SYNTHESIS AND LIQUID-CRYSTALLINE PROPERTIES

OF 4-(HEPTYLOXY)-n-(ARYL)BENZALDIMIN-2-OLS

Yu. G. Galyametdinov and G. I. Ivanova

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The synthesis and liquid-crystalline properties of 4-(heptyloxy)-N-(aryl)benzaldimin-2-ols have been described. The compounds obtained have smectic and nematic mesomorphism. Alternation of the bleaching temperatures (T_{bl}) with variation of the length of the alkyl radical in the N-aryl fragment has been noted. The dependence of T_{bl} on the contribution of the substituent to the polarizability of the molecule γ^2 is expressed by the equation $T_{bl} = 9.7 + 1.7 \gamma^2$.

The azomethines used to obtain liquid-crystalline metal complexes in [1] were liquid crystals. The changes in the mesogenic properties of compounds upon the transition from ligands to the corresponding metal complexes can be traced in their case. We synthesized two series (I and II) of substituted Schiff bases for the purpose of establishing the correlation between their structure and liquid-crystalline properties:



 $X = OC_nH_{2n+1}$, n = 1-12(I); X = H, F, Cl, Br, NO₂, CN, CH₃, C₄H₉, C₇H₁₅, N(CH₃)₂(II).

The syntheses were carried out by reacting 4-n-heptyloxyphenyl-2-hydroxybenzaldehyde with the corresponding anilines in ethanol. The reaction products were purified by recrystallization from ethanol or hexane or by reprecipitation by ethanol from chloroform. The azomethines obtained are crystalline substances of bright yellow or yellowish-green color. The composition and structure of the compounds was confirmed by the data from elemental analysis and IR spectroscopy, and the individuality was confirmed by thin-layer chromatography.

The liquid crystalline (mesogenic) properties of the azomethines were investigated with the aid of polarization microscopy. The temperatures of the phase transitions and types of mesophases found are presented in Tables 1 and 2, from which it is seen that all the compounds obtained, with the exception of compound 1 in Table 2, display liquid-crystalline properties and form a smectic or nematic mesophase. Some members of the series are polymorphous, i.e., they have two or even three (compound 9 in Table 2) mesogenic modifications.

The main factor determining the types of mesophases and temperatures of the phase transitions of the mesogens is the anisotropy of the dipole and dispersion intermolecular interactions. The latter, in turn, depends on the geometric anisotropy of the molecule and the anisotropy of the molecular polarizability.

In series I the electronic influence of the substituents X does not vary significantly as n is varied, although variation of the ratio of the length of the molecule to its width, i.e., the anisotropy of its shape, does occur.

An even-odd effect is known for the thermodynamic parameters of the phase transitions of liquid crystals with a normal paraffin chain. The compounds of series I investigated display (Fig. 1) alternation of the temperatures of the mesophase-isotropic-liquid transition (the bleaching temperatures T_{b1}) as a function of the number of atoms in the substituent X. This effect is caused by the anisotropy of the contributions of the polarizability of the substituents to the longitudinal (α_{\parallel}) and axial (α_{\perp}) components of the polarizability of the molecule [3]. The increment in α_{\parallel} is greater for a homolog with an odd number of atoms in

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Compound	n	T, °C			Width of
		K → S [*] _C	$K(S_C) \rightarrow N$	$M \rightarrow I$	mesophase ΔT, °C
(1)	í	90,0	-	106,9	16,9
(2)	2	82,6		126,5	43,9
(3)	3	78,6	82,3	110,0 495 7	30,9 58.7
(4)	4 5	59.8	107,4	120,7	61.3
(6)	6	59.7	122.7	126.5	66.8
$(\tilde{7})$	7	67,5	-	126,6	59,1
(8)	8	64,7		127,4	62,7
(9)	9	69,0	-	124,3	55,3
(10)	10	70,9	-	126 ,6	55,7
(11)	1 1	71,8	-	124,3	52,5
(12)	12	76.6	-	125,0	48,4

TABLE 1. Temperature of the Phase Transitions of the Compounds of Series I

*Phase: K - crystalline, S_C - smectic C, N - nematic, M - mesophase, I - isotropic liquid.



Fig. 1. Dependence of the temperature of the phase transitions on the number of atoms in the side chain in the compounds of series I: a) Isotropic liquid; b) nematic phase; c) smectic phase; d) crystalline phase.

Fig. 2. Dependence of the bleaching temperature T_{bl} $(T_{M \rightarrow I})$ of N-arylated azomethines on the anisotropy of the polarizability of the corresponding substituted benzenes γ^2 .

the substituent X than for a compound with an even number of atoms; therefore, the anisotropy of the polarizability of the molecule is greater and T_{bl} is higher in the former case. As the length of the substituent is increased above m = 8, reduction of the alternation of T_{bl} is observed, since the mobility of the chain increases and the contributions of the polarizabilities for the even and odd homologs become closer as the number of atoms in the chain is increased.

