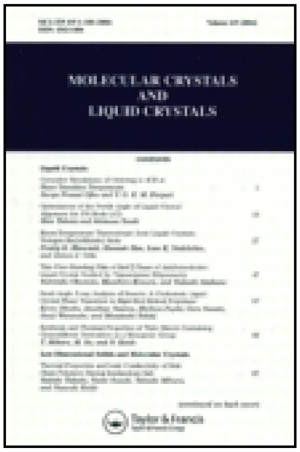


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Mesomorphous Properties of Azo- and Azoxyarylethanes as Potential Stationary Phases in Gas Chromatography

A. Ziólek [a], R. Dabrowski [a] & Z. Witkiewicz [a]
[a] Military Technical Academy, 01 489 Warsaw 49

Version of record first published: 20 Apr 2011.

To cite this article: A. Ziólek, R. Dabrowski & Z. Witkiewicz (1984): Mesomorphous Properties of Azo- and Azoxyarylethanes as Potential Stationary Phases in Gas Chromatography, Molecular Crystals and Liquid Crystals, 109:2-4, 107-123

To link to this article: http://dx.doi.org/10.1080/00268948408078700

Mol. Cryst. Liq. Cryst., 1984, Vol. 109, pp. 107–123
0026-8941/84/1094-0107/$18.50/0

Mesomorphous Properties of Azo- and Azoxyarylethanes as Potential Stationary Phases in Gas Chromatography

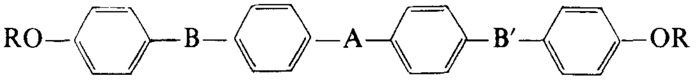
A. ZIÓŁEK, R. DĄBROWSKI, and Z. WITKIEWICZ
Military Technical Academy, 01 489 Warsaw 49

(Received December 21, 1982; in final form December 29, 1983)

Two series of compounds have been synthesized: 1,2-bis(4′-butoxybenzeneazobenzene-4)ethanes and 1,2-bis(4′-butoxybenzeneazoxybenzene-4)ethanes. The effects of lateral substituents (CH_3, Cl, CN) on temperature are tested as well as the molar enthalpies and entropies of their phase transitions determined. The application of those compounds as liquid-crystalline stationary phases in gas chromatography is suggested.

INTRODUCTION

Bi- and trinuclear compounds yielding liquid crystals are most frequently tested in view of their possible applications in displays. Another interesting application of those liquid crystals are stationary phases for gas chromatography. In some cases the liquid crystals used in the displays are also used in gas chromatography.[1] Often, however, liquid crystals with molecules consisting of four and even more benzene rings connected by such groups as, e.g., COO, CH=N, N=N, are used in chromatography, especially for separating polycyclic hydrocarbons. The liquid crystals with such molecules reveal wide mesophase ranges and low vapour pressures owing to which they are not easily removed from the chromatographic column. Such liquid-crystalline stationary phases often allow the simultaneous separation of mixtures of isomers with equal molecular weights as well as mixtures of compounds with molecular weights differing considerably. The long, rigid molecules yield in their majority crystals that have high melting points and in which we observe, on transition from the crystal phase, one or even several smectic phases, and their nematic phase often occurs in a narrow temperature range in the vicinity of the clearing point. On the other hand, nematics whose nematic phase is in the direct vicinity of the solid phase are often more suitable for use in gas chromatography since the best separations in the nematic phase are achieved in the neighbourhood of the melting point. If an flexible separating group is introduced into the molecule between the rings, the rigidity of the molecule decreases and the melting point is lowered what produces greater nematogeneity of the molecule. This concept was realized in practice by Janini *et al.*[2,3] with respect to Schiff's bases obtained from 1,2-di(4-aminophenyl)ethane (compounds of formula **1**):



1

where A and B are the groups separating the benzene rings: A = —CH$_2$—CH$_2$—, B = —CH=N— and B′ = —N=CH—, while R is an alkyl, C_nH_{2n+1} (n = 1–10).

