Irradiation Experiments. In each experiment 100 ml of the purified organic compound was placed in one of the tubes (7a or 7b). During irradiation, the compound was distilled from one tube to the other by keeping the distillation tube at a somewhat higher temperature than the receiver tube. When the distillation was complete the temperature difference between the tubes was reversed and the distillation repeated in the opposite direction. Reversals of direction of distillation were repeated until the end of the irradiation. The pressure of the vapors in the cell was adjusted by controlling the temperature at both tubes, 7a and 7b.

The inert gases which were added in some experiments flowed through the cell slowly at a controlled pressure. After 1 hr of irradiation the products and the remaining starting material were collected in one tube and analyzed. The relative quantities of the products were then estimated by the peak areas of the gas chromatogram.

Central Linkage Influence upon Mesomorphic and Electrooptical Behavior of Diaryl Nematics. A General Proton Magnetic Resonance Method Employing a Lanthanide Shift Reagent for Analysis of Isomeric Azoxybenzenes

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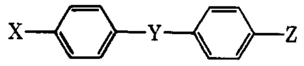
Abstract: The influence of the central linkage on the mesomorphic and electrooptical behavior of diaryl structures with low-temperature nematic potential is examined. The nematic to isotropic transitions for a wide variety of diaryl structures exhibit a parallel behavior for center linkage variation within a homologous series. No corresponding parallelism for the crystal to nematic transitions is present. The relative ordering of nematic thermal stability for 15 central linkages is examined for the 4-*n*-butyl-4′-methoxydiaryl derivatives. Low-temperature diaryl nematic systems are possible with a wide variety of central linkages. Several of these systems are examined with regard to the influence of the central linkage upon their ability to light scatter when electrically activated. Application of a new lanthanide shift reagent, tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)-europium(III), [Eu(fod)$_3$], to determine isomeric distributions of several unsymmetrical azoxybenzene mixtures is described. Upfield shifts are observed for protons on the 4,4′ substituents. This anomaly is discussed in terms of the expression for the pseudocontact interaction.

The majority of reported[2] nematic mesophases occur at substantially elevated temperatures. Recent discoveries utilizing the nematic mesophase as an anisotropic solvent for spectroscopy[3] and as a substrate exhibiting an important electrooptical response[4] have placed increasing importance on the development of room temperature nematic activity. Within the diaryls,



whether as single compounds[5] or mixtures,[6] this search has been primarily restricted to anils. We were concerned with the influence of the central linkage upon diaryl structures with low temperature nematic potential.

A structural problem related to the assignment of oxygen in unsymmetrical diaryls with an azoxy central linkage arose. The presence of a formal negative charge on oxygen makes azoxybenzenes relatively strong Lewis bases and susceptible to structural elucidation *via* lanthanide shift reagents. Both the emergence[7] of shift reagents as tools for structure determination and the recent disclosures[8] related to the polarizing and structural influence of central linkages upon mesomorphic activity within the diaryls prompted us to report our results.

Results

The relative ordering of nematic thermal stability for 15 central linkages is shown in Table I and the effect of central linkage variation within a homologous series in Figure 1. The results of the influence of the central

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(1) (a) Wright-Patterson Air Force Base; (b) Wright State University.

(2) W. Kast in "Landolt-Bornstein," 6th ed, Vol. II, Part 2a, Springer-Verlag, Berlin, 1960, p 266.

(3) Nmr and esr: (a) C. T. Yim and F. R. Gilson, *Can. J. Chem.*, **47**, 1057 (1969); (b) P. Diehl and C. L. Khetrapal, *Mol. Phys.*, **15**, 633 (1968); (c) A. Saupe, *Angew. Chem., Int. Ed. Engl.*, **7**, 97 (1968); (d) C. F. Schwerdtfeger and P. Diehl, *Mol. Phys.*, **17**, 417 (1969). Ir and uv: (e) R. A. Levenson, H. B. Gray, and G. P. Ceasar, *J. Amer. Chem. Soc.*, **92**, 3653 (1970).

(4) (a) G. H. Heilmeier and J. E. Goldmacher, *Proc. IEEE*, **57**, 34 (1969); (b) G. H. Heilmeier, A. Zanoni, and L. A. Barton, *ibid.*, **56**, 1162 (1968).

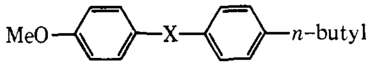
(5) (a) J. A. Castellano, J. E. Goldmacher, L. A. Barton, and J. S. Kane, *J. Org. Chem.*, 33, 3501 (1968); (b) J. A. Castellano and M. T. McCaffrey "Liquid Crystals and Ordered Fluids," J. F. Johnson and R. S. Porter, Ed., Plenum Press, New York, N. Y., 1970, p 293; (c) J. E. Goldmacher and M. T. McCaffrey, ref 5b, p 375; (d) I. Teucher, C. M. Paleos, and M. M. Labes, *Mol. Cryst. Liquid Cryst.*, **11**, 187 (1970); (e) H. M. Rosenberg and R. A. Champa, *ibid.*, 191 (1970); (f) H. Kelker and B. Scheurle, *Angew. Chem., Int. Ed. Engl.*, **8**, 884 (1969); (g) H. Kelker and B. Scheurle, *J. Phys. (Paris), Suppl.*, **30**, C4-104 (1969).

(6) (a) J. S. Dave, P. R. Patel, and K. L. Vasanth, *Mol. Cryst. Liquid Cryst.*, **8**, 93 (1969); (b) J. S. Dave and J. M. Lohar, *J. Chem. Soc. A*, 1473 (1967).

(7) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

(8) (a) M. J. S. Dewar and R. S. Goldberg, *ibid.*, **92**, 1582 (1970); (b) H. Kelker, B. Scheurle, R. Hatz, and W. Bartsch, *Angew. Chem., Int. Ed. Engl.*, **9**, 962 (1970).

Table I. Central Linkage Variation

	-X-		Crystal to nematic, °C	Nematic to isotropic, °C
1	$-CH{=}CH-$	Enantiotropic	118	121
2	$-C{\equiv}C-$	Monotropic 37; crystal to isotropic 49		
3	$-N{=}N-$	Enantiotropic	32[a]	49[a]
4	$-O\overset{\overset{O}{\Vert}}{C}O-$	Mesophase not observed; mp 28°		
5	-O-	Mesophase not observed; liquid at room temp		
6	None	Mesophase not observed; mp 69°		
7	$-CH{=}N-$	Enantiotropic	21[b]	46[b]
8	$-N{=}CH-$	Enantiotropic	46[c]	49[c]
9	$-CH{=}\overset{\overset{O^-}{\vert}}{N_+}-$	Monotropic 53; crystal to isotropic 113		
10	$-\overset{\overset{^-O}{\vert}}{N_+}{=}CH-$	Monotropic 70; crystal to isotropic 108		
11	$-N{=}\overset{\overset{O^-}{\vert}}{N_+}-$	Enantiotropic	41[d]	74[d]
12	$-\overset{\overset{^-O}{\vert}}{N_+}{=}N-$	Enantiotropic	42[d]	77[d]
13	$-\overset{\overset{O}{\Vert}}{C}O-$	Monotropic 24; crystal to isotropic 40		
14	$-O\overset{\overset{O}{\Vert}}{C}-$	Monotropic ~22; crystal to isotropic 63		
15	$-\overset{\overset{O}{\Vert}}{C}NH-$	Mesophase not observed; mp 145°		

[a] Lit.[8b] c → n = 32, n → i = 42, extremely light sensitive. [b] Lit. c → n = 20,[5f] 22,[8b] n → i = 41,[5f] 47–48.[8b] [c] Lit.[5e] c → n = 46, n → i = 48. [d] Structure assignment based upon the lit.[8b] values: **11**, c → n = 41, n → i = 69; **12**, c → n = 43, n → i ≥ 71 is subject to considerable ambiguity due to the depressed n → i values.

linkage upon electrically induced light scattering appear in Figure 2.