Thus, in the case of the compounds of series I, the thermostability of the mesophase is determined by the anisotropy of the contribution of the polarizability of X (in the homologs with a number of atoms in X up to 7) and the change in the geometric anisotropy of the molecule (when m > 8). As is seen from Fig. 1, an increase in the length of the chain in the substituent results in enhancement of the intermolecular interaction. This is evinced by the decrease in the size of the region for the existence of the less ordered nematic phase and the expansion of the temperature range for the more ordered smectic mesophase.

The geometric dimension of the para substituents in series II and the first two members of series I are close, allowing us to assume that anisotropy of the shape of the molecules is similar for the compounds of this series.

Compound		T, °C			Width of
	X	K → S _A	$K(S_A) \rightarrow N$	$M \rightarrow I$	mesophase ΔT, °C
(1) (2) (3) (4) (5) (6) (7) (8) (9) (10) (11)	H p-F p-Cl p-Br p-CN p-NO ₂ p-CH ₃ p-C ₄ H ₉ p-C ₄ H ₉ p-C ₇ H ₁₅ ‡ p-(CH ₃) ₂ N m-F	[72,5] * 72,0 81,4 76,0 48,7 † 44,6 † [27,3] *	- - - - 94.5 64.9 64.6 95.6 104.2 -	50.9 73.0 122.0 129.4 121.0 101.5 78.9 85.9 97.7 111.0 36	$ \begin{array}{c c} 0\\ 50.0\\ 54.0\\ 41.0\\ 25.5\\ 14.0\\ 37.2\\ 53.2\\ 6.8\\ - \end{array} $

TABLE 2. Temperatures of the Phase Transitions in Compounds of Series II

*A monotropic phase, which appears from the isotropic melt upon cooling. *The K \rightarrow S_C transition. *There is an S_C \rightarrow S_A transition at 94°C [2].

One special feature of the substituents in series II is the fact that a significant change in the electronic structure of the N-phenyl fragment can occur under their action due to the inductive and resonance influences of X. The thermal stability of the compounds of series II may be determined (a) by the contribution of the polarizability of the substituent to the total polarizability and polarity of the molecule and (b) by the changes in the conditions of the π conjugation in the CH-N-C₆H₄-X fragments and the conformation of the molecule under the effects of X.

The influence of noncoplanarity on the liquid-crystalline properties of some azomethines was considered in [4]. It was noted that the presence of an intramolecular hydrogen bond between the proton of the o-hydroxy group and the lone pair of the nitrogen atom worsens the condition for its conjugation with the phenyl ring. The introduction of alkoxy substituent with stronger donor properties reduces the effect of the π conjugation, and the molecule becomes more planar. The dispersion attraction of the planar molecules is stronger, and the temperature for the transition from the crystal to the mesophase is higher for them. In our case, as is seen from the data in Tables 1 and 2, the temperature of the substituents X. This is apparently due to the sharper difference between the electronic properties of the substituents X in the series under investigation in comparison to the properties of the radicals considered in [4].

It was noted in [5] that a strong electronic interaction of the substituent may result in changes in the coplanarity and the conditions for π conjugation between the fragments of the molecule, which may influence the values of the components of the principal tensor of the polarizability of the molecule. These changes in the anisotropy of the molecular polarizability should influence the thermostability (T_{bl}) of mesogens.

In order to evaluate the role of electronic effects in the overall influence of a substituent on the bleaching temperature, we determined the correlation between the values of T_{bl} of the compounds of series II, along with compounds 1 and 2 of series I, and the constants σ , R, \mathcal{F} . The Hammett constant σ takes into account the combined resonance and inductive influence of the substituent X, the constant \mathcal{F} reflects the contribution of the field effects, and R is the resonance effect of the substituent X.

None of the sets of constants of the substituents correlates with T_{bl} , indicating the absence of a unique relationship between the electronic parameters of a substituent and the energy of the intermolecular interactions determining the thermostability of the liquid-crystalline phase of the compound.

Nevertheless, the value of $T_{\rm bl}$ correlate linearly with the values of the anisotropy of the polarizability γ^2 of the corresponding monosubstituted benzenes [6] (Fig. 2) in accordance with the equation

$$T_{\rm b1} = 9.7 + 17 \,\gamma^2; \, r = 0.96. \, n = 8 \tag{1}$$

The existence of this correlation allows us to conclude that the changes in the thermostability of the mesophases of the compounds of series II and compounds 1 and 2 from series I, which are similar to them, are determined by the additive contributions of the anisotropy of the polarizability of the respective substituents to the total anisotropy of the polarizability of the molecules.

Correlations similar to (1) were observed separately for donor and acceptor substituents in cholesterol benzoates in [7]. The existence of two correlations was attributed by Cherkashina et al. to a manifestation of an effect of direct polar conjugation in the benzene fragment. In fact, taking into account the high acceptor ability of the esteric fragment ($\sigma = 0.44$ [8]), we should expect an effect due to its polar conjugation with donor substituents such as OCH₃ and OC₂H₅. The existence of a linear correlation and the deviation of T_{bl} from it only for a strong donor, viz., a dimethylamino group, allow us to postulate a small magnitude for the effect of the direct polar conjugation of the substituents in series II studied here.