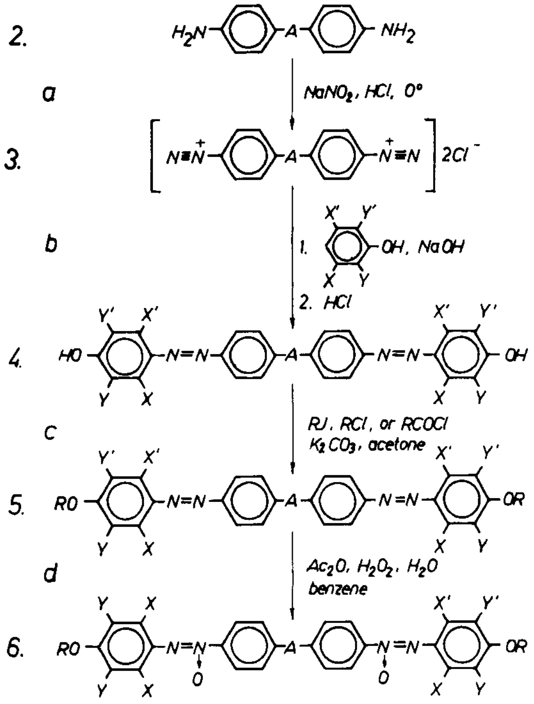
In our earlier works[4-7] we found that good separating properties with respect to isomers of benzene geometric derivatives and other compounds are revealed by liquid-crystalline azo and azoxy compounds. We thought it interesting therefore to synthesize similar compounds with separating groups such as A = —CH$_2$—CH$_2$ and B = B′ = —N=N— or N=N(O) in formula 1. As regards trinuclear compounds, it occurred that apart from changing the character of the terminal substituents of the elongated molecule, the introducing of lateral substituents producing the branching of the molecule is also a convenient method of controlling the melting and clearing points and kind of mesophase.[8-13] We decided to test whether in the case of compounds of formula 1 similar effects will be observed after introducing such lateral substituents as CH$_3$, Cl and CN.

The compounds of formula 1 can be regarded intermediary between the low molecular liquid-crystalline compounds and liquid-crystalline polymers, which attract ever increasing interest.[14,15] The information obtained on the effect of lateral substituents on the mesogeneity of compounds of formula 1 may also be useful for planning syntheses of polymeric liquid crystals containing mesogenous groups with lateral substituents in the main chain of the molecules. In the present work we only describe the method of obtaining azo and azoxy compounds of formula **1** as well as their mesogenic and thermodynamic properties. The effect of lateral substituents on the separating ability of the relevant stationary phases with respect to disubstituted naphthalene isomers and the application of those phases for separating polynuclear aromatic hydrocarbons are described in other works.[16,17]

RESULTS AND DISCUSSION

Synthesis of the compounds and their structure

Bis-azo and bis-azoxy compounds of formula **1** have been synthesized according to the reaction scheme shown in Figure 1 from 1,2-di-(4-aminophenyl)ethane (A = $-CH_2-CH_2-$) or (in one case) from



$A = -CH_2-CH_2-$ or $-CH=CH-$

$X = H-$ or CH_3-, $Cl-$ $\quad Y = H-$ or CH_3-, $Cl-$, $CN-$

$X' = H-$ or CH_3- $\quad Y = H-$

FIGURE 1 Scheme of the synthesis of bis-azo and azoxy compounds.

4,4′-diamino-trans-stilbene (A = trans—CH=CH—). 1,2-di(4-aminophenyl)ethane was obtained by reducing 1,2-di(4-nitrophenyl)ethane with hydrazine in alcoholic solution in the presence of Raney nickel.[18] 4,4′-di-nitro-trans-stilbene was reduced with zinc in hydrochloric acid,[19] when only 4,4′-diamino-trans-stilbene is produced. 1,2-di-(4-nitrophenyl)ethane and 4,4′-dinitrostilbene have been obtained according to Ref. 20 by passing through the alkaline methanol solution of *p*-nitrotoluene a stream of oxygen (in the case of the former compound) or a stream of air (in the case of the latter compound). Diazotization (step a) and coupling (step b) were conducted in the standard, generally adopted way. Commercially available phenols (phenol, *o*-cresol, *m*-cresol, *o*-chlorophenol, *m*-chlorophenol, 3,5-xylenol) were used. Only cyanophenol was produced from *o*-cyanoanisole.[21] The alkylation with butyl iodide or benzyl chloride and acylation (step c) of the obtained bis-azophenols (compounds **4**) were carried out in the presence of potassium carbonate in acetone or cyclohexanone at the boiling point of those solvents. The reactions proceed slower in acetone as compared with cyclohexanone however, only due to that the substrates are readily soluble and the reaction products insoluble in acetone and the latter precipitate in the course of the reaction so they are only slightly contaminated. This facilitates the further purification of the products by recrystallization.

