| 3 | $CH_3$ | $C_3H_7$ | 74 | 116 |
| 4 | $CH_3$ | $C_4H_9$ | 82 | 101 |
| 5 | $CH_3$ | $C_5H_{11}$ | 70 | 106 |
| 6 | $CH_3$ | $C_6H_{13}$ | 72 | 95 |
| 7 | $CH_3$ | $C_7H_{15}$ | 76 | 99 |
| 8 | $C_2H_5$ | $CH_3$ | 121 | 136 |
| 9 | $C_2H_5$ | $C_2H_5$ | 103 | 141 |
| 10 | $C_2H_5$ | $C_3H_7$ | 91 | 139 |
| 11 | $C_2H_5$ | $C_4H_9$ | 78 | 126 |
| 12 | $C_2H_5$ | $C_5H_{11}$ | 68 | 127 |
| 13 | $C_2H_5$ | $C_6H_{13}$ | 64 | 117 |
| 14 | $C_2H_5$ | $C_7H_{15}$ | 87 | 118 |
| 15 | $C_3H_7$ | $CH_3$ | — | 114 (109)[(a)] |
| 16 | $C_3H_7$ | $C_2H_5$ | 99 | 119 |
| 17 | $C_3H_7$ | $C_3H_7$ | 96 | 118 |
| 18 | $C_3H_7$ | $C_4H_9$ | 77 | 107 |
| 19 | $C_3H_7$ | $C_5H_{11}$ | 80 | 110 |
| 20 | $C_3H_7$ | $C_6H_{13}$ | 80 | 102 |
| 21 | $C_3H_7$ | $C_7H_{15}$ | 83 | 104 |
| 22 | $C_4H_9$ | $CH_3$ | 107 | 117 |
| 23 | $C_4H_9$ | $C_2H_5$ | 103 | 125 |
| 24 | $C_4H_9$ | $C_3H_7$ | 98 | 124 |
| 25 | $C_4H_9$ | $C_4H_9$ | 84 | 114 |
| 26 | $C_4H_9$ | $C_5H_{11}$ | 82 | 116 |
| 27 | $C_4H_9$ | $C_6H_{13}$ | 81 | 109 |
| 28 | $C_4H_9$ | $C_7H_{15}$ | 84 | 111 |
| 29 | $C_5H_{11}$ | $CH_3$ | 101 | 104 |
| 30 | $C_5H_{11}$ | $C_2H_5$ | 86 | 114 |
| 31 | $C_5H_{11}$ | $C_3H_7$ | 88 | 113 |
| 32 | $C_5H_{11}$ | $C_4H_9$ | 86 | 104 |
| 33 | $C_5H_{11}$ | $C_5H_{11}$ | 78 | 107 |
| 34 | $C_5H_{11}$ | $C_6H_{13}$ | 73 | 100 |
| 35 | $C_5H_{11}$ | $C_7H_{15}$ | 77 | 104 |
| 36 | $C_6H_{13}$ | $CH_3$ | 101 | 108 |
| 37 | $C_6H_{13}$ | $C_2H_5$ | 95 | 116 |
| 38 | $C_6H_{13}$ | $C_3H_7$ | 89 | 115 |
| 39 | $C_6H_{13}$ | $C_4H_9$ | 80 | 108 |
| 40 | $C_6H_{13}$ | $C_5H_{11}$ | 82 | 111 |
| 41 | $C_6H_{13}$ | $C_6H_{13}$ | 70 | 106 |
| 42 | $C_6H_{13}$ | $C_7H_{15}$ | 78 | 107 |
| 43 | $C_7H_{15}$ | $CH_3$ | 101 | 100 |
| 44 | $C_7H_{15}$ | $C_2H_5$ | 99 | 109 |
| 45 | $C_7H_{15}$ | $C_3H_7$ | 89 | 109 |
| 46 | $C_7H_{15}$ | $C_4H_9$ | 77 | 104 |
| 47 | $C_7H_{15}$ | $C_5H_{11}$ | 79 | 106 |
| 48 | $C_7H_{15}$ | $C_6H_{13}$ | 78 | 101 |
| 49 | $C_7H_{15}$ | $C_7H_{15}$ | 80 | 105 |

