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Liquid Crystals: Transition Point Studies of 4(4′)-Alkoxyformyloxy-4′(4)-alkylazoxybenzenes

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Abstract—A series of 4(4′)-alkoxyformyloxy-4′(4)-alkylazoxybenzenes has been prepared. The transition temperatures have been determined and the applicability of the spectral shift reagent Eu(fod)$_3$ to determine the mole percent of six isomeric mixtures was demonstrated.

Recently we reported an empirical method to estimate the nematic–isotropic (NI) transition of para substituted biaryls containing any combination of five central and 35 terminal substituents.⁽¹⁾ The five central substituents are azo, azomethine, azoxy, nitrone and ester. Of the five central substituents, the azoxy central linkage generally leads to nematic liquid crystals with the greatest thermal stability.

Melting points of organic compounds are not easily predicted. However, of the several room temperature or nearly room temperature nematic liquid crystals reported, all contain a para alkyl substituent. Alkyl substituents, although their effect on the NI transition is quite variable and usually leads to lower thermal stability, do as a general rule, lower the melting point substantially more than the other substituents studied.

A low melting point, however, is only one of several criteria to be considered in the design of biaryl compounds for low-temperature nematic phases. For example, although some trans azo compounds exhibit a low crystal–nematic transition (CN), the azo central linkage is extremely susceptible to light-induced trans-cis isomerization which destroys its nematic character. Azomethines, although slightly less sensitive to light, are easily hydrolyzed in the presence of moisture. The azoxy central linkage imparts color to the compound which may be a drawback, depending on the intended application. The ester central linkage, on the other hand, is colorless. It would seem, therefore, that the selection of a central linkage for a biaryl structure will involve a comparison of several properties.

Because of the superior nematic thermal stability of azoxy biaryls and the decreased melting points of alkyl substituted azoxybenzenes, we have studied a series of para alkyl substituted azoxybenzenes.

1. Results and Discussion

In general, the melting points of organic compounds are depressed on admixture with a second component. The melting range of a mixture may be quite broad while the melting range of a eutectic mixture is narrow. However, if a true binary mixture is formed, the melting point of the eutectic mixture can be determined from the onset of melting of a mixture of non-eutectic composition.(2)†

Recently Steinsträsser and Pohl reported the preparation of a series of 4-alkoxy-4′-alkylazoxybenzenes under reaction conditions which led to eutectic mixtures containing one-third mole percent of the higher melting component.(3) However, there doesn't appear to be a theoretical basis for this composition being the optimum for all mixtures.(4) We have not tried to generate the eutectic mixture but have instead carried out routine oxidations of azo biaryls, isolated the azoxy biaryls by chromatography and crystallization, and recorded the melting ranges of the mixtures obtained. Through the use of the melting range and the onset of melting, we have determined the eutectic melting point of the mixtures. The mole percent and structure of the major and minor isomers of the mixtures were determined through the use of NMR peak integrations utilizing Eu(fod)$_3$. The NI transitions of the azoxy isomeric mixtures are reported in Table 1.

An inherent difficulty in the synthesis of unsymmetrically substituted azoxybenzenes is the production of pairs of structural isomers which differ only in the relative position of the oxygen atom. Since the NI transitions of azoxy isomers are generally quite close,(5) the

† The formation of true binary eutectic mixtures for these compounds is indicated by the combination of pure components for several of these mixtures and also observed in Ref. 3.

