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Liquid Crystalline Properties of Substituted Azo- and Azoxy-benzenes. I[1]

Kei Murase and Haruaki Watanabe

Ibaraki Electrical Communication Laboratory, Nippon Telegraph and Telephone Public Corporation, Tokai, Ibaraki 319—11

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In order to obtain low-temperature mesomorphic materials, thirty-two *p*-alkyl-*p*′-alkoxy-azo- and -azoxybenzenes have been synthesized. The former have been made by the condensation of *p*-*n*-alkylnitrosobenzenes and *p*-*n*-alkoxyanilines, and the latter, by the oxidation of the former. Twenty-nine of the compounds show nematic behavior. In the majority of cases, the nematic temperature range of the azoxy compounds, which have been considered to consist of two isomers synthesized simultaneously, is appreciably wide.

In order to use a new electro-optic effect of nematic liquid crystals[2] to display elements, the present authors are studying the preparation of new mesomorphic materials[3,4] which, it is hoped, will exhibit nematic behavior at a low and wide temperature range, and will respond at high speeds and with high contrast ratios to an applied electric field.

Many compounds of *p*,*p*′-di-*n*-alkoxy-benzylideneanilines, -azobenzenes, and -azoxybenzenes are well known to show mesomorphism.[5] Recently, almost all the compounds of *p*-*n*-alkoxybenzylidene-*p*′-*n*-alkylanilines have been found to be mesomorphic.[3,6,7] Because their less polar alkyl substituents make the molecular interactions weak, they show mesomorphic transitions at much lower temperatures than the corresponding *p*,*p*′-dialkoxybenzylideneanilines.

For the same reason, it was presumed that *p*-*n*-alkyl-*p*′-*n*-alkoxy-azo- or -azoxy-benzenes would be mesomorphic in a low temperature range. This work was carried out to ascertain the validity of this assumption. Thirty-two new compounds have been synthesized in this work; some of them have recently been studied by a method different from ours, and the same results have been shown.[8,9,10]

Experimental

The transition temperatures were determined with a Mitamura Riken micro hot stage. The NMR spectra were measured on a JEOL C-60 HL apparatus, using CCl_4 as the solvent.

Raw Materials. *p*-Nitrotoluene and *p*-ethylnitrobenzene were purchased from commercial sources and were not distilled further. *p*-*n*-Propylnitrobenzene (bp 96—100 °C/2 mmHg) and *p*-*n*-butylnitrobenzene were prepared by the nitration of the corresponding *n*-alkylbenzenes. *p*-Anisidine and *p*-phenetidine were purchased from commercial sources and were not refined. *p*-*n*-Propoxyaniline (bp 74—75 °C/1.5 mmHg), *p*-*n*-butoxyaniline (bp 103—104 °C/1.5 mmHg), and *p*-*n*-hexyloxyaniline (bp 155—158 °C/5 mmHg) were prepared by the reduction of corresponding *p*-*n*-alkoxynitrobenzenes.[11]

Preparation of p-*Alkylnitrosobenzenes.* *General Procedure*: A solution of *p*-*n*-alkylnitrobenzene (14—18 g) in 60 ml of ethanol and an aqueous solution of ammonium chloride (5.4 g) were mixed and then kept at 60—65 °C. Zinc dust (15 g) was added to the mixture under vigorous stirring for two or three minutes. Then the zinc oxide was removed and the filtrate was cooled at dry ice-methanol temperature. The resulting solid was filtered and washed with benzene. After vacuum drying white *p*-alkylphenylhydroxylamine was obtained in a 10—20% yield.

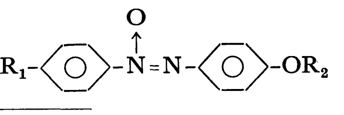
Then, a solution of the hydroxylamine (3 g) in 100 ml of ethanol was poured into an ice-cooled aqueous solution of $FeCl_3 \cdot 6H_2O$ (10.8 g). By extraction with ether, the green *p*-*n*-alkylnitrosobenzene was separated. The yield was about 90%.

