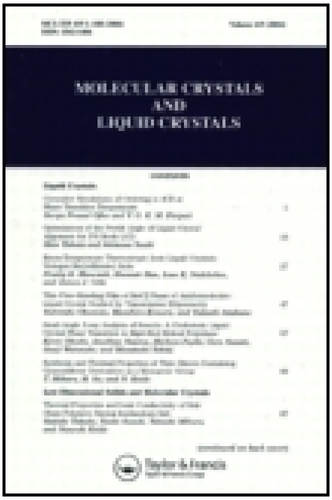

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Liquid Crystals. VIII. Nematogenic Compounds with a Terminal Dimethylaminoethoxy Group[1]

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Liquid Crystals. VIII. Nematogenic Compounds with a Terminal Dimethylaminoethoxy Group[1]

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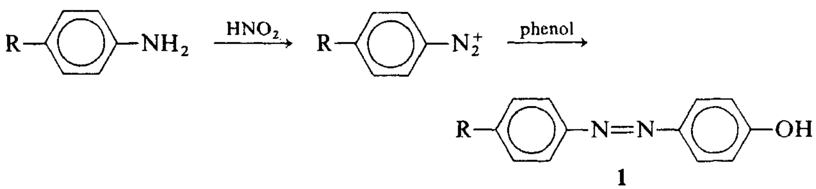
Six *p,p'*-disubstituted azo- and azoxybenzenes in which one of the terminal groups is 2-N,N-dimethylaminoethoxy, and their hydrochlorides have been synthesized. The three azoxybenzene derivatives exhibit nematic mesomorphism. Neither the azobenzenes nor any of the salts are liquid crystalline.

INTRODUCTION

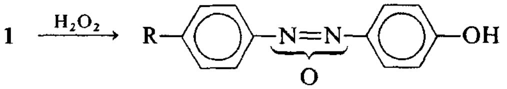
The well-known presence of mesomorphic substances in living systems prompted one of us (D.C.S.) to speculate as to the possible effects of synthetic compounds that are both physiologically active and mesomorphic on living organisms. As a first step in exploring this idea, a substituent found in a number of pharmaceuticals, 2-N,N-dimethylaminoethoxy, was introduced into two molecular systems known to exhibit liquid crystallinity to see if it is compatible with mesomorphism. The results of this preliminary investigation are reported below.

RESULTS AND DISCUSSION

The *p*-substituted *p'*-hydroxyazobenzenes (**1**) were prepared by diazotization of the appropriate *p*-substituted anilines, and coupling of the resulting diazonium chlorides with phenol (Eq. 1).[3] Recrystallization of the crude products from ethanol-water (50:50) gave rust-colored solids. The corresponding hydroxyazoxybenzenes (**2**) were obtained by oxidation of the azophenols (**1**) with hydrogen peroxide in acetic acid (Eq. 2).[4] After recrystallization from benzene-petroleum ether, the methyl- and ethoxy-substituted compounds were rust-colored, the methoxy-substituted derivative was yellow orange. The dimethylaminoethoxy group was introduced by means of a Williamson reaction in ethanol between the potassium salt of the azo- or azoxyphenol and dimethylaminoethyl chloride (Eq. 3).[5] The yellow products (**3**) were recrystallized from ligroin and converted to their hydrochlorides (**4**) by treatment with HCl in absolute ethanol (Eq. 4). Recrystallization of the salts from absolute ethanol gave lustrous yellow to orange plates. The results are summarized in Table I.



1 (1)



2 $(R{=}CH_3, CH_3O, C_2H_5O)$ (2)

$$\underset{\textbf{1}\text{ or }\textbf{2}}{ArOH} \xrightarrow{KOH} ArOK \xrightarrow{(CH_3)_2NCH_2CH_2Cl} \underset{\textbf{3a}\text{ (azo) or }\textbf{3b}\text{ (azoxy)}}{ArOCH_2CH_2N(CH_3)_2} \qquad (3)$$

$$\textbf{3} + HCl \longrightarrow \underset{\textbf{4a}\text{ (azo) or }\textbf{4b}\text{ (azoxy)}}{ArOCH_2CH_2\overset{+}{N}H(CH_3)_2 \quad Cl^-} \qquad (4)$$

$(Ar{=}RC_6H_4N_2C_6H_4 \text{ or } RC_6H_4N_2(O)C_6H_4)$

Preparation of the hydroxyazobenzenes (Eq. 1) was straightforward. Oxidation of these to the corresponding azoxybenzenes (Eq. 2) also went smoothly. However, it should be pointed out that two isomeric products would be expected from this reaction, one with the NO group on the R side and the other with the NO group on the OH side. Previous research in these laboratories has shown that, for $R{=}CH_3O$, this is indeed the case. The isomers were separated by fractional crystallization or column chromatography and found to melt at 135° and 156°. In the present work, no attempt was made to separate the isomeric hydroxyazoxybenzenes, so the amino derivatives prepared from them may well be mixtures of isomers also.