TABLE 1 Transition Temperatures of 4(4′)-Alkoxyformyloxy-4′(4)-alkylazoxybenzenes

R	R′	CN(°C)	NI(°C)
C_3H_7	C_5H_{11}	38–42	79
C_4H_9	C_4H_9	24–38	70
C_4H_9	C_5H_{11}	28–47	67.5
C_5H_{11}	CH_3	45–59	100
C_5H_{11}	C_2H_5	53–64	92.5
C_5H_{11}	C_3H_7	64–74	81.5
C_5H_{11}	C_4H_9	28–49	80.5
C_5H_{11}	C_5H_{11}	27–32	81.5
C_5H_{11}	C_6H_{13}	33–35	81
C_6H_{13}	CH_3	44–45	89
C_6H_{13}	C_2H_5	33–38	81.5
C_6H_{13}	C_3H_7	38–66	70.5
C_6H_{13}	C_4H_9	22–24	72
C_6H_{13}	C_5H_{11}	23–25	72
C_6H_{13}	C_6H_{13}	31–42	73

NI transition of the pure components can be approximated from that of the mixture. The melting range and, to a large extent, the nematic range of these mixtures are determined by the isomer distribution. A rapid and unambiguous method of determining this critical composition has recently been reported.(6) The technique is based on the use of a paramagnetic shift reagent, $Eu(fod)_3$,(7) and a comparison of the shifted NMR spectra with the spectrum of the untreated mixture. The spectrum of the untreated azoxybenzene gives the misleading appearance of a single, pure compound. Addition of $Eu(fod)_3$ separates the coincidental isomeric methyl resonances. Identification of the isomers was deduced from the unusual bidirectional shifting observed for this particular $Eu(fod)_3$-azoxybenzene adduct.† The isomer, 4′-methoxyformyloxy-4-methylazoxybenzene, with the N→O function nonadjacent to the aromatic ring containing the alkyl group shows an upfield shift in the benzylic protons. (See Fig. 1 for the specific case where the benzylic protons are methyl.) This was used to identify the structural isomers based on similar shifts of the benzylic protons in 4(4′)-*n*-butyl-4′(4)-methoxyazoxybenzene mixtures and pure isomers.(6) By integration

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† The upfield shift has been attributed to an angular term in the expression for the pseudocontact interaction which produces the spectral shifts.