Preparation of p-*Alkyl*-p′-*alkoxyazobenzenes.* *General Procedure*: A solution of *p*-*n*-alkylnitrosobenzene (3 g) in 25 ml of ethanol and a solution of an equimolar quantity of the appropriate *p*-*n*-alkoxyaniline in 10 ml of acetic acid were cooled with ice-water and then mixed. After the cooling had been continued for about an hour, an orange-red crystalline product was given by filtration in a 70—90% yield. The product was recrystallized twice from a methanol solution. IR(KBr): 1580 (N=N), 1255 (C-O-C) and 835 (*p*-subst. benzene-ring) cm^{-1}. NMR(CCl_4): τ 2.20 and 2.28 (double d, $J=9$ Hz, inner aromatic 4H), 2.87 and 3.20 (double d, $J=8$ Hz, outer aromatic 4H).

Preparation of p-*Alkyl*-p′-*alkoxyazoxybenzenes.* *General Procedure*: The azobenzene (6 g) was dissolved in acetic acid (90 ml) and then warmed to 60—70 °C. While the solution was being stirred continuously, a 90-ml portion of aqueous hydrogen peroxide (30%) was added. After the color of the solution became yellow, cold water (100 ml) was added. Then the product was extracted with *n*-hexane (300 ml). The yield was 55—85%. The additional recrystallization of the product was done twice. IR (Nujol): 1565—70 and 1280 ($N=N\rightarrow O$), 1255 (C-O-C) and 835 (*p*-subst. benzene-ring) cm^{-1}. NMR (CCL$_4$): τ 1.80 (m, inner aromatic 4H), 2.81 and 3.20 (double d, $J=8$ Hz, outer aromatic 4H).

Results and Discussion

Sixteen compounds of *p*-*n*-alkyl-*p*′-*n*-alkoxyazoxybenzenes were synthesized, and all were converted into the corresponding azoxybenzenes (strictly speaking, each of the compounds seems to be a mixture of Compounds I and II[10]) by oxidation.



(I),

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[1] Presented in part at the 25th Annual Meeting of the Chemical Society of Japan, Oct., 1971 (Osaka).

[2] G. H. Heilmeier, L. A. Zanoni, and L. A. Barton, *Proc. IEEE.*, **56**, 1162 (1968).

[3] K. Murase, This Bulletin, **45**, 1772 (1972).

[4] K. Murase, *Chem. Lett.*, **1972**, 471.

[5] Cf., for example, W. Kast, "Landort-Börnsteins Tabellen," 6th ed., Bd II (2a), 288 (1960).

[6] H. Kelker and B. Scheurle, *Angew. Chem.*, **81**, 903 (1969).

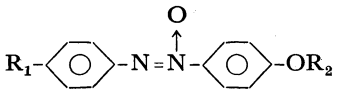
[7] J. B. Flannery and W. Haas, *J. Phys. Chem.*, **74**, 3611 (1970).

[8] H. Kelker and B. Scheurle, *Angew. Chem.*, **82**, 984 (1970).

[9] R. Steinsträsser, *Z. Naturforsch.*, **B26**, 577 (1971).

[10] R. Steinsträsser and L. Phol, *Tetrahedron Lett.*, **1971**, 1921.

[11] G. O. Gutekunst and H. L. Gray, *J. Amer. Chem. Soc.*, **44**, 1741 (1922).


(II)

The structures of the obtained compounds were confirmed by means of their IR and NMR spectra. Although *p,p'*-dialkyl and *p,p'*-dialkoxy compounds were expected to have also been produced by exchange reaction,[12] it can be concluded from the characterization of the NMR spectra of the aliphatic protons that the obtained compounds do not contain those mentioned above.

Contrary to Steinsträsser's result,[10] the difference in NMR spectra between Compounds I and II was not apparent in ours. Therefore, the isomer compositions of the azoxybenzenes are ambiguous.

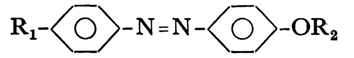
The elemental compositions of the obtained compounds were also confirmed. The analyzed C, H, and N contents are in fair agreement with the calculated values.

The transition temperatures of the obtained compounds are shown in Tables 1 and 2. It is apparent from these results that the majority of the compounds show nematic behavior in the relatively low temperature range, which is appreciably wide, especially in the azoxybenzenes. The wide nematic range of the azoxy compounds gives evidence that each of them consists of two isomers synthesized simultaneously.