(a) Monotropic

TABLE 2 *p*-Alkoxy-*p*′-acyloxyazoxybenzene Isomers



| No. | $R_1$ | $R_2$ | Transition Temperatures, °C Nematic Range | Smectic Range | $\Delta H_f$ (cal/mole) CN or CS | SN | NL | $\Delta S$ (cal/°K mole) CN or CS | SN | NL | $R_f$[(b)] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $CH_3$ | $CH_3$ | 125–133 | — | 6326.3 | — | 160.2 | 16.18 | — | 0.40 | 0.367 |
| 2 | $CH_3$ | $C_2H_5$ | 82–127 | — | 2535.0[(a)] | — | 171.0 | 7.16 | — | 0.43 | 0.409 |
| 3 | $CH_3$ | $C_3H_7$ | 78–130 | — | 3121.9 | — | 175.8 | 11.27 | — | 0.44 | 0.456 |
| 4 | $CH_3$ | $C_4H_9$ | 87–116 | — | 4592.0 | — | 164.7 | 12.80 | — | 0.43 | 0.554 |
| 5 | $CH_3$ | $C_5H_{11}$ | 73–120 | — | 4032.2 | — | 198.4 | 11.72 | — | 0.51 | 0.586 |
| 6 | $CH_3$ | $C_6H_{13}$ | 77–110 | — | 3873.3 | — | 156.6 | 11.16 | — | 0.41 | 0.658 |
| 7 | $CH_3$ | $C_7H_{15}$ | 72–114 | — | 5886.7 | — | 207.2 | 17.21 | — | 0.54 | 0.694 |
| 8 | $C_2H_5$ | $CH_3$ | 98–151 | — | 3388.1[(a)] | — | 307.9 | 9.18 | — | 0.73 | 0.311 |
| 9 | $C_2H_5$ | $C_2H_5$ | 99–152 | — | 4172.0[(a)] | — | 250.3 | 11.34 | — | 0.59 | 0.373 |
| 10 | $C_2H_5$ | $C_3H_7$ | 84–151 | — | 4391.4 | — | 265.2 | 12.41 | — | 0.63 | 0.440 |
| 11 | $C_2H_5$ | $C_4H_9$ | 69–136 | — | 4906.3 | — | 224.9 | 14.52 | — | 0.55 | 0.415 |
| 12 | $C_2H_5$ | $C_5H_{11}$ | 81–138 | — | 6538.2 | — | 312.8 | 18.63 | — | 0.76 | 0.575 |
| 13 | $C_2H_5$ | $C_6H_{13}$ | 66–129 | — | 5214.4 | — | 251.3 | 15.43 | — | 0.63 | 0.586 |
| 14 | $C_2H_5$ | $C_7H_{15}$ | 77–130 | — | 6653.4 | — | 279.7 | 19.17 | — | 0.70 | 0.601 |
| 15 | $C_3H_7$ | $CH_3$ | 86–123 | — | 1190.1[(a)] | — | 219.8 | 3.32[(a)] | — | 0.56 | 0.451 |
| 16 | $C_3H_7$ | $C_2H_5$ | 89–118 | — | 2076.2[(a)] | — | 187.0 | 5.83[(a)] | — | 0.48 | 0.487 |
| 17 | $C_3H_7$ | $C_3H_7$ | 77–127 | — | 4097.2 | — | 215.5 | 11.77 | — | 0.54 | 0.544 |
| 18 | $C_3H_7$ | $C_4H_9$ | 70–117 | — | 5693.9 | — | 191.3 | 16.75 | — | 0.49 | 0.601 |
| 19 | $C_3H_7$ | $C_5H_{11}$ | 69–119 | — | 5172.3 | — | 218.3 | 15.26 | — | 0.56 | 0.637 |
| 20 | $C_3H_7$ | $C_6H_{13}$ | 67–111 | — | 5540.6 | — | 218.9 | 16.34 | — | 0.57 | 0.731 |
| 21 | $C_3H_7$ | $C_7H_{15}$ | 68–115 | — | 5476.5 | — | 246.8 | 16.13 | — | 0.64 | 0.762 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 22 | $C_4H_9$ | $CH_3$ | 81–130 | — | 4782.2(a) | — | 288.6 | 13.59 | — | 0.72 | 0.430 |
| 23 | $C_4H_9$ | $C_2H_5$ | 82–134 | — | 6287.0 | — | 239.4 | 17.86 | — | 0.59 | 0.409 |
| 24 | $C_4H_9$ | $C_3H_7$ | 79–135 | — | 4802.4 | — | 210.0 | 13.76 | — | 0.52 | 0.508 |
| 25 | $C_4H_9$ | $C_4H_9$ | 66–118 | — | 5322.6 | — | 236.8 | 16.18 | — | 0.61 | 0.549 |
| 26 | $C_4H_9$ | $C_5H_{11}$ | 64–125 | — | 5385.6 | — | 268.8 | 16.08 | — | 0.67 | 0.617 |
| 27 | $C_4H_9$ | $C_6H_{13}$ | 64–120 | — | 5408.1 | — | 262.7 | 16.14 | — | 0.67 | 0.634 |
| 28 | $C_4H_9$ | $C_7H_{15}$ | 63–122 | — | 5689.7 | — | 292.5 | 16.98 | — | 0.74 | 0.679 |
| 29 | $C_5H_{11}$ | $CH_3$ | 83–118 | — | 4938.5 | — | 194.9 | 13.99 | — | 0.50 | 0.420 |
| 30 | $C_5H_{11}$ | $C_2H_5$ | 71–124 | — | 3866.8(a) | — | 160.2 | 11.31 | — | 0.41 | 0.484 |
| 31 | $C_5H_{11}$ | $C_3H_7$ | 66–126 | — | 4603.7 | — | 210.9 | 13.70 | — | 0.53 | 0.521 |
| 32 | $C_5H_{11}$ | $C_4H_9$ | 58–117 | — | 5607.4(a) | — | 207.4 | 17.15 | — | 0.53 | 0.590 |
| 33 | $C_5H_{11}$ | $C_5H_{11}$ | 59–119 | — | 4241.5(a) | — | 210.9 | 12.89 | — | 0.54 | 0.622 |
| 34 | $C_5H_{11}$ | $C_6H_{13}$ | 58–115 | 54–57 | 4587.7 | 230.7 | 156.6 | 14.20 | 0.70 | 0.41 | 0.590 |
| 35 | $C_5H_{11}$ | $C_7H_{15}$ | 67–117 | 58–56 | 6926.8 | 315.2 | 259.9 | 21.24 | 0.93 | 0.67 | 0.692 |
| 36 | $C_6H_{13}$ | $CH_3$ | 82–123 | — | 3734.4(a) | — | 245.6 | 10.70(a) | — | 0.62 | 0.415 |
| 37 | $C_6H_{13}$ | $C_2H_5$ | 68–128 | — | 4454.8(a) | — | 214.6 | 13.14 | — | 0.54 | 0.473 |
| 38 | $C_6H_{13}$ | $C_3H_7$ | 66–128 | — | 6086.4 | — | 280.3 | 18.17 | — | 0.70 | 0.537 |
| 39 | $C_6H_{13}$ | $C_4H_9$ | 68–119 | — | 4919.3 | — | 214.9 | 14.51 | — | 0.55 | 0.601 |
| 40 | $C_6H_{13}$ | $C_5H_{11}$ | 66–122 | — | 5372.5 | — | 304.9 | 15.99 | — | 0.77 | 0.622 |
| 41 | $C_6H_{13}$ | $C_6H_{13}$ | 72–119 | 60–71 | 5878.8 | 357.8 | 276.9 | 17.76 | 1.04 | 0.71 | 0.654 |
| 42 | $C_6H_{13}$ | $C_7H_{15}$ | 80–121 | 62–79 | 5812.4 | 299.2 | 259.6 | 17.45 | 0.85 | 0.66 | 0.702 |
| 43 | $C_7H_{15}$ | $CH_3$ | 77–117 | — | 1838.9(a) | — | 236.8 | 5.25 | — | 0.61 | 0.457 |
| 44 | $C_7H_{15}$ | $C_2H_5$ | 75–119 | — | 2860.8(a) | — | 172.8 | 8.22 | — | 0.44 | 0.521 |
| 45 | $C_7H_{15}$ | $C_3H_7$ | 61–123 | — | 3526.3 | — | 175.1 | 10.65 | — | 0.44 | 0.596 |
| 46 | $C_7H_{15}$ | $C_4H_9$ | 71–117 | 69–70 | 5339.5 | 370.8 | 185.4 | 15.75 | 1.08 | 0.48 | 0.628 |
| 47 | $C_7H_{15}$ | $C_5H_{11}$ | 78–120 | 68–77 | 3995.9 | 328.0 | 238.6 | 11.75 | 0.94 | 0.61 | 0.644 |
| 48 | $C_7H_{15}$ | $C_6H_{13}$ | 85–117 | 61–84 | 5038.0 | 356.4 | 242.0 | 15.22 | 1.00 | 0.62 | 0.654 |
| 49 | $C_7H_{15}$ | $C_7H_{15}$ | 90–118 | 62–89 | 5520.6 | 340.5 | 349.6 | 16.53 | 0.94 | 0.89 | 0.718 |