All of the compounds examined in this study were obtained *via* conventional synthetic techniques as detailed in the Experimental Section. Structural assignments were made by routine spectroscopic methods with the exception of the azoxy isomers, **11** and **12**. Figure 3 depicts the separation of the coincident resonances of the nonequivalent protons from both structural isomers with tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium(III), $[Eu(fod)_3]$. Comparison of the shifting patterns in Figure 4 with those of the known 4- and 4′-methoxyazoxybenzenes[9] and the two isoelectronic nitrones, **9** and **10**, allows the oxygen position to be unambiguously assigned. Table II summarizes the data which illustrate the generality of this technique.

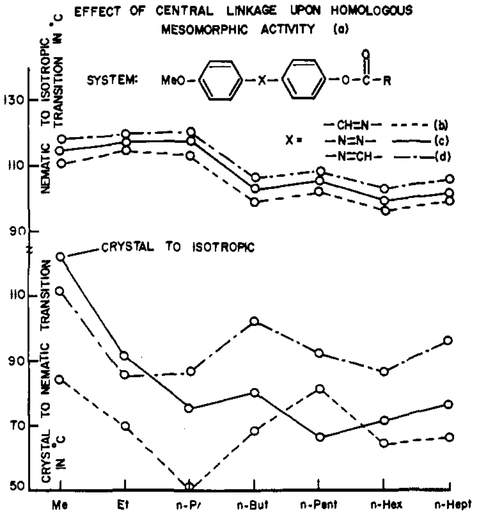


Figure 1. (a) Partial literature data: anil (b), Me to *n*-Pent;[5g] azo (c), Me to *n*-Hept [D. Vorlander, *Z. Phys. Chem.*, **126**, 449 (1927)]; anil (d), Me[2] give several incorrect values.

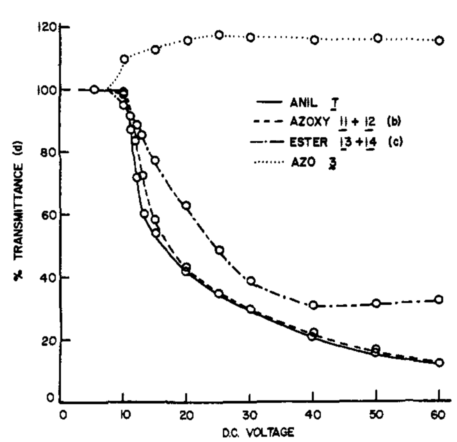


Figure 2. (a) At 22° with materials having $1-2 \times 10^{10}$ Ω cm resistance encapsulated in a 25-μ layer between two SnO_2 electrodes. Microscopic examination revealed light scatter due to a dynamic[4] mechanism. (b) Mole ratio **11**:**12** = 1:1; nematic range 18–75°. (c) Mole ratio **13**:**14** = 2:1; nematic range 14–23°. (d) The decrease in intensity of a collimated white light source passed through the cell due to light scatter >3°.

Discussion

The terminal substituents X, Z = methoxy, *n*-butyl were selected for study of the effect of central linkage variation upon nematic mesomorphic thermal stability since these are the substituents associated with the only known enantiotropic, room temperature, nematic: *N*-(4′-methoxybenzylidene)-4-*n*-butylaniline.[5f] Considerable mesomorphic activity was observed for the diaryls in Table I and established the relative ordering of nematic thermal stability as a function of the central linkage, though room temperature nematic activity remained unique to the anil,[5f] **7**. Improvement in nematic thermal stability was associated with a corresponding rise in crystalline stability. Mesomorphic activity was not observed with linkages which distorted the molecular geometry from the required[10] rod-shaped structure; yet, rigidly enforcing a

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(9) C. S. Hahn and H. H. Jaffe, *J. Amer. Chem. Soc.*, **84**, 949 (1962).

(10) (a) G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press, New York, N. Y., 1962; (b) G. W. Gray, *Mol. Cryst. Liquid Cryst.*, **7**, 127 (1969).

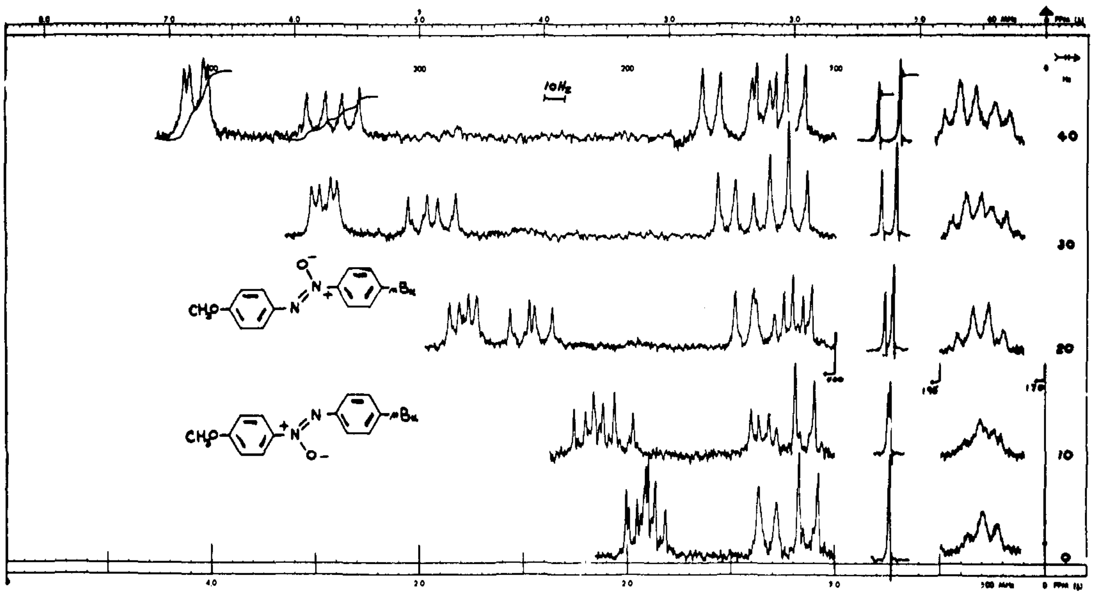


Figure 3. 60-MHz pmr spectra of mixture (28 mg, 1.0×10^{-4} mol) in 0.5 ml of CCl_4 containing 0–40 mg (4.0×10^{-5} mol) of $Eu(fod)_3$. Frequency offsets of 170, 195, and 400 Hz were used for $ArCH_2$–, MeO–, and aromatic protons, respectively.