In order to quantitatively compare the capacities of benzoyl and azomethine fragments for polar conjugation, we determined the value of the σ constant of the latter. The value $\sigma = 0.29$ was obtained from data on the ¹⁹F NMR chemical shifts of compounds 2 and 11 (Table 2). The correlations presented in [9] were used for the calculation. The acceptor ability of an azomethine fragment ($\sigma = 0.29$) is lower than that for a benzoyl fragment ($\sigma = 0.44$), and this fact is responsible for the smaller role of the effects of direct polar conjugation in the azomethines investigated in comparison to the cholesterol derivatives. Thus, in the case of mesogens with the general formula YC₆H₄X, the donor-acceptor properties of the fragment cause either the appearance of two correlations of type (1) or the deviation of the points for substituents X with pronounced donor (when Y is an acceptor) or acceptor (when Y is a donor) properties from Eq. (1).

As is seen from Fig. 2, the point corresponding to the cyano group deviates from correlation (1). The acceptor ability of the cyano group with respect to a benzene ring is lower than that of the nitro group. Therefore, the deviation noted cannot be caused by conjugation effects. The capacity of the cyano group for additional coordination, however, is known, and it may result in a type of packing of the molecules with X = CN in the mesophase different from that of the remaining compounds of series II. This may have an effect on the character of the intermolecular interactions and ultimately on the thermostability of the compound. Elucidation of this question would require a separate investigation.

EXPERIMENTAL

The compounds were obtained by boiling equivalent amounts of 4-n-heptyloxy-2-hydroxybenzaldehyde and the respective substituted aniline in ethanol for 15-30 min. In the case of X with acceptor properties, the reaction time was increased to 5-6 h, and acetic acid was employed as the catalyst. The reaction products were purified by recrystallization from ethanol, chloroform, or hexane. The individuality of the compounds was established by TLC on Silufol UV-254 plates, and the eluent was a chlorform-hexane mixture. The composition and structure of the compounds synthesized were confirmed by the data from elemental analysis and IR spectroscopy. The formation of the Schiff bases was characterized by the band of the stretching vibrations of the C=N bond in the azomethine group at 1620-1600 cm⁻¹, as well as by the broad band for the OH group with a center at 3008 cm⁻¹.

The temperatures of the phase transitions and the types of mesophase were determined on a Boetius microscope. The IR spectra of solutions of the compounds in CCl₄ were recorded on a Specord 75 IR spectrometer. The ¹⁹F NMR spectra were obtained on a Tesla BS-487 spectrometer with the use of CF₃COOH as an external reference. The chemical shifts relative to fluorobenzene for the para- and meta-substituted derivatives are, respectively: $\delta_p^F = -2.79$; $\delta_m^F = -3.59$.

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AZIDE-TETRAZOLE TAUTOMERISM OF DIAZIDODIAZINES

AND THEIR BENZO ANALOGS

V. P. Krivopalov, S. G. Baram,

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A. Yu. Denisov, and V. I. Mamatyuk

It has been discovered with the aid of IR and NMR spectroscopy that 5-azidotetrazolo[1,5-a]quinazoline exists in solutions in a tautomeric equilibrium with ditetrazolo[1,5-a:1',5'-c]quinazoline, and the thermodynamic and kinetic characteristics of the equilibrium have been determined. Azide-tetrazole tautomerism is not observed under these conditions for ditetrazolo[1,5-a:5',1'-c]pyrazine, 6-azidotetrazolo[1,5-b]pyridazine, and their benzo analogs.

An azido group in an α position to an aza atom of a heterocycle is capable of undergoing reversible intramolecular addition with the formation of an annelated tetrazole (T). The tautomeric conversions of such heteroaromatic azides (A) represent an important factor, which determines their reactivity, biological activity, and physical properties [1-3].



Investigation of azide-tetrazole equilibria have also revealed an effect of benzoannelation on the direction of the cyclization of the azido group when two inequivalent reaction centers are present in the molecule [4]. In our opinion, diazidodiazines and their benzo analogs are convenient models for investigations in this area. The structures of the tautomers of diazidobenzodiazines (see below) were previously established in a number of studies with the use of chemical, but not spectroscopic, methods.

In the present work we used the methods of NMR and IR spectroscopy to study the structures of diazidodiazines^{*} and their benzo analogs^{*} in solutions of 3,6-diazidopyridazine (IAA) (the numbering is given as 1,4- in the scheme), 1,4-diazidophthalazine (IIAA), 2,3-diazidopyrazine (IIIAA), and 2,3-diazidoquinoxaline (IVAA), as well as the benzo analogs 2,4diazidopyrimidine (VAA) and 2,4-diazidoquinazoline (VIAA).

*The numbering of the atoms in the schemes, which does not correspond to the IUPAC rules, was selected for the sake of convenience in comparing the parameters of the NMR spectra.

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