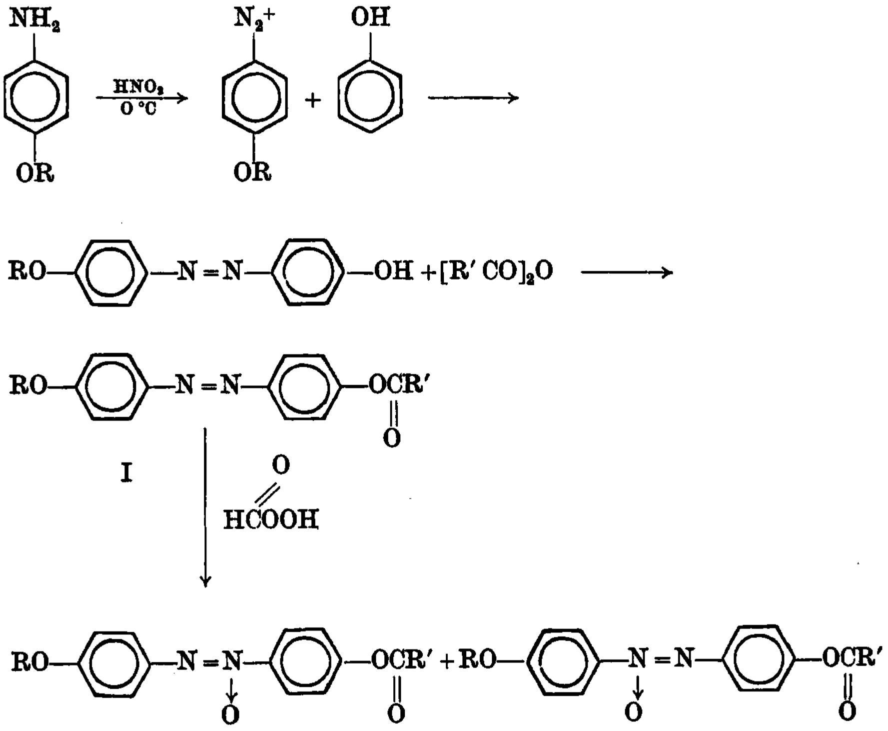
(a) Solid-solid transitions prior to observed melting point.