The Williamson synthesis (Eq. 3) was not successful with K_2CO_3 as the base, but proceeded nicely with KOH, particularly when the free amine,

TABLE I

Substituted azo- and azoxybenzenes and hydrochlorides of the amine derivatives[a]

			Transition temp., °C		
Formula	R	Yield, %	M. pt.	N-I	Lit.
1	CH_3	55	153		153[6]
1	CH_3O	70	142		142[6]
1	C_2H_5O	70	126		126[6]
2	CH_3	70	159		
2	CH_3O	68	133		135[7]
2	C_2H_5O	70	90[b]		
3a	CH_3	35	77		
3a	CH_3O	50	92		93[6]
3a	C_2H_5O	51	110		
3b	CH_3	40	68	80	
3b	CH_3O	32	54	78	
3b	C_2H_5O	40	66	112	
4a	CH_3	62	186		
4a	CH_3O	76	191[c]		
4a	C_2H_5O	71	192		
4b	CH_3	62	194		
4b	CH_3O	72	196		
4b	C_2H_5O	66	187		

[a] Satisfactory analytical data (±0.3% for C, H and N) were reported for all new compounds listed in the table. Elemental microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Transition temperatures were determined with a Reichert Thermopan polarizing microscope equipped with a Kofler micro hot stage.

[b] This intermediate gave the desired dimethylaminoethoxy derivative, but the elemental analysis indicates that it was isolated as the hemihydrate.

[c] This salt had been prepared before,[6] exhibited a melting point of 230°C, and had the correct analysis (60.78% C, 6.70% H, 12.54% N). A possible explanation for the discrepancy in melting points is polymorphism: i.e., a different crystalline modification may have been obtained in the earlier synthesis.

dimethylaminoethyl chloride, was used rather than its hydrochloride (converted to the free amine with KOH *in situ*).

All three of the dimethylaminoethoxy azoxy compounds exhibited a nematic mesophase, but the corresponding azo compounds did not. This is in agreement with earlier observations[8] indicating that *p*-disubstituted azoxybenzenes are more nematogenic than their azo analogs. Apparently, the bulky dimethylamino group broadens the rodshaped molecule sufficiently to inhibit nematic mesophase formation by the azo compounds, whereas the lateral dipole provided by the N—O bond provides enough additional

Analytical data for Table I

		%C		%H		%N	
Formula	R	Calcd.	Found	Calcd.	Found	Calcd.	Found
2	CH_3	68.41	68.59	5.30	5.47	12.27	12.16
2	C_2H_5O[a]	62.92	63.22	5.62	5.72	10.48	10.19
3a	CH_3	72.06	72.08	7.47	7.71	14.83	14.68
3a	CH_3O	68.21	68.01	7.07	6.91	14.04	13.89
3a	C_2H_5O	68.98	68.72	7.40	7.50	13.41	13.25
3b	CH_3	68.21	67.92	7.07	7.29	14.04	13.82
3b	CH_3O	64.74	64.67	6.71	6.73	13.32	13.21
3b	C_2H_5O	65.63	65.45	7.04	7.17	12.76	12.61
4a	CH_3	63.84	63.71	6.93	7.06	13.14	13.08
4a	CH_3O	60.80	60.57	6.60	6.71	12.51	12.23
4a	C_2H_5O	61.10	61.19	6.84	6.84	11.81	11.88
4b	CH_3	60.80	60.96	6.60	6.64	12.51	12.54
4b	CH_3O	58.03	58.16	6.30	6.36	11.94	11.90
4b	C_2H_5O	58.46	58.60	6.54	6.55	11.36	11.45

[a] Calculated for the hemihydrate, $C_{14}H_{14}N_2O_3 \cdot 1/2\,H_2O$.

intermolecular attraction in the azoxy compounds to counteract this steric effect.

The hydrochlorides were prepared because of their higher solubility in water and, thus, greater ease of administration into and compatibility with biological systems. Their lack of thermotropic mesomorphism is not surprising. Sterically, the trialkylammonium chloride group is very bulky, and, being salts, they have high melting points—about 100° higher than those of the free amines. In addition, hydrogen bonding via the N—H moiety may encourage the adoption of a non-linear molecular arrangement in the melt. It had been hoped, however, that their solutions would exhibit lyotropic mesomorphism. This did not prove to be true. A variety of solvents were tested: water, diethylene glycol, diglyme, glycerol, DMF, DMSO, and mixtures of the organic solvents with water. None of the salt solutions displayed liquid crystallinity. This may have been due, in part, to the steric and hydrogen bonding effects mentioned above, but another likely possibility is that the miscibilities of the salts with the solvents were simply not high enough to provide the concentrated solutions that are necessary for lyotropic behavior.

Despite this disappointing result, the thermotropic nematic mesomorphism of the azoxy compounds demonstrates that the dimethylaminoethoxy function and, presumably, other related physiologically active groups are compatible with liquid crystallinity, and encourages further research in this direction.

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1. (a) This work was supported by grants from the Research Council of the University of North Carolina at Greensboro. (b) From the M.S. thesis of M.H.A., The University of North Carolina at Greensboro, 1979. (c) Previous paper in this series: J. P. Schroeder, submitted to *Mol. Cryst. Liq. Cryst.* (in press). (d) N and I are abbreviations for nematic and isotropic.
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