The oxidation of bis-azo compounds **5** was conducted using peracetic acid obtained from a 30% H_2O_2 solution and acetic anhydride. Bis-azo compounds **5** are poorly soluble in the oxidizing mixture and their oxidation in suspension proceeds with difficulty. To increase the solubility of those bis-azo compounds the reaction mixture was diluted with benzene, when a homogeneous system was obtained what lead to a significant acceleration of the reaction.

Oxidation of the bis-azo compounds obtained from ortho-substituted phenols yields mixtures of position isomers of the bis-azo compounds with the oxygen atom attached to the first or the second nitrogen atom.

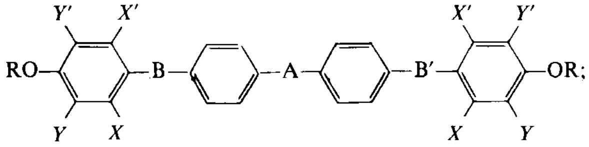
Oxidation of the bis-azo compounds obtained from meta-substituted phenols yields only one isomer of the bis-azo compound in which the oxygen atom is bound to the nitrogen atom more distant from the lateral substituent.

A more detailed description of the preparation and purification of the compounds is given in the experimental part.

The structure of the synthesized compounds has been confirmed by IR, UV-VIS absorption spectra and analyses, the results of which are given in Table I.

TABLE I

Comparison of the phase-transition temperatures and of positions λ_{max} of the long-wave π-π^* band in the UV-VIS spectrum for compounds of formula:



; B = B′ with the exception of compound 1

Compound 1	A 2	B 3	R 4	Y 5	Y' 6	X 7	X' 8	Phase transition temperatures, °C $K_1 \to K_2$ 9	Phase transition temperatures, °C $K \to I$ or S_A or N 10	Phase transition temperatures, °C $S_A \to N$ 11	Phase transition temperatures, °C $N \to I$ 12	λ_{max} nm 13
4a	CH_2-CH_2	N=N	H	H	H	H	H		258			
4b	CH=CH	N=N	H	H	H	H	H		> 360[a]			
4c	CH_2-CH_2	N=N	H	H	H	CH_3	H		200			
4d	CH_2-CH_2	N=N	H	H	H	Cl	H		214			
4e	CH_2-CH_2	N=N	H	CH_3	H	H	H		230			
4f	CH_2-CH_2	N=N	H	Cl	H	H	H		208			
4g	CH_2-CH_2	N=N	H	CN	H	H	H		212			
4h	CH_2-CH_2	N=N	H	H	H	CH_3	CH_3		210			
1[b]	CH_2-CH_2	CH=N	C_4H_9	H	H	H	H		159	188	303	
5a	CH_2-CH_2	N=N	C_4H_9	H	H	H	H		201		310	352
5b	CH=CH	N=N	C_4H_9	H	H	H	H		250	300	360	400
5c	CH_2-CH_2	N=N	C_4H_9	H	H	CH_3	H		116 or 120[c]		229	357
5d	CH_2-CH_2	N=N	C_4H_9	H	H	Cl	H	123	136		235	357
5e	CH_2-CH_2	N=N	C_4H_9	CH_3	H	H	H		193		253	350
5f	CH_2-CH_2	N=N	C_4H_9	Cl	H	H	H	175	179	197	256	352

TABLE I (*Continued*)

Compound 1	A 2	B 3	R 4	Y 5	Y' 6	X 7	X' 8	Phase transition temperatures, °C $K_1 \to K_2$ 9	$K \to I$ or S_A or N 10	$S_A \to N$ 11	$N \to I$ 12	λ_{max} nm 13
5g	CH_2—CH_2	N=N	C_4H_9	CN	H	H	H		197	212	283	350
5h	CH_2—CH_2	N=N	C_4H_9	H	H	CH_3	CH_3	104	115		204	345
5i[d]	CH_2—CH_2	N=N	C_4H_9CO	H	H	H	H		165	184	303	
5j	CH_2—CH_2	N=N	$C_4H_9C_6H_4CO$	H	H	H	H		200[e]	229	360	338
5k	CH_2—CH_2	N=N	$C_6H_5CH_2$	H	H	H	H		225	250	310	346
6a	CH_2—CH_2	N=N[g] ↓ O	C_4H_9	H	H	H	H		137	290	330	352
6c	CH_2—CH_2	N=N ↓ O	C_4H_9	H	H	CH_3	H		157	167	268	365
6d	CH_2—CH_2	N=N ↓ O	C_4H_9	H	H	Cl	H		171		260	365
6f	CH_2—CH_2	N=N[g] ↓ O	C_4H_9	Cl	H	H	H	132	143[f]	243	262	352

[a] With decomposition.