(b) $R_f$ values for thin-layer chromatography on Brinkmann F-254 silica gel plates (0.25 mm thick) with benzene as solvent.

graphic integration of the peaks at the various temperatures. The instrument constant was determined by calibrating with a number of standard compounds.

## 3. Discussion

*p*-Azoxyanisole and *p*,*p*′-dialkoxyazoxybenzenes are among the most widely known materials that form liquid crystals. Most of the definitive synthetic work on this class of materials was performed some years ago. Attempts to prepare azoxy compounds which exhibit nematic properties at ambient temperatures have been reported only very recently. Steinstrasser and Pohl(11) reported the preparation of a series of *p*-alkyl-*p*′-alkoxy- and *p*-alkyl-*p*′-acyloxy-azoxybenzenes which had melting points below 40 °C. Our investigation was concerned with the preparation of a series of *p*-alkoxy-*p*′-acyloxyazo and azoxy benzenes which were prepared according to the following synthetic route:



I

The *p*-substituted groups were normal alkyl chains containing from one to seven carbon atoms. The transition temperatures and thermodynamic properties are presented in Tables 1 and 2.

In order to facilitate a better understanding of the effects of changes in molecular structure as a function of mesomorphic behavior, a series of phase transition plots were constructed. These illustrate the changes in the phase transition temperatures and changes in entropy with an increase in the length of an alkyl chain attached to one of the terminal positions of the molecule.

The general relationships that hold true for the majority of homologous series of mesomorphic compounds(12) also hold true for the series of azo compounds; that is, a regular alternation of the nematic-isotropic transition temperatures occurs when the temperatures are plotted against the number of carbon atoms in the alkyl chain. In addition, the melting points decrease with increasing length of the alkyl chain (Fig. 1). Since the melting characteristics of a compound are largely determined by the strength of intermolecular interactions in the crystal lattice, it follows that a reduction in the strength of these interactions by the separation of the active centers of charge would produce lower melting materials.

In this series monotropic behavior was observed for the *p*-alkoxyphenylazo-*p'*-phenyl acetates when the alkoxy portion contained one, three and seven carbon atoms. When the chain length was five carbon atoms a very narrow nematic phase was observed. When the alkoxy portion contained two carbon atoms increasing the chain length in the ester portion resulted in a compound ($n = 5$) with the lowest crystal-nematic transition in the series. The greatest thermal stability was also observed in this set at $n = 1$ as well as the broadest mesomorphic ranges.

As the ether portion is extended a gradual decrease in the magnitude of the nematic–isotropic transition is seen. A difference of 24 °C between the high and the low NL in the ethoxy homologs to a difference of 9 °C in the heptyloxy homologs was observed.

No smectic mesomorphism occurred for any member of this particular series. Even though an increase in the chain length of both the alkoxy and the acyloxy portions of the molecule generally results in decreased terminal and increased lateral interactions, the lack of a dipole operating across the long axis of the molecule at the

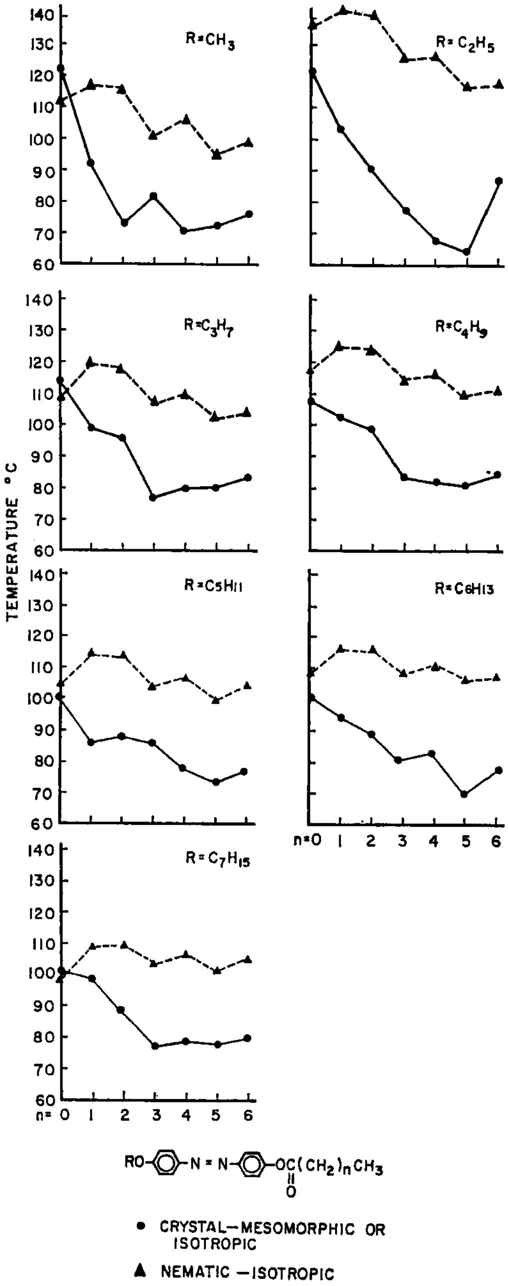


Figure 1. Phase transition plots for the *p*-alkoxy-*p*′-acyloxyazobenzenes.

central linkage does not provide the molecule with sufficient lateral attractive forces to induce smectic formation, at least for the seven alkoxy members of the series that were prepared.