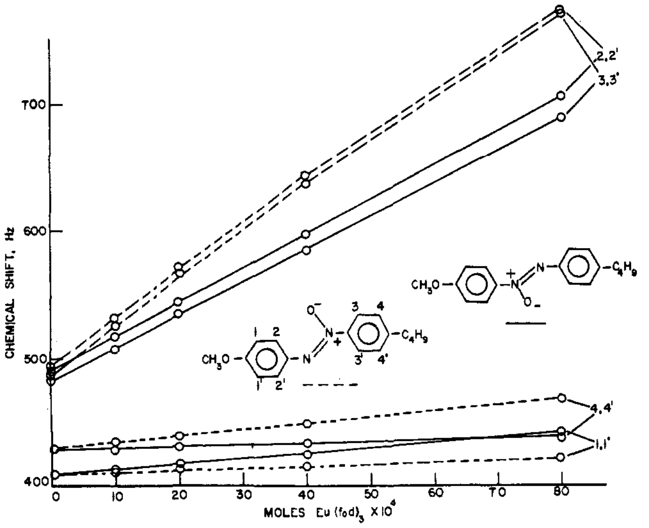
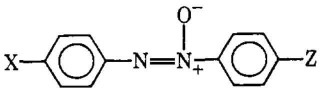


Figure 4. Chemical shifts of aromatic protons with added $Eu(fod)_3$.

linear structure with the acetylenic linkage did not lead to exceptional nematic thermal stability. Further, within a homologous series (Figure 1), the central linkage exerted an uneven influence on the intermolecular forces controlling crystalline breakdown to the nematic mesophase but gave predictable, parallel nematic to isotropic transitions. This latter behavior was found to be typical for a wide variety of liquid crystals, monotropic as well as enantiotropic, where X, Z = alkyl, alkoxy, acyloxy, alkylcarbonato and Y = anil, azo, azoxy, ester. The relative ordering of nematic thermal stabilities (Table I), coupled with the expected parallel nematic to isotropic trends within homologous series differing only in the central linkage (Figure 1), allows a very rapid, semiquantitative assessment of the isotropic transition temperature expected for any potential diaryl nematic, provided that at least one complete homologous series including its terminal substituents is known.

The relatively low crystalline transitions indicated in Table I suggest that room temperature nematic systems are possible for a wide variety of central linkages if eutectic mixtures with different X, Z substituents[11] are used. The isomeric azoxy mixtures appear to be especially appropriate[12] since the lack of stereospecificity in the oxidation[9] of unsymmetrical azo compounds makes them easily available and the identical terminal substituents promote good eutectic mixing.

Table II. Determination of Isomeric Distributions from Integration of Shifted Spectra



Mixture	Isomer	X	Z	% composition
1	a	CH_3O	n-C_4H_9	55
	b	n-C_4H_9	CH_3O	45
2	a	CH_3O	H	44
	b	H	CH_3O	56
2′	a	CH_3O	H	(74.4)[a]
	b	H	CH_3O	(25.6)[a]
3	a	CH_3	H	52
	b	H	CH_3	48
4	a	C_2H_5O	n-C_4H_9	47
	b	n-C_4H_9	C_2H_5O	53
5	a	Cl	n-C_4H_9	47
	b	n-C_4H_9	Cl	53
6	a	Cl	H	50
	b	H	Cl	50
7	a	CH_3O	$OCOCH_3$	55
	b	$OCOCH_3$	CH_3O	45

[a] Mixture 2′ was made up of 75.0% (by weight) of pure isomer a and 25.0% of b and served as an accuracy and assignment check. The numbers in parentheses are the average of four spectral integrations.

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(11) Several low-temperature nematic mixtures (<30–70°) are now known for 4-alkylcarbonato-4′-alkoxyphenylbenzoates: J. A. Castellano, M. T. McCaffrey, and J. E. Goldmacher, *Mol. Cryst. Liquid Cryst.*, in press.

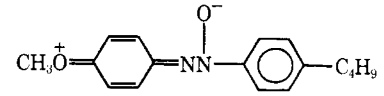
(12) Several isomeric azoxy mixtures with nematic ranges from 20–30 to 70–80° have been prepared by L. E. Knaak, these laboratories, with X, Z = alkyl, alkylcarbonato.

The low-temperature nematic substrates in Table I presented a unique opportunity to examine the electro-optical properties of several substrates differing only in the central linkage. As shown in Figure 2, the decrease in the intensity of a collimated white light source due to continuous light scatter varied widely for the substrates studied. While the anil and azoxy linkages were rather similar, the ester and azo[13] linkages gave distinctly different behavior. When 4-*n*-butyl-4′-methoxyazobenzene was electrically activated, transient scattering equivalent to the anil and azoxy values was observed, followed by clearing and an actual increase in the light transmission due to removal of the light scatter provided by the random domain orientation in the unactivated state. Thinner layers of the electrically activated 4-*n*-butyl-4′-methoxyazobenzene dramatically decreased the intensity of cross-polarized light thus indicating the partial formation of a homeotropic alignment from which no light scattering is expected.[4] Although the substantial differences shown in Figure 2 tend to support the important role proposed[4] for the off-axis dipole, two observations are disquieting: (1) the virtual identical behavior associated with the anil and azoxy linkages; (2) 4-*n*-butyl-4′-methoxystilbene, which like the azo molecule possesses no permanent central dipole, light scatters continuously at 119°. We are continuing our investigation of this phenomenon.

In general, oxidation of unsymmetrically substituted azobenzenes produces pairs of trans isomers differing only in the relative position of the oxygen atom.[9] Even though the isomers can be physically separated by tedious column chromatographic or fractional recrystallization procedures, the problem of assigning the position of the oxygen in the pure isomers still remains. The azoxy isomers, **11** and **12**, could be fractionally recrystallized from the mixture obtained *via* peracetic acid oxidation of 4-*n*-butyl-4′-methoxyazobenzene. The presence of a formal negative charge in these molecules makes them relatively strong Lewis bases. This fact and the use of shift reagents for structure elucidation[7] prompted us to study the effect of adding our recently introduced lanthanide shift reagents[14] to the mixtures. One of these improved materials, tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium(III), [Eu(fod)$_3$], was used with the axozybenzene mixtures in the hope of separating the coincident resonances of the nonequivalent aromatic protons from both structural isomers.