[b] Ref. 2; B′ = —N=CH—.

[c] The compound melts at 116°C and crystallizes yielding a form of higher melting point.

[d] Ref. 18.

[e] See remarks in text.

[f] The transition S_C, $S_C \to S_A$ is observed at 183°C.

[g] The mixture of isomers.

The electron spectra of the obtained compounds **5a** and **6a** are characteristic for 4,4′-disubstituted azo- and azoxybenzene, respectively.[22] In the UV-VIS range they have two bands related to the electron transition $\pi \rightarrow \pi^*$ (one is more intensive with maximum at about 350 nm, and one weaker with maximum at about 250 nm). The azo compound reveals, besides, a band of small intensity and flattened maximum in the visible range of 400–450 nm which is related to the $n \rightarrow \pi^*$ transition in the azo group. Such a structure of the spectrum indicates that the $—CH_2—CH_2—$ group separates effectively both aromatic systems of the molecule; those systems absorb UV-VIS radiation almost independently. Substitution of the saturated $—CH_2—CH_2—$ bridge by the vinylene $—CH{=}CH—$ group, making possible—as it should have been expected—the coupling of π electrons of both aromatic systems, produces significant changes in the electron spectrum: λ_{max} is shifted batochromically from 352 nm for **5a** to 400 nm for **5b**. The introduction of one substituent (CH_3 or Cl) in position ortho to the azo bridge produced no major changes in the electron spectrum. It was only after the second, successive group was substituted in position ortho with respect to the azo bridge that a distinct hypsochromic shift of both bands $\pi \rightarrow \pi^*$ was observed (Figure 2). This fact points to a change in the spatial orientation of the benzene rings about the azo bonds what leads to the decreased effectiveness of π-electron coupling in the auxochromic system. It occurs that similar effects in the electron molecular spectra are brought about also by introducing large terminal groups—the butylbenzoyl or benzyl ones (compounds **5j** and **5k**). For molecules containing rigid fragments the linear conformation is favoured also in solution.[23] In the presence of rigid terminal substituents (like in **5j** or **5k**) a more linear geometry of the molecule is probably obtained, and the angles of bonds in the environment of the azo group are deforming from the optimal value for to realize the coupling of the benzene ring π-electrons and the nitrogen bridge.

Phase transitions

In the following we shall discuss the effects of the functional groups at the main chain of the molecule in the terminal and internuclear positions on the temperatures and types of phase transitions, as well as of substituents in lateral positions on the temperatures, molar enthalpies and entropies of phase transitions in the synthesized compounds **5** and **6**. In general it can be stated that all the alkyloxy- and acyloxybis-azo and azoxy compounds **5** and **6** are enantiotropic liquid