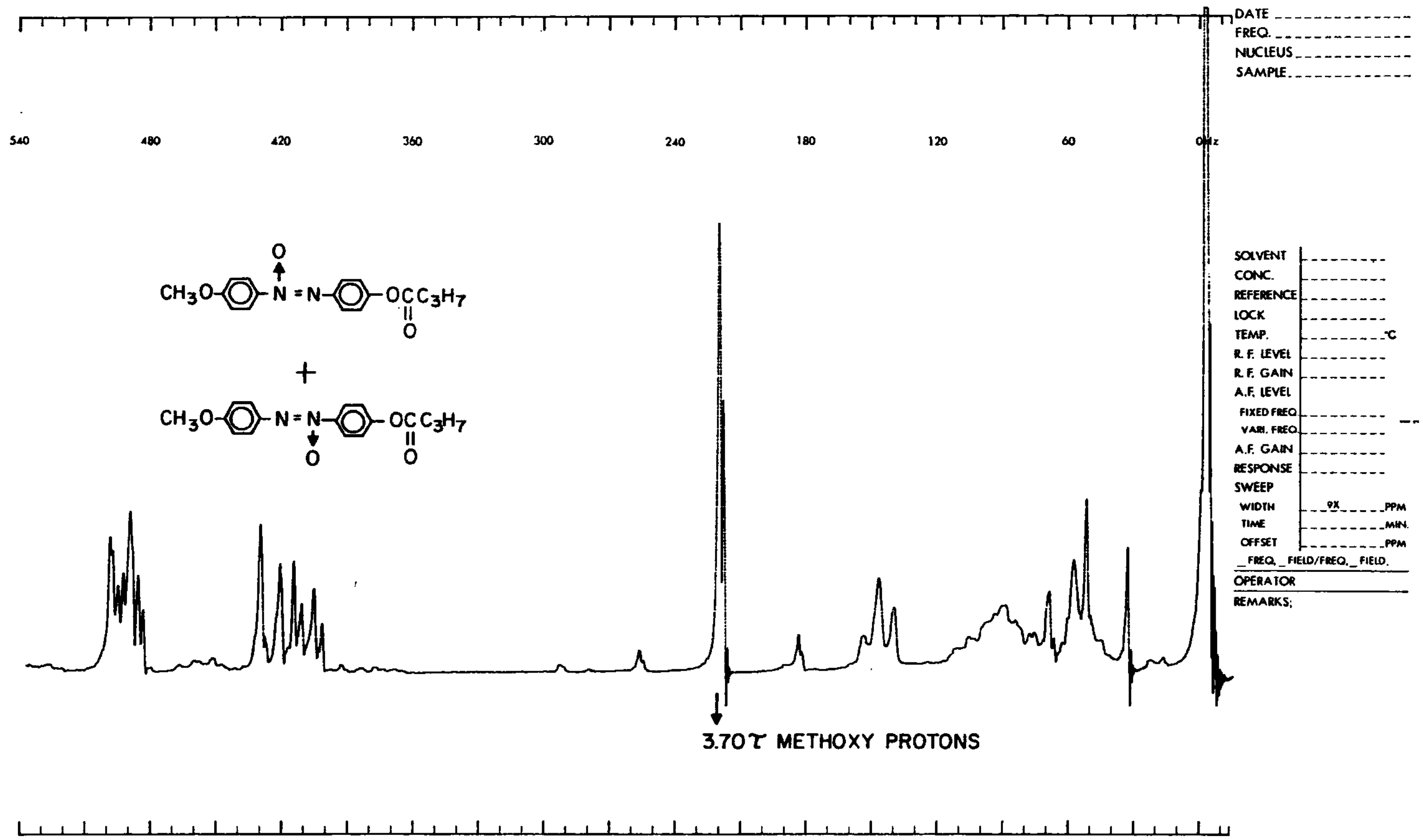
As will be seen with the azoxy compounds and the previously reported benzylidene anilines, the presence of the dipole does induce smectic behavior in the highest homologs.

The $p$-alkoxy-$p'$-acyloxyazoxybenzenes have much broader mesomorphic ranges, greater nematic thermal stabilities and lower crystal–nematic transitions than the corresponding azo series. This behavior is most certainly a result of the transverse dipole created by the addition of the oxygen atom at the central linkage. However, since the oxygen atom protrudes laterally from the molecule, the lateral attractive forces induced by the dipole are somewhat lessened by the increased breadth of the molecule. Consequently, terminal interactions are strong enough to ensure higher nematic thermal stabilities when compared with the corresponding azo compounds.

The co-planar conformation of the aromatic rings in the azobenzene molecule may also partly explain the higher melting points of series I when compared with the azoxy compounds of series II. The presence of the oxygen atom in the azoxy molecule disrupts the co-planarity of the rings thus contributing to a less densely packed crystal lattice which results in lower melting compounds.

A further complicating factor affecting the melting point is the fact that the individual azoxy homologs are really mixtures of the two possible isomers; the oxygen can be attached to the nitrogen nearest the alkoxy portion of the molecule or to the nitrogen farthest from the alkoxy group. NMR studies conducted by Steinsträsser(11) on the series of $p$-alkyl-$p'$-alkoxy and $p$-alkyl-$p'$-acyloxyazoxybenzenes confirmed that a mixture of the two isomers does exist. Separation of the isomers by gas–liquid chromatography has also been reported.(13) Our own limited NMR studies showed that a marked splitting of the alkoxy proton signals occurs in the spectra obtained with the compounds of series II. One example is shown in Fig. 2.