The shifting influence of a rare earth complex has been attributed primarily to a pseudocontact interaction operating through space.[15] In a particular Eu(fod)$_3$–azoxybenzene adduct, the distance of an aromatic proton from the europium will depend upon which oxygen atom is coordinated.[16] Since protons nearest to the metal cation will be affected most, it should be possible to assign protons to specific isomers based on the magnitude of their induced shifts.

The Eu(fod)$_3$ was added in 10-mg increments (1×10^{-5} mol) to 0.5-ml CCl$_4$ solutions containing 10^{-4} mol of each of the azoxybenzenes shown in Table II. Spectra were obtained at 60 MHz with a Varian HA-60IL spectrometer. The chemical shifts of the aromatic protons of both isomers were carefully monitored as the shift reagent was added. In all of the mixtures, the induced shifts were sufficiently large and selective to permit the unambiguous assignment of all of the protons. Figure 3 is a typical set of shifted spectra. In the absence of Eu(fod)$_3$, the spectrum is relatively compressed and uninformative. After the addition of only 10 mg of the europium complex, the spectrum reveals the presence of two pairs of AA′BB′ spectra. Spectral separation of the two isomers increases with further addition of the shift reagent until the two spectra are practically first order and readily amenable to spin decoupling and integration. The assignments were made from the coupling constants and from decoupling and integration experiments on the shifted spectra. Further confirmations were provided by direct comparisons with spectra obtained from the two isoelectronic nitrones, **9** and **10**, the 4- and 4′-methoxyazoxybenzenes,[9] and from the shifted spectra of a pure azoxy isomer. Figure 4 shows that a plot of the induced shifts as a function of added Eu(fod)$_3$ exhibited slightly steeper slopes for the 2,2′ and 3,3′ protons of one of the isomers. This was attributed to the following resonance effect



which increases the Lewis basicity of that particular isomer. In both isomers, the slopes of the 2,2′ and 3,3′ protons were parallel, indicating similar positions with respect to the europium metal. Molecular models using Prentice-Hall framework atoms with 1 in. = 1 Å were constructed. An assumed colinearity of the N–O–Eu– places the center of the metal ion approximately equidistant to the centers of both sets of protons ortho to the center group. From this position in the coordinated adduct, the europium would be expected to interact with the 2,2′ and 3,3′ protons to nearly the same extent.

As expected, all of the aromatic protons underwent the expected unidirectional shifts upon addition of increasing amounts of the shift reagent. However, the methoxy protons, as well as the methylene protons adjacent to the phenyl ring, experienced minor shifts in *both* directions. In Figure 3, for example, the separations of the methoxy singlet and methylene triplet result from induced shifts in opposite directions. Careful examination of the shifted spectra reveals that in one of the structural isomers, the methoxy protons are shifted upfield while the methylene protons move downfield. The effect is reversed in the other isomer; *i.e.*, the methoxy shifts upfield and the methylene down.

A possible explanation for these anomalous shifts can be found in the expression for the pseudocontact shift,[7] $\Delta H = k(3\cos^2\phi - 1)/r^3$. The parenthetic term becomes negative for values of ϕ, the O–metal–proton internuclear angle, between 55 and 125°. Thus, it is possible for the sign of the pseudocontact expression to be reversed and for the induced shift to be in the oppo-

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(13) This phenomena is general for X, Z = alkyl, methoxy and X, Z = alkylcarbonato, methoxy.

(14) R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, **93**, 1522 (1971).

(15) G. H. Wahl and M. R. Peterson, *Chem. Commun.*, 1167 (1970).

(16) Treatment of 4-*n*-butyl-4′-methoxyazobenzene with Eu(fod)$_3$ caused no noticeable spectral shifts. This experiment eliminated further consideration of the ether oxygen as a potential coordination center in the 4-alkoxyazoxybenzenes.

site direction. In the above, more basic isomer, for example, the values of ϕ measured from the assumed position of the europium in the adduct were 95° to the methoxy and 45° to the methylene protons. In terms of the $(3 \cos^2 \phi - 1)$ dependence, this predicts slight upfield and downfield shifts for the $-OCH_3$ and $-CH_2-$ protons, respectively. In the other isomer, the internuclear angles are 40° to the methoxy and 87° to the methylene. Again, these figures coincide with the reversed shifts observed in this isomer. Similar shifts were observed for all mixtures except 6 which contains no protons in the para substituent.

For each mixture in Table II, integration of either the aromatic protons ortho to the center group or the methyl singlets yielded the isomer distributions. In mixture 3, for example, the methyl resonances were separated by 25 Hz after treatment with 40 mg of shift reagent (mole ratio of Eu(fod)$_3$ to donor = 0.4). In mixture 7, as in the other alkoxy mixtures, the ether methyl resonances separate, one moving upfield slightly and the other downfield. The ester methyls also separate but with both peaks shifting downfield, suggesting coordination at the carbonyl oxygen. Thus the applicability of the technique extends to compounds with two coordination sites.

In the continuing search of potentially useful liquid crystal materials, the above method is a simple and unambiguous way of establishing the isomeric distribution as well as determining the stereospecificity of different oxidation schemes.

Experimental Section[17]

***trans*-4-*n*-Butyl-4′-methoxystilbene.** 4-*n*-Butylbenzaldehyde (3.6 g, 0.02 mol) was reduced with an excess of lithium aluminum hydride in ether. After stirring for 2 hr, the excess hydride was destroyed with 4 equiv of water. The precipitated salts were filtered and washed with ether. The ether was removed under reduced pressure and the residue taken up in 5 ml of pentane–ether (1:1). This was added to 10 ml of concentrated hydrochloric acid at 0°. After stirring vigorously for 3 hr, the reaction mixture was extracted with small portions of pentane–ether. The combined extracts were washed with 5% aqueous sodium bicarbonate and brine and dried (MgSO$_4$). The pentane–ether was removed *in vacuo* and the residue distilled to give 3.6 g of 4-*n*-butylbenzyl chloride, bp 69–77° (1.4 mm). This was used without further purification.

A solution of 2.88 g (0.011 mol) of triphenylphosphene, 2.04 g (0.011 mol) of 4-*n*-butylbenzyl chloride, and 10 ml of dry benzene was heated at reflux overnight. After cooling, 9.2 ml of 1.55 *N* *n*-butyllithium was added under a nitrogen atmosphere. After stirring for 2.5 hr, 1.85 g (0.014 mol) of anisaldehyde was added dropwise and the mixture allowed to stir for 3 days at room temperature. Water was added and the mixture extracted with ether. The combined extracts were washed with 10% aqueous sodium bisulfite and brine and dried (MgSO$_3$). When most of the solvent had been removed by rotatory evaporation, the *trans*-4-*n*-butyl-4′-methoxystilbene [0.8 g; mp 117.6–118.2° (c $\rightarrow$ n), 120.0–120.3° (n $\rightarrow$ i)] was obtained as a white crystalline solid by the addition of ethanol and cooling: ir (KBr) 6.25, 7.74, 8.0, 8.54, 9.74, 10.33, 12.0 μ; uv max (MeOH) 230 nm (ϵ 13,000), 307 (30,900), 322 (32,000); nmr (CCl$_4$) δ 0.7–2.0 (7 H, m), 2.56 (2 H, t, J = 7 Hz), 3.71 (3 H, s), 6.74 (2 H, d, C-1′1 H's, J_{12} = 8.5 Hz), 6.9 (2 H, d, C-4′4 H's, J_{34} = 8.0 Hz) 7.26 (2 H, d, C-3′3 H's, J_{34} = 8.0 Hz), 7.29 (2 H, d, C-2′2 H's, J_{12} = 8.5 Hz), 6.82 (2 H, s).