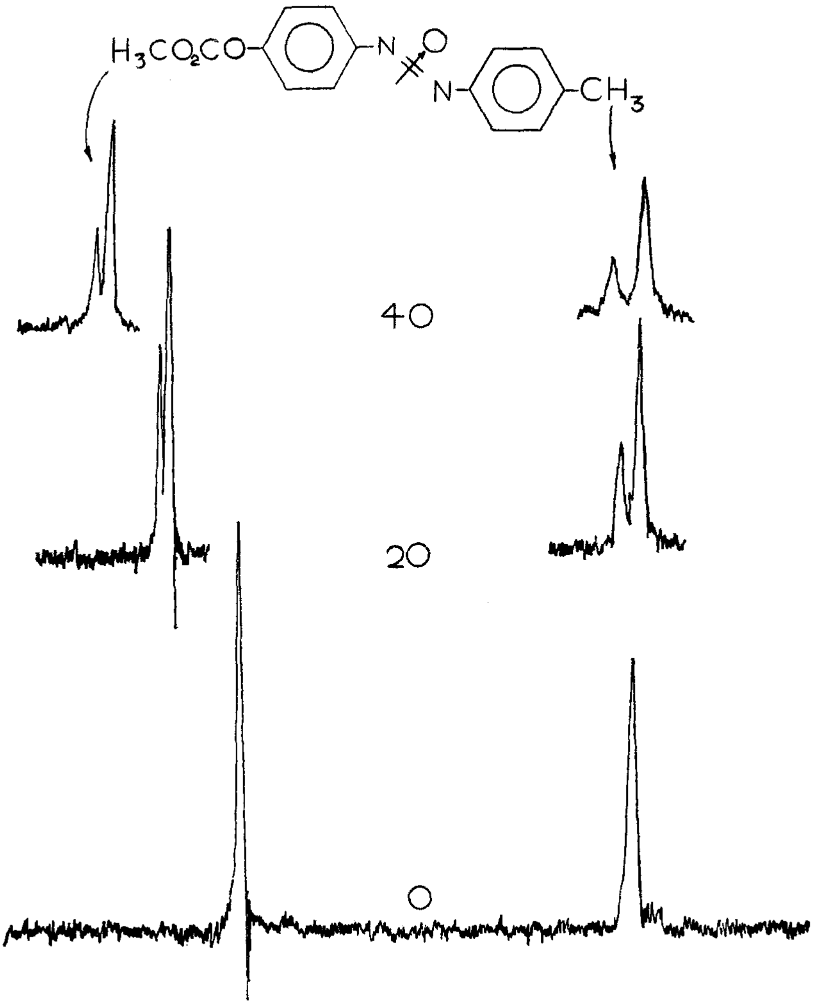


Figure 1. Induced spectral separations of methyl resonances in 4′(4)-methoxyformyloxy-4(4′)-methylazoxybenzene. The predominant isomer is 4′-methoxyformyloxy-4-methylazoxybenzene. Numbers are milligrams of $Eu(fod)_3$ added to 100 μmoles of the azoxybenzene mixture in 0.5 ml CCl_4.

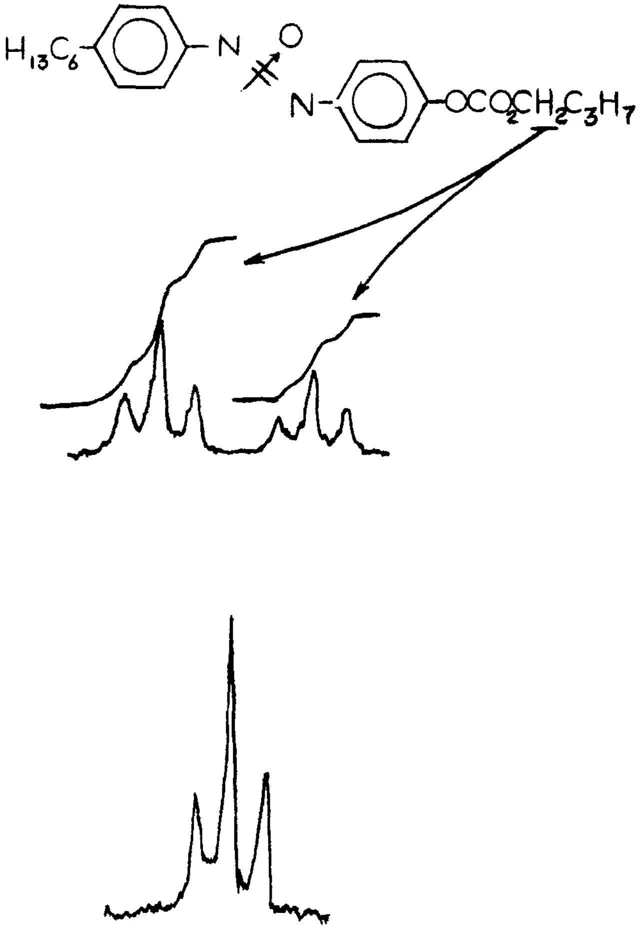
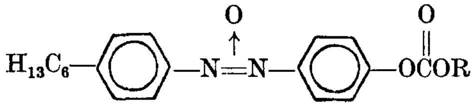


Figure 2. Separation of coincidental, isomeric methylene resonances of 4′(4)-butoxyformyloxy-4(4′)-hexylazoxybenzene induced by 40 mg of Eu(fod)$_3$. The bottom triplet is the same methylene absorption in the absence of the shift reagent.

of the separated peaks, the relative mole percents of the two isomers were determined. (See Fig. 2.)

The percent composition and melting ranges of several of the isomeric mixtures are given in Table 2. Those mixtures with a narrow melting range have an approximate 2:1 ratio of isomers corresponding to previous reports. In one case ($R = C_3H_7$) the isomer ratios were reversed and a melting range of 28 ° was obtained.