When the alkoxy chain in series II contained one carbon atom and the acyloxy chain contained from one to seven carbon atoms, the melting points observed were higher than the corresponding azo analogs (Fig. 3). For example, the first member of series II has a crystal–nematic transition which occurs at a fairly high temperature.



3.70 τ METHOXY PROTONS

Figure 2. NMR spectrum of isomeric *p*-methoxy-*p*′-butanoyloxyazoxybenzenes.

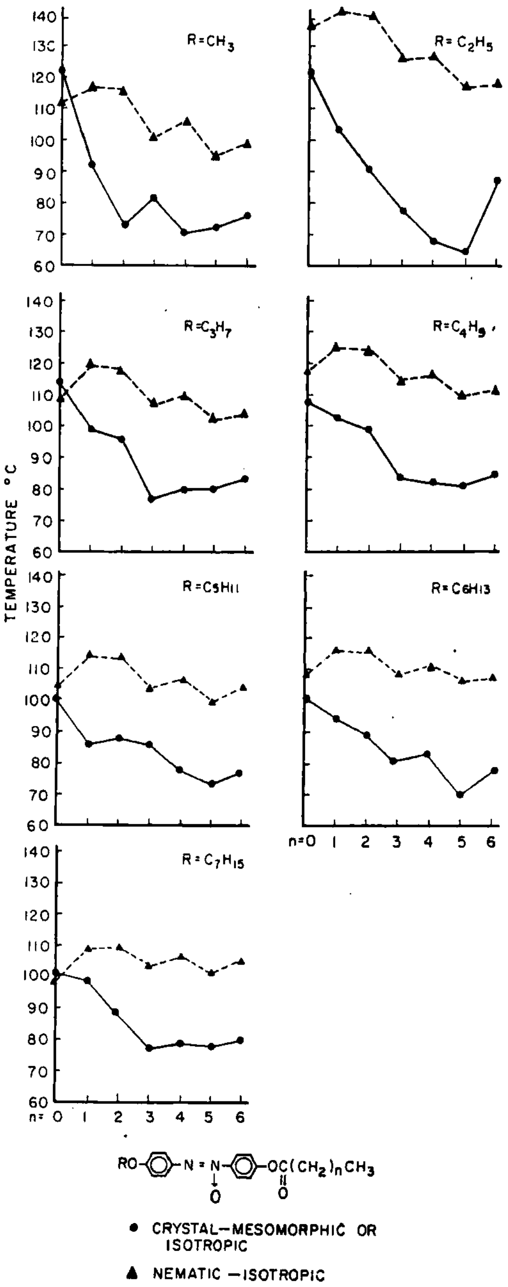


Figure 3. Phase transition plot for the *p*-alkoxy-*p*′-acyloxyazoxybenzenes.

The analogous azo compound showed monotropic behavior. This is also the only azoxy compound to exhibit a mesomorphic range of less than 29 °C.

When the alkoxy group contained two carbon atoms, the broadest mesomorphic ranges in the series were observed—an average of 59 °C. These compounds also had the highest nematic thermal stabilities.

With the alkoxy chain lengths at three and four carbon atoms, the longer ester chains produce small decreases in the crystal-nematic transition while the nematic-isotropic transitions show typical odd-even effects. The mesomorphic ranges for the last five homologs in this series level off at approximately 55 °C.

With the alkoxy chain set at five carbon atoms, an increase in the length of the ester chain resulted in the lowest melting compounds of the series. Because of reduced terminal interactions due to the separation of the polarizable ester linkage and subsequent increase in the lateral interactions, smectic behavior was introduced. The ranges are relatively small to begin with but gradually increase as the ether chain is extended to seven carbon atoms. As observed by Gray,(12) an increasing chain length causes increases in the smectic thermal stability because of a decrease in the ratio of terminal to lateral cohesions.

A comparison of transition temperatures for *p*-alkoxy-*p*′-acyloxy-azoxybenzenes, azobenzenes and benzylidene anilines was made in order to evaluate the effects of the central linkage on mesomorphic behavior. In 1938, Weygand and Gabler(14) conducted a similar study of *p*,*p*′-dialkoxy azoxybenzenes, azobenzenes and benzylidene anilines. Their results for compounds with chain lengths of five carbon atoms or less indicated a pattern for nematic thermal stabilities as follows: azoxy greater than azo greater than Schiff base. Young, Haller and Aviram(15) in their work on homologous nitrones made the same comparisons, the nitrone falling between the azoxy and azo in stability for its nematic phase.