4-*n*-Butyl-4′-methoxydiphenylacetylene. The procedure was a modification of one reported[18] by L. I. Smith and M. M. Falkof. To a solution of 266 mg (0.001 mol) of *trans*-4-butyl-4′-methoxystilbene in 5 ml of ether was added a slight excess of bromine. When the product precipitated immediately, additional ether was added. After 15 min, the dibromide was filtered and washed with ether until white.

The dibromide was added to a solution of 1.2 g of potassium hydroxide in 15 ml of absolute ethanol. The mixture was brought to reflux and stirred for 3 days. After cooling, the mixture was decanted onto ice. The resulting solid was filtered, dissolved in ether, and dried (MgSO$_4$). After removal of the ether and molecular distillation of the residue (0.1 mm, bath temperature 190°), 171 mg of the acetylene was obtained which contained trace amounts of the stilbene and the vinyl bromides (as indicated by mass spectral analysis). Preparative tlc on silica gel HF impregnated with silver nitrate (15%) followed by crystallization from petroleum ether and sublimation gave a pure sample of 4-*n*-butyl-4′-methoxydiphenylacetylene: mp 46–47° (c $\rightarrow$ i), 37° monotropic; ir (KBr) 4.2 (w), 6.25, 6.1, 7.8, 8.03, 8.4, 8.55, 8.82, 9.04, 9.75, 11.95, 12.22 μ; nmr (CDCl$_3$) δ 0.7–1.8 (7 H, m), 2.58 (2 H, t, J = 7 Hz), 3.77 (3 H, s), 6.83 (2 H, d, C-1′1 H's, J_{12} = 9.1 Hz), 7.08 (2 H, d, C-4′4 H's, J_{34} = 1.0 Hz), 7.42 (2 H, d, C-3′3 H's, J_{34} = 8.0 Hz), 7.44 (2 H, d, C-2′2 H's, J_{12} = 9.1 Hz); high-resolution mass spectrum (70 eV) *m/e* molecular ion 264.1521 (calcd for $C_{17}H_{20}O$, 264.1514).

4-*n*-Butylphenyl 4′-Anisoyl Carbonate. 4-Methoxyphenyl chloroformate (3.6 g, 0.02 mol) was placed in 15 ml of dry benzene and 4-*n*-butylphenol [3.0 g (0.02 mol) in 3.4 g (0.02 mol) of pyridine] added to the stirred solution. The solution was stirred for 14 hr, the pyridine hydrochloride filtered, and the benzene removed under reduced pressure. The remaining oil was chromatographed with hexane on alumina yielding 3.8 g (63%) of a slowly crystallizing oil. Recrystallization from hexane gave a solid: mp 28.0–29.5°; ir (neat) 5.7, 6.7, 8.1, 8.54, 9.7, 12.07 μ.

4-*n*-Butyl-4′-methoxydiphenyl Ether. A modification of the procedure[19] of H. E. Ungnode and E. F. Orwoll was utilized. 4-*n*-Butylphenol (3.0 g, 0.02 mol) was added to a potassium hydroxide solution (1.12 g, 0.02 mol, in 10 ml of H$_2$O). The water was removed under reduced pressure and the resultant powder dried at 100° *in vacuo*. Copper powder (0.3 g) and 4-bromoanisole (4.68 g, 0.025 mol) were added to the dry salt; the mixture was heated to 150–160°. When no further increase in product formation was noted by glpc analysis, the mixture was decanted onto 100 ml of 10% HCl and the organic layer extracted with ether. After drying (MgSO$_4$), the ether was removed under reduced pressure and the residue chromatographed with hexane on 100 g of activity II alumina yielding an oil which after distillation gave 2.7 g (53%) of a clear oil: bp 145–148° (0.005 mm): ir (neat) 6.2, 6.7, 8.1, 9.65, 11.45, 11.85 (shoulder), 12.05 μ; nmr (CCl$_4$) δ 0.7–1.8 (7 H, m), 2.5 (2 H, t, J = 7 Hz), 3.78 (1 H, s), 6.67–7.1 (8 H, m).

4-*n*-Butyl-4′-methoxybiphenyl. Acetic anhydride (4.08 g, 0.04 mol) was added dropwise to a solution of 4-*n*-butylaniline (5.97 g, 0.04 mol) in 10 ml of dry benzene. The mixture was brought to reflux and stirred overnight. After removal of 5 ml of benzene by distillation, the reaction mixture was allowed to cool. Addition of petroleum ether initiated crystallization. After concentration of the mother liquor, a total of 7.3 g of *N*-(4-*n*-butylphenyl)acetamide was obtained.

To a solution of *N*-(4-*n*-butylphenyl)acetamide (1.91 g, 0.01 mol), 14 ml of glacial acetic acid, 2 g of freshly fused potassium acetate, 4 ml of acetic anhydride, and 1 g of phosphorus pentoxide was added dropwise while stirring at 8–10° a solution of nitrosyl chloride dissolved in 3 ml of acetic anhydride until the reddish color of the nitrosyl chloride persisted ($\sim$1 g). After a total of 30 min, the reaction mixture was poured onto crushed ice. The crystalline, yellow *N*-nitroso(4-*n*-butylphenyl)acetamide was filtered, washed with cold water, and air-dried. The *N*-nitroso(4-*n*-butylphenyl)-acetamide (2.0 g) was added in one portion to 10 ml of anisole previously distilled from sodium. The amide dissolved with the evolution of nitrogen and the temperature rose to approximately 50°. After stirring overnight, the dark reaction mixture was filtered, the anisole removed by distillation under reduced pressure, and the residue trap to trap distilled (0.3 mm, 200° bath). The distillate (460 mg), a mixture of three major components (in the approximate ratio of 6:1:1/ortho:meta:para as indicated by glpc analysis-SE-30 column at 100°), was placed on a 3 ft, activity I, alumina column and eluted with hexane. Initial fractions contained only 4-*n*-butyl-2′-methoxybiphenyl (mp 17–18°, petroleum ether) while later fractions contained a mixture of the 4,2′ isomer enriched in 4-*n*-butyl-4′-methoxybiphenyl. Further purification

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(17) Satisfactory elemental analyses were obtained for each new, previously unreported compound. Mesomorphic transitions determined in bulk and with an American optical polarizing microscope equipped with Mettler FP-2 heating–cooling unit.