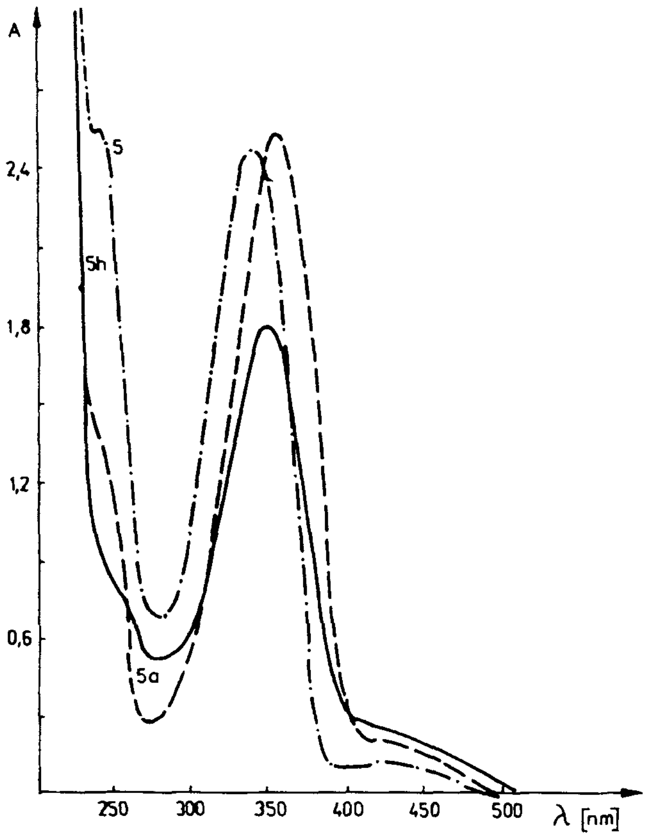


FIGURE 2 Comparison of the electron spectra of the bis-azo compounds: **5a**—compound with no lateral substituent, the butyloxy group being in the terminal position; **5h**—compound with two methyl groups in positions ortho and ortho′; **5j**—compound with no lateral substituent, the benzoyl group being in the terminal position.

crystals as distinguished from bis-azophenols **4** which are not mesogenic (Table I). Compounds **5** and **6** reveal a wide range of the mesophase (of 100° and more), with the exception of meta-substituted azo compounds which have a narrower mesophase range.

For all compounds tested in this work in which the smectic phase was observed we found on the basis of miscibility with other smectics and of characteristic textures (fan-like or pseudo-isotropic) that the phase is of A type. In the case of compound **6f**, which has two smectic phases, the one existing at the lower temperature was assigned to type C, and that existing at the higher temperature to also type A. Some doubts still exist as to the kind of smectic phase in compound **5j** which reveals a peculiar behaviour. That compound has a fan-like texture characteristic of a smectic of type A, but its mixtures with the remaining smectic compounds tested in this work show a very strong extension of the nematic range at the cost of the smectic one. The smectic phase is destroyed in that compound when it is mixed with a relatively small quantity of another smectic A. This peculiarity is the object of our study and will be described in a separate publication.

Effect of the groups separating the benzene rings on the melting and clearing points and on the type of the mesophase

The data summarized in Table I show that substituents A and B in the main chain, when the terminal substituent is $—OC_4H_9$, produce a strong varying of the type of the mesophase and the phase transition temperatures. Compound **5a** (A = $—CH_2—CH_2—$, B = B′ = —N=N—) has only the nematic phase. The change of the symmetric azo group, —N=N—, to the unsymmetrical azoxy, —N=N(O), or azomethine, —CH=N—, group also contributes to the tendency of smectic phase formation. The azoxy compound **6a** has a very stable smectic phase which extends almost over the whole mesophase range from 137° to 290°, furthermore, only one type of the smectic phase S_A in the whole temperature range is observed. The azomethin compound **1** is a smectic in the range of 30° above the melting point. This ability to form smectic phases is due to the polarity of the unasymmetrical groups —N=N(O) and —CH=N—. The dipole-dipole and dipole induced dipole molecular interactions inhibit mutual parallel displacements of the molecules and stabilize the smectic ordering. The azoxy and azomethine groups also lower significantly the melting points of the azo compounds, however, no greater differences in the clearing points are observed; the clearing points of azoxy compounds are higher by not more than 20°. The latter behaviour is different than that observed for compounds which do not contain the flexible ethylene group, $—CH_2—CH_2—$, where the observed differences in T_{N-I} between the azo and azoxy compounds are greater. The lowering of the melting point of azomethine and azoxy compounds as compared with the azo compounds can probably be related to the non-planar arrangement of the benzene rings in the neighbourhood of the —N=N(O) and —CH=N— groups.[24] That produces and advanced irregularity of the shape of the molecule and in the case of molecules of such a considerable size may inhibit the formation of a closely packed crystalline lattice. The lack of greater differences in the clearing points irrespective of which group, —N=N—, —CH=N— or

—N=N(O)—, is present follows from that the molecule includes the ethylene group. The molecule conformation states, allowing for a more or less inhibited rotation on that group, are strongly temperature dependent and it is those states that are chiefly responsible for the clearing temperature of those compounds. The substitution of the group $—CH_2—CH_2—$ by the —CH=CH— group apart from increasing—as expected—the rigidity and coplanarity of the molecules also raises significantly the melting and clearing points as well as the smectogenic properties (see compound **5b**).