TABLE 2 Percent Composition and Melting Range of Some 4(4′)-Alkoxyformyloxy-4′(4)-alkylazoxybenzenes



R	$\overset{\overset{O}{\uparrow}}{N}{=}N$	$N{=}\overset{\overset{O}{\uparrow}}{N}$	Melting Range °C
CH_3	70	30	1
C_2H_5	62	38	5
C_3N_7	28	62	28
C_4H_9	61	39	2
C_5H_{11}	70	30	2
C_6H_{13}	79	21	11

TABLE 3 Elemental Analyses[a]

R	R′	%C Calc.	%C Found	%H Calc.	%H Found	%N Calc.	%N Found
C_3H_7	C_5H_{11}	68.08	68.36	7.08	7.26	7.56	7.76
C_4H_9	C_4H_9	68.08	68.21	7.08	7.25	7.56	7.54
C_4H_9	C_5H_{11}	68.72	68.87	7.34	7.15	7.29	7.42
C_5H_{11}	CH_3	66.65	66.57	6.48	6.58	8.18	8.18
C_5H_{11}	C_2H_5	67.39	67.35	6.79	6.80	7.86	7.96
C_5H_{11}	C_3H_7	68.08	68.05	7.08	7.17	7.56	7.86
C_5H_{11}	C_4H_9	68.72	68.89	7.34	7.49	7.29	7.25
C_5H_{11}	C_5H_{11}	69.32	69.41	7.59	7.70	7.03	7.33
C_5H_{11}	C_6H_{13}	69.87	69.96	7.82	8.06	6.79	6.86
C_6H_{13}	CH_3	67.39	67.69	6.79	7.03	7.86	8.02
C_6H_{13}	C_2H_5	68.08	67.98	7.08	7.20	7.56	7.69
C_6H_{13}	C_3H_7	68.72	68.81	7.34	7.42	7.29	7.25
C_6H_{13}	C_4H_9	69.32	69.57	7.59	7.76	7.03	7.26
C_6H_{13}	C_5H_{11}	69.87	69.66	7.82	7.96	6.79	6.84
C_6H_{13}	C_6H_{13}	70.39	70.22	8.03	7.86	6.57	6.62

[a] Elemental analyses were carried out by the Analytical Branch, AFML/LPA, Wright-Patterson Air Force Base, Dayton, Ohio.

Two of the presently reported mixtures are nematic at room temperature and several just above room temperature. However, the nematic thermal stabilities of these mixtures are several degrees lower than the earlier reported cases of 4(4′)-*n*-butyl-4′(4)-methoxyazoxybenzene.⁽³⁾

2. Experimental Section

Melting points were measured on an American Optical polarizing microscope equipped with a Mettler FP-2 heating stage. Column chromatography was carried out with MCB chromatographic grade alumina or silica gel.

4(4′)-Alkyl-4′(4)-hydroxyazoxybenzenes To a solution of 2g of 4-alkyl-4′-hydroxyazobenzene⁽⁸⁾ in 25 ml of methylene chloride was added 40% peracetic acid (1 :1.5 mole ratio). The two phase system was stirred vigorously overnight. The methylene chloride phase was separated and washed twice with water, twice with 5% $NaHCO_3$, and thrice with water. The methylene chloride was removed under reduced pressure and the residue placed on a short silica gel column (20 g). Elution was effected using ether : petroleum ether, increasing the ether from 10–33%. Combination of the azoxy fractions typically afforded 1.5 g of product which was used in the carbonate preparation without further purification.

4(4′)-Alkoxyformyloxy-4′(4)-alkylazoxybenzenes To a solution of 100 mg 4-alkyl-4′-hydroxyazoxybenzene in 10 ml of dry benzene was added 2 mole equivalents of dry pyridine. The solution was stirred vigorously while 2 mole equivalents of alkylchloroformate was added dropwise. After 4–6 hours of continuous stirring, the benzene solution was filtered from the precipitate of pyridine hydrochloride and the precipitate was washed with benzene. The benzene was then washed with two 20 ml portions of H_2O, the benzene distilled at reduced pressure and absolute ethanol added to azeotrope residual H_2O. The crude product was then chromatographed through a column of 30 g silica gel, eluted with petroleum ether: ether (9:1) and the azoxy fraction recrystallized from hexane. See Table 1 for CN transition temperatures.

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