(18) L. I. Smith and M. M. Falkof, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 350.

(19) H. E. Ungnode and E. F. Orwoll, ref 18, p 566.

of the fractions enriched in the 4,4′ isomer by recrystallization from petroleum ether at reduced temperatures (Dry Ice–2-propanol bath) afforded the 4-*n*-butyl-4′-methoxybiphenyl as a white crystalline solid: mp 68.5–69.0° (c → i); ir (KBr) 6.2, 6.65, 7.75, 7.93, 8.22, 8.45, 9.62, 12.2, 12.78 μ; nmr (CCl_4) δ 0.7–1.4 (7 H, m), 2.58 (2 H, t, J = 7 Hz), 3.73 (3 H, s), 6.6–7.5 (8 H, m).

***N*-(4-Methoxyphenyl)-α-(4-*n*-butylphenyl)nitrone.** To a solution of 2.16 g (0.014 mol) of 4-nitroanisole in 10 ml of ethanol was added 0.81 g of ammonium chloride dissolved in a minimum volume of water. The system was purged with nitrogen and cooled to 20°. Small portions of zinc dust totaling 3.6 g (90% pure) were added such that the temperature did not exceed 25°. After 50 min, the reduction was complete as indicated by glpc analysis (SE-30). The precipitated zinc oxide was filtered and washed with small portions of chilled ethanol and water, respectively, under nitrogen. The hydroxylamine crystallized as light yellow needles after the volume of the filtrate had been increased to 125 ml by the addition of brine and cooling in an ice–salt bath for 1 hr. The product (1.5 g, 76%) was filtered, washed with cold brine and water, dried in a vacuum desiccator for 5 hr, and used without further purification.

To 1.5 g (10.8 mmol) of 4-methoxyphenylhydroxylamine were added 1.94 g (12.0 mmol) of 4-*n*-butylbenzaldehyde and 2 ml of absolute ethanol. After the mixture was stirred for 8 hr, the solid was then filtered. Recrystallization from ether gave 2.7 g (89%) of the nitrone as white needles: mp 107–108.2° (c → i), monotropic 70.4° (n → i) after sublimation (120°, 0.05 mm); ir (KBr) 6.23, 6.68–7.2, 7.65, 7.98, 8.51, 5.58, 9.43, 9.72, 11.18, 11.82, 11.95, 12.23 μ; uv max (MeOH) 231 nm (ε 7500), 325 (16,500); nmr ($CDCl_3$) δ 0.7–1.9 (7 H, m), 2.63 (2 H, t, J = 7 Hz), 3.83 (3 H, s), 6.95 (2 H, d, C-1′1 H's, J_{12} = 9.1 Hz), 7.21 (2 H, d, C-4′4 H's, J_{34} = 8.5 Hz), 7.74 (2 H, d, C-2′2 H's, J_{12} = 9.1 Hz), 7.85 (1 H, s), 8.32 (2 H, d, C-3′3 H's, J_{34} = 8.5 Hz).

***N*-(4-*n*-Butylphenyl)-α-(4-methoxyphenyl)nitrone.** Anisaldehyde (170 mg, 1.26 mmol) was added to 200 mg (1.20 mmol) of 4-*n*-butylphenylhydroxylamine (prepared by the zinc, ammonium chloride, ethanol reduction of 4-*n*-butylnitrobenzene). A few drops of ethanol were added and the mixture was allowed to stand overnight. The product was vacuum filtered and washed with a small amount of ethanol to afford 310 mg (90%) of the nitrone: white needles; mp 112.2–113.5° (c → i), monotropic 52.4° (n → i) after sublimation (120°, 0.05 mm); ir (KBr) 6.23, 6.63, 7.58, 7.97, 8.4, 8.54, 9.34, 9.74, 11.15, 11.76, 11.97, 12.18, 12.5 μ; uv max (MeOH) 240 nm (ε 11,600), 332 (27,600); nmr ($CDCl_3$) δ 0.7–1.9 (7 H, m), 2.63 (2 H, t, J = 7 Hz), 3.85 (3 H, s), 6.98 (2 H, d, C-1′1 H's, J_{12} = 9.1 Hz), 7.23 (2 H, d, C-4′4 H's, J_{34} = 8.7 H), 7.69 (2 H, d, C-3′3 H's, J_{34} = 8.7), 7.85 (1 H, s), 8.41 (2 H, d, C-2′2 H's, J_{12} = 9.1 Hz).

4-*n*-Butyl-4′-methoxyazoxybenzene and 4′-*n*-Butyl-4-methoxyazoxybenzene. 4-*n*-Butyl-4′-methoxyazobenzene (9.6 g, 0.036 mol) was added to 50 ml of 30% peracetic acid and the mixture stirred at 50° for 12 hr. The solution was then poured onto ice water and extracted with ether; the ether was dried ($MgSO_4$) and removed under reduced pressure. The residue was chromatographed on 200 g, activity II, neutral alumina with hexane as eluent. The rapidly moving yellow band was collected yielding 8.2 g (80%) of a yellow oil: mp 16–18° (c → n), 75.1–75.3° (n → i); uv max (MeOH) 347 nm (ε 22,400), 240 (12,900); nmr (see body of paper). Upon standing, one isomer (rhomboid crystals) preferentially separated. By fractional crystallization from hexane both isomers were subsequently obtained with isomeric purities >99% as shown by the nmr, $Eu(fod)_3$ technique. 4-Butyl-4′-methoxyazoxybenzene (platelet crystals): mp 41.5–42.5° (c → n), 76.9–77.0° (n → i); ir (KBr) 6.23, 6.66, 6.8, 7.5, 7.89, 8.6, 8.9, 9.0, 9.07, 9.7, 10.9, 11.87 μ. 4′-Butyl-4-methoxyazoxybenzene (rhomboid crystals): mp 40.5–41.5° (c → n), 74.2–74.3° (n → i); ir (KBr) 6.22, 6.65, 6.8, 7.5, 7.92, 8.4, 8.6, 8.9, 9.68, 10.94, 11.9 μ.

4-*n*-Butylphenyl 4′-Anisoate. A solution of 4-*n*-butylphenol [3 g (0.02 mol) in 25 ml of pyridine] was added to 4-anisoyl chloride (3.4 g, 0.02 mol) which had been dissoved in 50 ml of pyridine. The solution was refluxed for 2 hr, and the pyridine solution was extracted twice with 100 ml of water and dried (Na_2SO_4). Removal of the pyridine under reduced pressure yielded an oil which was chromatographed on alumina with petroleum ether as eluent yielding 3.2 g (56%) of a clear liquid which when recrystallized from hexane gave a solid: mp 40.0–40.5° (c → i), 24° monotropic; ir (KBr) 5.82, 6.25, 6.66, 7.64, 7.97, 8.4, 8.6, 9.44, 9.26, 11.4, 11.3, 12.78, 13.0, 14.4 μ; uv max (MeOH) 260 nm (ε 23,000); nmr (CCl_4) δ 0.7–1.9 (7 H, m), 2.57 (2 H, t, J = 7 Hz), 3.75 (3 H, s), 6.82 (2 H, d, C-1′1 H's, J_{12} = 8.8 Hz), 7.02 (4 H, s, C-3′3,4′4 H's), 8.03 (2 H, d, C-2′2 H's, J_{12} = 8.8 Hz).