Smectic phases are also observed in azo compounds **5i**, **5j** and **5k** as a result of replacing of the butoxy group in the terminal positions by the benzyloxy, butylbenzoyloxy or valeryloxy ones. In such compounds the smectic phases exist only in a narrow temperature interval of 20–30° above the melting point. The benzyloxy and especially the butylbenzoyloxy group in the terminal position increases the fraction of rigid elements in the molecule and elongates the latter. Then the possibility of free rotation on the carbon-carbon bridge of $—CH_2—CH_2—$ decreases what contributes to the increased stability of the mesophase. Compound **5j** reveals the widest nematic mesophase range in the tested series of bis-azo compounds and despite having as many as six benzene rings in the molecule reveals a relatively low melting point, not exceeding 200°. We found that this compound reveals when used as a stationary phase good separating properties with respect to many high-boiling mixtures of compounds inclusive of polynuclear aromatic hydrocarbons.[17]

Effect of lateral groups on the melting and clearing points

The lateral substituents: CH_3, Cl and CN appear in the tested compounds in the external rings in position meta or ortho to the azo or azoxy groups. Those substituents lower the clearing points of the compounds irrespective of which of the two positions with respect to the azo or azoxy group they occupy. The substituent in position ortho lowers the clearing point more (by about 80°) than when it appears in the meta position (only by 30–60°). The greatest lowering of T_{N-I} was observed when two substituents were present, one in position ortho and the other one in position ortho′ (compound **5h**). The observed decrease was smaller, however, than the doubled depression of the clearing point produced on introducing one substituent. The ortho-substitution of the benzene ring external with respect to the azo groups lowers the melting point in a similar degree as the clearing point, thus the range of the mesophase of the compounds is not affected, but is only shifted towards lower temperatures. In azoxy compounds that reveal low melting points the lateral substituent produces no further lowering of the melting point, and when it appears in ortho-position it may even raise that point. This is due to that ortho-substituted azoxy compounds have only one isomer, while the remaining azoxy compounds may be mixtures of even three position isomers.

The substituents in meta position lower but slightly the melting points, so the mesophase range is also narrowed. When the chlorine atom or the cyano group is present in azo compounds in the meta position, the compounds are smectics, though only in a narrow temperature range. That property becomes more pronounced when the azo group is replaced by the azoxy one. On the other hand, if the substituent is present in the ortho position, the occurrence of smectic phases is not observed neither in the azo nor in the azoxy compounds, with the exception of compound **6c**.

Effect of the lateral groups on the molar melting and clearing enthalpies and entropies

Table II summarizes the determined molar melting and clearing enthalpies, ΔH_{melt} and $\Delta H_{N \to I}$ as well as the calculated values of ΔS_{melt} and $\Delta S_{N \to I}$.

Azo compounds **5c** to **5h** meta- and ortho-substituted with —Cl, —CH_3 or —CN groups have higher molar melting enthalpies than the non-substituted compound, **5a**, whereas the molar clearing enthalpy is smaller than (if polar groups are present (—Cl, —CN)) and approximately equal to (if the methyl substituent is present) the molar

TABLE II

Molar melting and clearing enthalpies and entropies of the azo compounds as well as the differences of the clearing points ($\Delta T_{N \to I}$) and melting points (ΔT_m) between the non-substituted and laterally substituted compounds

Compound	$\Delta H_{K \to N}$ kJ mole^{-1}	$\Delta S_{K \to N}$ J mole^{-1} K^{-1}	$\Delta H_{N \to I}$ kJ mole^{-1}	$\Delta S_{N \to I}$ J K^{-1} mole^{-1}	$\Delta T_{N \to I}$ °C	ΔT_m °C
5a	24.7	52.2	4.0	6.9	0	0
5c	50.9	130.6	3.7	7.3	81	85
5d	46.4	113.4	2.0	3.9	75	65
5e	34.2	73.3	4.3	8.3	57	8
5f	43.0	95.1	3.1	5.9	54	22
5g	40.9	87.0	1.2	2.1	27	4
5h	38.4	98.9	3.3	6.9	106	86

enthalpy of the non-substituted compound **5a**. The ortho-substituted compounds **5c**, **5d** and **5h** show higher molar melting enthalpies than the meta-substituted ones **5e**, **5f** and **5g**. The value of ΔH_{melt} decreases, depending on the substituent, in the order: o-CH_3 > o-Cl > o,o'-di-CH_3 > m-Cl > m-CN > m-CH_3. The high molar melting enthalpy of ortho-substituted compounds may be due to that the conformation of the tested compound also changes in the melting process. This conclusion follows from the observation of compound **5c**, where the occurrence of two melting points was detected.† Compound **5c** melts at 116° after which, when heated slowly, crystallizes spontaneously and melts again at 120°. Compounds **5d** and **5h** of the same series also show a polymorphous transformation in the solid state at a temperature about 10° below the melting point.