The deviations in the transition temperatures of some of the obtained compounds from those of the analogous compounds which have two *n*-alkoxy groups as the *para* substituents[13] are shown in Table 3. As expected, all the transition temperatures of the obtained compounds are much lower than those of the comparable analogues.

Consequently, the materials obtained in this study may be used in the practical display so far as the transition temperature is concerned. Further study of the electro-optic effect of these materials is now in progress; the results will be presented in a subsequent paper.

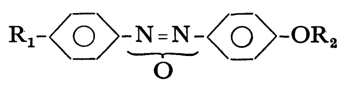
TABLE 1. TRANSITION TEMPERATURES OF SYNTHSIZED AZO COMPOUNDS,



Substituents		Transition temperatures (°C)		
R_1	R_2	mp	CNpt.	NLpt.
CH_3	CH_3	110 (111)[a]		(64)[a]
CH_3	C_2H_5	120 (118)[a]		90 (87)[a]
CH_3	n-C_3H_7	91		
C_2H_5	CH_3	80 (80)[a]		41 (37)[a]
C_2H_5	C_2H_5	102 (97)		80 (60)
C_2H_5	n-C_3H_7	91		
C_2H_5	n-C_4H_9	69 (68)[a]		68 (67)[a]
C_2H_5	n-C_6H_{13}		67	69
n-C_3H_7	CH_3		58 (60)[a]	69 (69)[a]
n-C_3H_7	C_2H_5		88 (88)[a]	100 (100)[a]
n-C_3H_7	n-C_3H_7	86		74
n-C_3H_7	n-C_4H_9		74	85
n-C_3H_7	n-C_6H_{13}		65	81
n-C_4H_9	CH_3		31 (32)[a,b]	46 (42[b], 47[a])
n-C_4H_9	C_2H_5		47 (48)[a,b]	84 (81[b], 83[a])
n-C_4H_9	n-C_3H_7	62[c]	(67)[a]	54[c] (68)[b]

a) Ref. 9, b) Ref. 8, c) Recrystallized only once.

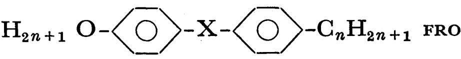
TABLE 2. TRANSITION TEMPERATURES OF SYNTHESIZED AZOXY COMPOUNDS,



Substituents		Transition temperatures (°C)		
R_1	R_2	mp	CNpt.	NLpt.
CH_3	CH_3	98		
CH_3	C_2H_5		105	114
CH_3	n-C_3H_7	88		62
C_2H_5	CH_3		38 (37[a])	71 (71[a])
C_2H_5	C_2H_5		54	100
C_2H_5	n-C_3H_7	72		68
C_2H_5	n-C_4H_9		47	85
C_2H_5	n-C_6H_{13}		51	81
n-C_3H_7	CH_3		41	94
n-C_3H_7	C_2H_5		55	119
n-C_3H_7	n-C_3H_7		52	90
n-C_3H_7	n-C_4H_9		44	102
n-C_3H_7	n-C_6H_{13}		58	98
n-C_4H_9	CH_3		18 (19[b], 16[b])	73 (75—76[b], 76[a])
n-C_4H_9	C_2H_5		45	98
n-C_4H_9	n-C_3H_7		49 (39[a])	73 (78[a])

a) Ref. 10, b) Ref. 8.

TABLE 3. DEVIATIONS IN THE TRANSITION TEMPERATURES OF



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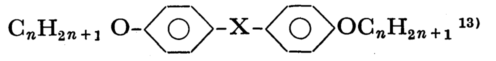

[13]

n	Deviations in transition temperature (°C)			
	X: $-N=N-$		X: $-\overset{\overset{O}{\uparrow}}{N}=N-$	
	CNpt or mp	NLpt	CNpt or mp	NLpt
1	−45		−18	
2	−57	−70	−80	−68
3	−60		−64	−32

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[12] Y. Ogata, M. Tsuchida, and Y. Takagi, *J. Amer. Chem. Soc.*, **79**, 3397 (1957).

[13] C. Weygand and R. Gabler, *Ber.*, B **71**, 2399 (1938).