4-Methoxyphenyl 4′-*n*-Butylbenzoate. A solution of 4.3 g (0.024 mol) of 4-*n*-butylbenzoic acid, 6.0 g of thionyl chloride, and a drop of dimethylformamide was heated at reflux overnight. The excess thionyl chloride was removed under reduced pressure and the residue vacuum transferred to give 4.6 g of the acid chloride, which was dissolved in 30 ml of pyridine with 3.0 g (0.024 mol) of 4-methoxyphenol added. After standing overnight, the reaction mixture was decanted onto ice. The precipitate was filtered, washed with water, taken up in ether, and dried ($MgSO_4$). The ether was removed *in vacuo* and the residue recrystallized from ether–hexane to afford a white solid (5.7 g, 80%): mp 63° (c → i), 22° monotropic; ir (KBr) 5.8, 6.22, 6.65, 7.88, 8.02, 8.37, 8.54, 9.1, 9.25, 9.33, 9.78, 11.5, 12.1, 12.26, 12.5, 13.18, 13.43, 14.42 μ; nmr (CCl_4) δ 0.7–1.9 (7 H, m), 2.64 (2 H, t, J = 7 Hz), 3.70 (3 H, s), 6.76 (2 H, d, C-1′1 H's, J_{12} = 9.0 Hz), 7.08 (2 H, d, C-2′2 H's, J_{12} = 9.0 Hz), 7.18 (2 H, d, C-4′4 H's, J_{34} = 8.0 Hz), 8.02 (2 H, d, C-3′3 H's, J_{34} = 8.0 Hz).

4-*n*-Butylphenyl-4′-anisamide. 4-*n*-Butylaniline (5.09 g, 0.040 mol) was added to a solution of 4-anisoyl chloride [6.00 g (0.035 mol) in 25 ml of pyridine] and refluxed for 2 hr. The solid which precipitated after pouring into ice-cold 10% hydrochloric acid was extracted into ether–benzene and washed with 10% hydrochloric acid and water, and the ether–benzene layer was dried ($MgSO_4$). Removal of the solvent under reduced pressure left a solid which when recrystallized from benzene gave 6.3 g of white needles (65%): mp 145.5–146.0°; ir (KBr) 3.02, 6.08, 6.24, 6.65, 7.1, 7.6, 7.7, 8.0, 8.5, 9.05, 9.75, 11.1, 11.7, 11.9, 12.12, 13.1 μ; uv max (MeOH) 275 nm (ε 22,600); nmr (C_7D_6O) δ 0.7–1.8 (7 H, m), 2.54 (2 H, t, J = 7 Hz), 3.78 (3 H, s), 6.94 (2 H, d, C-1′1 H's, J_{12} = 8.8 Hz), 7.07 (2 H, d, C-4′4 H's, J_{34} = 8.5 Hz), 7.67 (2 H, d, C-3′3 H's, J_{34} = 8.5 Hz), 7.91 (2 H, d, C-2′2 H's, J_{12} = 8.8 Hz), 9.32 (1 H, s).

4-*n*-Butyl-4′-methoxyazobenzene (4,4′-Substituted Azobenzenes). The azo compounds were prepared either by utilizing a modification of the procedure as reported by J. L. Hartwell and L. F. Fieser[20] or by H. D. Anspon.[21]

The appropriate 4-substituted aniline (0.15 mol) was added to 60 ml of distilled water and dilute hydrochloric acid [45 g of concentrated hydrochloric acid (0.43 mol) diluted to 150 ml with distilled water] was added dropwise. The solution was cooled below 10° and sodium nitrite (0.15 mol in 25 ml distilled water) added dropwise. After allowing the solution to stir for 2 hr at 10°, it was added dropwise to a buffered sodium phenoxide solution (14.1 g of phenol, 0.15 mol; 6.00 g of sodium hydroxide, 0.15 mol; 18 g of sodium carbonate; all in 200 ml of distilled water) with vigorous stirring. The suspended solids were then filtered after neutralization with hydrochloric acid to pH 8 and dissolved in ether. After drying (Na_2SO_4) and removing the ether *in vacuo*, the initial solid residue was recrystallized from hexane yielding an orange solid in yields of 60–75% which were characterized as the expected 4-hydroxy-4′-alkylazobenzene.

The appropriate 4-hydroxy-4′-alkylazobenzene (0.01 mol) and an equivalent amount of sodium hydroxide (0.40 g, 0.01 mol) were dissolved in 100 ml of distilled water and heated until all solids were in solution. The appropriate iodoalkane (tenfold molar excess) was added and the mixturer efluxed overnight. The reaction mixture was then extracted with ether, and the ether was dried ($MgSO_4$) and removed under reduced pressure. The residue was chromatographed on activity II neutral alumina with petroleum ether as eluent. The yellow-orange band that moved rapidly down the column was collected and consisted of the expected azo derivative in yields of 60–80% after removal of solvent under reduced pressure. The azo compounds were recrystallized from hexane: 4-*n*-butyl-4′-methoxyazobenzene; mp 32° (c → n), 49° (n → i); ir (KBr) 6.25, 6.74, 8.03, 8.75, 8.84, 9.75, 11.95 μ; uv max (MeOH) 347 nm (ε 19,300), 238 (12,000), 433 (17,000); nmr (CCl_4) δ 0.7–1.9 (7 H, m), 2.6 (2 H, t, J = 7 Hz), 3.72 (3 H, s), 6.83 (2 H, d, C-1′1 H's, J_{12} = 8.8 Hz), 7.14 (2 H, d, C-4′4 H's, J_{34} = 8.5 Hz), 7.72 (2 H, d, C-3′3 H's, J_{34} = 8.5 Hz), 7.80 (2 H, d, C-2′2 H's, J_{12} = 8.8 Hz).

The appropriate 4-substituted nitrosobenzene (0.05 mol) was added to a solution (0.05 mol) of the appropriate 4-substituted aniline in 50 ml of glacial acetic acid. After stirring for 3 hr, 50 ml of crushed ice was added to the reaction mixture. The product was filtered and washed with water. The solid was taken up in ether and dried (Na_2SO_4), and the solvent was removed *in vacuo*. The residue was chromatographed on activity II, neutral alumina

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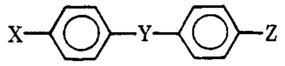
(20) J. L. Hartwell and L. F. Fieser, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 145.

(21) H. D. Anspon, ref 18, p 711.