The clearing temperature and the molar clearing enthalpies and entropies vary in the following orders:

$$T_{N\rightarrow I} H > m\text{-CN} > m\text{-Cl} > m\text{-CH}_3 > o\text{-Cl} > o\text{-CH}_3 > o\text{-}o'\text{-di-CH}_3$$

$$\Delta H_{N\rightarrow I} m\text{-CH}_3 > \mathrm{H} > o\text{-CH}_3 > o,o'\text{-di-CH}_3 > m\text{-Cl} > o\text{-Cl} > m\text{-CN}$$

$$\Delta S_{N\rightarrow I} m\text{-CH}_3 > o\text{-CH}_3 > o,o'\text{-di-CH}_3 > \mathrm{H} > m\text{-Cl} > o\text{-}U > m\text{-CN}$$

Highest molar clearing entropies are revealed by compounds with the CH_3 group irrespective of its position with respect to the azo group. For various groups the molar entropy varies in the order: CH_3 > Cl > CN. We observe hence, for the methyl substituent the greatest lowering of the clearing point and highest values of the molar clearing entropies and enthalpies.

Similar regularities have been found by Griffin and Dewar for laterally substituted trinuclear diesters.[9] The presence in the molecule of highly polar groups favours a better ordering of the molecules in the isotropic phase as compared with the weakly polar CH_3 group. That is why the transition from the isotropic phase to the nematic one is accompanied by relatively smaller change of the ordering of molecules with strongly polar groups as compared with those with weakly polar groups. The changes of entropy and enthalpy are thus proportional only to the obtained increase of ordering of molecules in the mesophase. This conclusion is confirmed by the observed fact that in a series of laterally substituted compounds with one lateral substituent

---

†That phenomenon was observed for certain monoamides[25] and also attributed to the inhibited rotation.

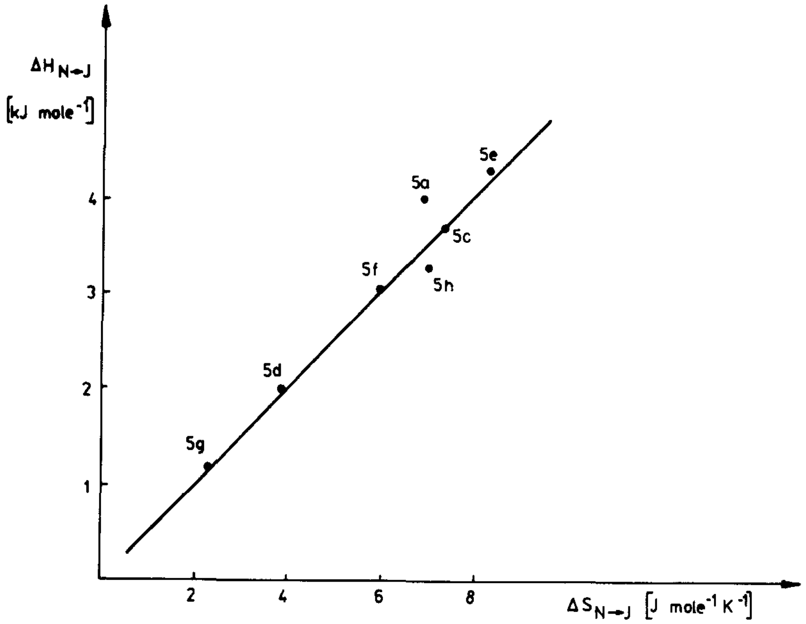


FIGURE 3 Variations of the molar clearing enthalpy with the molar entropy of a series of azo compounds.

one observes a nearly linear relationship between $\Delta H_{N \to I}$ and $\Delta S_{N \to I}$ (Figure 3) irrespective of the position of that substituent with regard to the azo group. No such correlations are observed between the clearing temperatures of the compounds and the values of their molar clearing enthalpies. This fact leads to the confirmation of the conclusions that the stability of the nematic phase is controlled chiefly by geometric factors and the capacity of the molecules to associate, and that the effects related to the displacement of electrons at the bonds and the resulting anisotropy of polarizability of the molecules are of secondary importance, as it was postulated by Wulf.[26]