In our study (Fig. 4), the azoxy homologs were found to have the highest stabilities, the benzylidene anilines the lowest, while the azo homologs fell intermediate between the two. This relationship is true for alkoxy chains with up to four carbon atoms and acyloxy chains with up to seven carbon atoms. However, when the alkoxy chain is increased from five to seven carbon atoms, the azo and

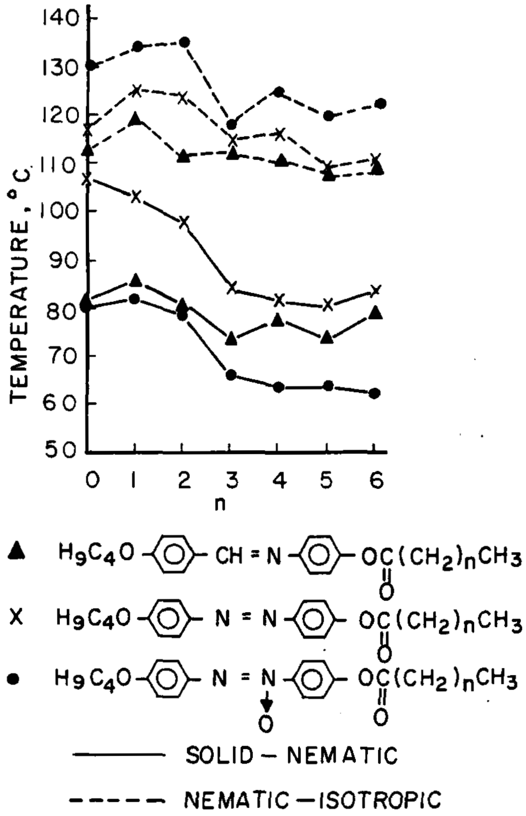


Figure 4. Phase transition plots for Schiff bases, azo and azoxybenzene derivatives.

benzylidene aniline stabilities overlap with the Schiff base stabilities predominating. The relationship of azoxy to azo remains the same throughout the entire series.

A study of the heats of transition for the azoxy derivatives showed no anomalous behavior. The enthalpies and derived entropies for the crystal-nematic transitions, as expected, showed no predictable trends when plotted against increasing chain length. However, the entropies for the nematic-isotropic transition when plotted against ascending chain length showed the now familiar odd-even relationship (Figs. 5 and 6). This has also been reported by Haller and Cox⁽¹⁶⁾ for substituted Schiff bases and by Arnold⁽¹⁷⁾ for *p,p*′-dialkoxyazoxybenzenes. The only definite conclusion that can be drawn from the

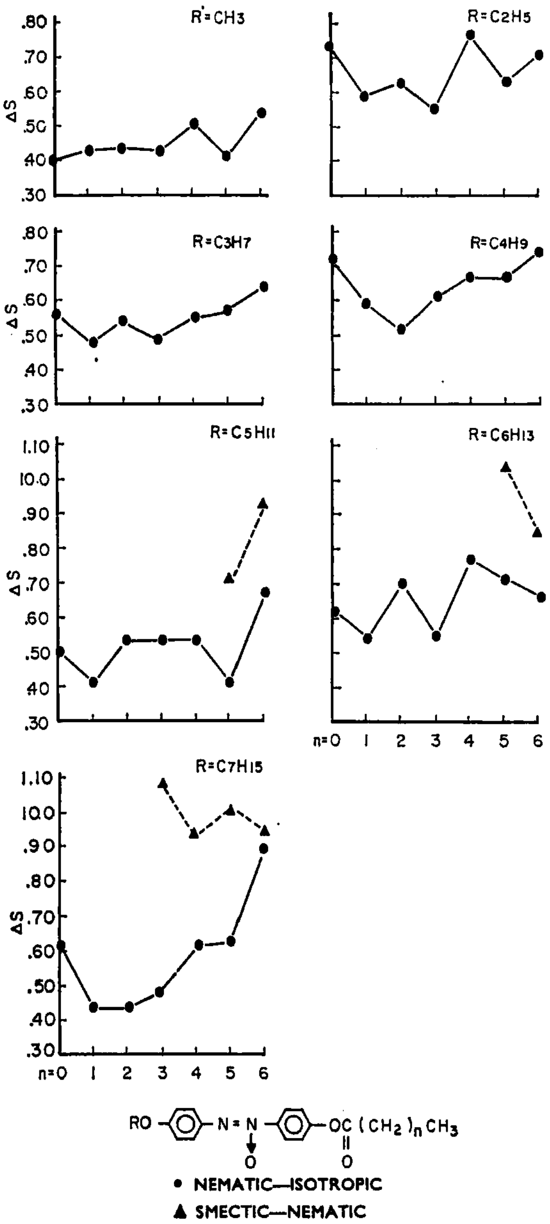


Figure 5. Entropy-chain length relationships for *p*-alkoxy-*p*′-acyloxyazoxybenzenes.