Table III



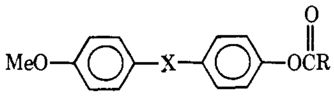
X	Y	Z	Transition temp, °C Obsd value	 Lit. value
n-Bu	N=N	OH	79.5–79.5	
H	N=N	OMe	55.0–55.5	54.5–55.5[a]
Bu	N=N	OEt	47–48 (c → n) 83.5–84.0 (n → i)	
Me	N=N	H	68.5–69.0	71[b]
Bu	N=N	Cl	71.0–71.5	
H	N=N	Cl	86.5–87.0	88–90[c]
H	$\overset{\overset{O^-}{\uparrow}}{{}^+N}{=}N$	OMe	71.5–73.0	66.5–67.5[d]
H	$N{=}\overset{\overset{O^-}{\uparrow}}{N^+}$	OMe	52.0–52.5	42–43[d]
Bu	$\underset{+}{\overset{\overset{O^-}{\uparrow}}{N}}{=}N$	OEt	32 (c → n) 102 (n → i)	
Bu	$\underset{+}{\overset{\overset{O^-}{\uparrow}}{N}}{=}N$	Cl	51–53 (c → n) 57 (n → i) 47 (s → n) monotropic	
H	$\underset{+}{\overset{\overset{O^-}{\uparrow}}{N}}{=}N$	Cl	60–63	
MeO	$\underset{+}{\overset{\overset{O^-}{\uparrow}}{N}}{=}N$	OAc	120 (c → n) 133 (n → i)	116 (c → n) 132 (n → i)
H	$\underset{+}{\overset{\overset{O^-}{\uparrow}}{N}}{=}N$	Me	36–45	
H	$N{=}\underset{+}{\overset{\overset{O^-}{\uparrow}}{N}}$	Me	64.0–64.5	65[e]

[a] W. R. Brode, I. L. Seldin, P. E. Spoerri, and G. M. Wyman, *J. Amer. Chem. Soc.*, **77**, 2763 (1955). [b] P. P. Birnbaum, J. H. Linford, and D. W. G. Style, *Trans. Faraday Soc.*, **49**, 735 (1953). [c] A. H. Cook, *J. Chem. Soc.*, 876 (1938). [d] See ref 9. [e] D. L. Webb and H. H. Jaffe, *J. Amer. Chem. Soc.*, **86**, 2419 (1964).

using petroleum ether–ether as the eluent. Collection of the yellow-orange band afforded the azo derivative in yields of 80–90% after removal of the solvent under reduced pressure and recrystallization from hexane; see Table III.

4,4′-Substituted Azoxybenzenes. With the exception of the ester-substituted azobenzenes (which were oxidized overnight with an equivalent amount of *m*-chloroperbenzoic acid in methylene chloride solution), the appropriate azo compound (0.01 mol) was dissolved in 40 ml of 40% peracetic acid and refluxed overnight. The solution was tested with KI–starch paper to make sure all peroxide was gone and then the solvent was removed under reduced pressure. The residue was chromatographed on 100 g of activity II, neutral alumina with petroleum ether as eluent. The rapidly moving yellow band was collected yielding the expected azoxy derivative in yields of 70–85% upon removal of solvent under reduced pressure. Glpc of the azoxy materials prior to recrystallization indicated only one peak on SE-30 and QF-1 columns. Nevertheless, the suspiciously broad melting points suggested a mixture. This was substantiated by complexing the azoxy materials with tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium(III).

Table IV



X	R	Transition temp, °C Crystalline to nematic	 Lit. value (ref)	 Nematic to isotropic	 Lit. value (ref)
CH=N	CH_3	84	81 (5g)	110.5	109 (5g)
	C_2H_5	70	68 (5g)	114.5	105 (5g)
	C_3H_7	51	50 (5g)	112.5	112 (5g)
	C_4H_9	68	60 (5g)	98.5	97 (5g)
	C_5H_{11}	82	83 (5g)	102.0	103 (5g)
	C_6H_{13}	64		97.0	97[a]
	C_7H_{15}	66	64[a]	99.0	
N=N	CH_3	122[b]	119[d]	114.5[c]	115[d]
	C_2H_5	92	91[d]	117.0	117[d]
	C_3H_7	76	75[d]	117.0	117[d]
	C_4H_9	80	80[d]	102.5	102[d]
	C_5H_{11}	66	66[d]	105.0	106[d]
	C_6H_{13}	71	71[d]	99.5	98[d]
	C_7H_{15}	77	76[d]	102.0	101[d]
N=CH	CH_3	112	112 (2)	118.0	128 (2)
	C_2H_5	85	85[a]	119.5	116[a]
	C_3H_7	86	86[a]	120.0	118[a]
	C_4H_9	102	102[a]	106.0	105[a]
	C_5H_{11}	92	92[a]	108.0	108[a]
	C_6H_{13}	87	87[a]	103.0	102[a]
	C_7H_{15}	96		106.0	

[a] R. Steinstrasser and L. Pohl, *Z. Naturforsch.*, **266**, 87 (1971). [b] Crystalline to isotropic transition. [c] Monotropic. [d] D. Vorlander, *Z. Phys. Chem.*, **126**, 449 (1927).

In the case of the 4′-methoxy- and 4-methoxyazoxybenzenes, resolution of the isomers[9] *via* six recrystallizations of the first plate-like and needle-like crystals of the respective isomers from hexane (obtained during preliminary phase of separation) afforded isomers of >99% purity as shown by the nmr, $Eu(fod)_3$ technique. See Table III.

***N*-(4′-Methoxybenzylidene)-4-acyloxyanilines, *N*-(4′-Acyloxybenzylidene)-4-methoxyanilines, and 4-Acyloxy-4′-methoxyazobenzenes.** These benzylidene and azobenzene esters were prepared by a modification of the Chattoway[22] procedure. In general, *N*-(4′-methoxybenzylidene)-4-hydroxyaniline (0.02 mol, prepared by heating at reflux an equal molar quantities of 4-anisaldehyde with 4-aminophenol in absolute ethanol for 1 hr) and sodium hydroxide (0.04 mol) were added to 60 ml of distilled water and cooled *via* the addition of ice. The appropriate anhydride (0.03 mol) was added with stirring at 0° (acylation temperatures were increased as the homologous series grew; *i.e.*, the best results with pentanoic and hexanoic anhydrides were achieved at 60°). After the mixture was stirred for 15–30 min, the precipitate was collected by vacuum filtration from the cooled reaction mixture, washed with cold 5% NaOH and water, and dried, respectively. Purification was achieved either by chromatography on alumina (ether elution) and crystallization or by direct crystallization from ethanol until observation of a constant nematic–isotropic transition. Yields ranged from 60 to 73%. *N*-(4′-Hydroxybenzylidene)-4-methoxyaniline and 4-hydroxy-4′-methoxyazobenzene were treated in a similar manner to yield the benzylidene esters with reversed anil linkage and the azobenzene esters, respectively See Table IV.

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(22) F. D. Chattoway, *J. Chem. Soc.*, 2495 (1931).