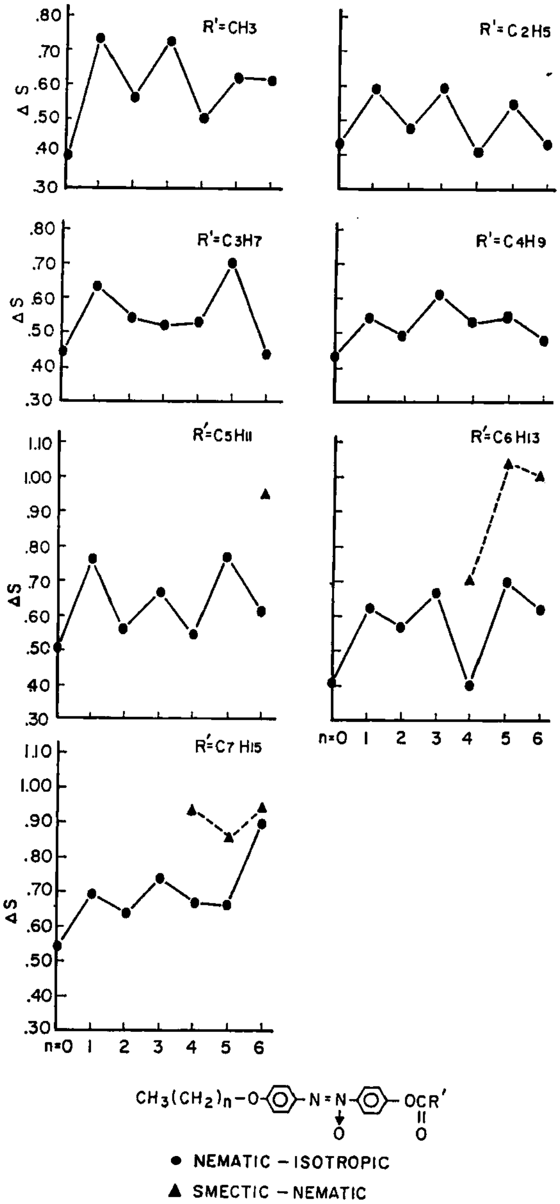


Figure 6. Entropy-chain length relationships for $p$-alkoxy-$p'$acyloxyazoxybenzenes.

rather familiar results is that the lack of sufficient increments of change in the entropy at the nematic–isotropic transition for each increase in the chain length indicates that terminal alkyl chains do not exist in a single elongated conformation in the nematic state. This is in agreement with the previously reported results of Young *et al.*(15)

## 4. Conclusions

Some general observations can now be made concerning mesomorphic azo and azoxybenzene derivatives:

(1) Azoxy compounds have more thermally stable nematic mesophases than their azo counterparts. This has been attributed to the presence of a transverse dipole in the azoxy group. The average difference between the nematic stabilities of the two series shows a maximum for the methyl ethers and a decrease through the propyl ethers, a minimum for the butyl ethers and an increase through the heptyl ethers.

(2) The melting points of azoxy compounds are lower than the corresponding azobenzenes. The co-planarity of the aromatic rings in the azo derivatives allows for dense packing in the crystal lattice and hence high melting points. A second contributing factor to the differences in melting point is that the azoxy derivatives are obtained as isomeric mixtures.

(3) The broadest mesomorphic ranges for both the azo and azoxy series[1] were observed when the alkoxy chain contained two carbon atoms and the acyloxy portion was increased through seven carbon atoms. The mesomorphic ranges for the azoxybenzenes steadily increase over the ranges for the azobenzenes as the alkoxy and acyloxy chain lengths are increased through seven carbon atoms.

(4) No smectic behavior was observed for the azo derivatives over the range covered. This is probably due to a lack of a transverse dipole at the central linkage. However, smectic behavior appeared in the azoxy series when the total of carbon atoms in both chains was 11, 12, 13 and 14. This trend is similar in other homologous series.

(5) The unusually small increments in entropy for nematic-isotropic transitions per increase in methylene group indicate that

terminal alkyl chains cannot exist in a single, elongated conformation in the nematic state.

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### REFERENCES

1. For the previous paper in this series, see C. S. Oh, Abstracts of Papers presented at the National ACS Meeting, Washington, D.C., September 1971.
2. Heilmeier, G. H., Zanoni, L. A. and Barton, L. A., *Proc. IEEE* **56,** 1162 (1968).
3. Heilmeier, G. H., Castellano, J. A. and Zanoni, L. A., *Mol. Cryst. and Liq. Cryst.* **83,** 293 (1969).
4. Castellano, J. A., Goldmacher, J. E., Barton, L. A. and Kane, J. S., *J. Org. Chem.* **33,** 3503 (1968).
5. Castellano, J. A. and Goldmacher, J. E.: U.S. Patent 3,540,796 (1970).
6. Goldmacher, J. E. and McCaffrey, M. T., *Liquid Crystals and Ordered Fluids*, Plenum Press, 1970, p. 375.
7. Castellano, J. A. and McCaffrey, M. T., *Liquid Crystals and Ordered Fluids*, Plenum Press, 1970, p. 293.
8. Satisfactory analysis was obtained for each compound. The purity of the materials was 99.9%.
9. Vogel, A. I., *Practical Organic Chemistry*, 3rd ed., 1966, p. 622.
10. Castellano, J. A., Green, J. and Kauffman, J. M., *J. Org. Chem.* **31,** 821 (1966).
11. Steinsträsser, R. and Pohl, L., *Tetrahedron Letters*, 1921 (1971).
12. Gray, G. W., *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, 1962.
13. Kelker, H., Scheurle, B., Hatz, R. and Bartsch, W., *Angew Chem.*, **82,** 987 (1970).
14. Weygard, C. and Gabler, R., *Chem. Ber.* **71B,** 2399 (1938).
15. Young, W. R., Haller, I. and Aviram, A., *IBM J. Res. Develop.* **15,** 41 (1971).
16. Haller, I. and Cox, R. J., *Liquid Crystals and Ordered Fluids*, Plenum Press, 1970, p. 393.
17. Arnold, H., *Mol. Cryst. and Liq. Cryst.* **2,** 63 (1966).