CONCLUSIONS

In the coupling reaction of the diazonium salt obtained from 1,2-di(4-aminophenyl)ethane and phenol or ortho-, possibly meta- substituted phenols, bis-(*p*-azophenols) are easily formed which transform in reaction with alkyl or acyl halides to liquid crystalline compounds revealing a wide range of the mesophase. Those compounds may be used as stationary phases in gas chromatography. The temperature range of the mesophase, its kind and stability may easily be controlled by the suitable choice of the lateral or terminal substituents or else by oxidation of the azo to azoxy compounds. The observed regularities in the effect of substituents in the inter-ring, terminal and lateral positions in the tested molecules allow us to postulate that the mesogenic properties of those molecules are determined in a paramount degree by the steric factors and polarity which controls the ordering of molecules in the mesophase. The substituents in the ring neighbouring the azo group in ortho-position inhibit the formation of smectic phases while those in meta-position favour their formation.

EXPERIMENTAL

Synthesis of 1,2-bis(4′-butoxybenzeneazobenzene-4)ethane (5a) and 1,2-bis(4′-butoxybenzeneazoxybenzene-4)ethane (6a)

Steps a and b. 20 g (0.094 mole) of 1,2-di(4-aminophenyl)-ethane were dissolved in hot 15% hydrochloric acid, subsequently cooled rapidly with vigourous mixing to 0° so as obtain a microcrystalline precipitate. A solution of sodium nitrite (13.5 g $NaNO_2$ in 75 cm^3 H_2O) was added dropwise to the hydrochloride suspension. The solution of the diazonium salt prepared in this way was poured with vigorous agitation to a preliminarily prepared sodium phenolate solution (18 g phenol, 0.188 mole, and 15.2 g NaOH, 0.38 mole, in 200 cm^3 H_2O) cooled to 5°. As the solutions combine, an orange-brown solid precipitates. The precipitate was filtered off after acidifying the solution with hydrochloric acid, washed with water, dried, and extracted with acetone. The acetone extracts were concentrated, and the formed orange-brown crystals were filtered off. After drying, 24 g (61% yield) were obtained of 1,2-bis(4′-hydroxybenzeneazobenzene-4)ethane (compound **4a**) of melting range 255–258° with decomposition.

The remaining bis-azophenols (compounds **4c**–**4h**) were obtained analogously by coupling the described diazonium salt with ortho- or meta-chlorophenol, ortho- or meta-cresol, *m*-cyanophenol, or 3,5-xylenol. 1,2-bis(4′-hydroxybenzeneazobenzene-4)ethane (compound **4b**) was obtained from 4,4′-diamino-trans-stilbene in an identical way. The melting points of compounds **4a**–**4h** are given in Table I.

Step c. 10.6 g (0.025 mole) of 1.2-bis(4′-hydroxybenzeneazobenzene-4)ethane were dissolved in 300 cm^3 anhydrous acetone upon which 13.8 g (0.075 mole) of *n*-butyl iodide and 27.6 g (0.2 mole) anhydrous potassium carbonate were added. The reaction mixture was refluxed on a water bath for 15 hours. On cooling the mixture was poured into water, the precipitate was filtered off and recrystallized from dioxane. 9.3 g (70% yield) of orange-red 1,2-bis(4′-butoxybenzeneazobenzene-4)ethane crystals were obtained with phase transition points *K* 201° *N* 310° *I*. The IR spectrum (KBr pellet) 1130 cm^{-1} band, Ar—N= bond. The UV-VIS spectrum (in chloroform) $\lambda_{\max} = 352$ nm (π-π^* band), $\lambda_{\max}$ 400–440 nm ($n - \pi^*$ transition in —N=N—). Anal. calcd. for:

$C_{34}H_{38}N_4O_2$:			
	C = 76.40%,	H = 7.11%,	N = 10.48%;
Found:	C = 76.28%,	H = 7.11%,	N = 10.28%.

The same procedure was used for alkylating bis-azophenol **4a** with benzyl chloride and acylation with butylbenzoyl chloride; alkylations of the remaining azophenols **4b**–**4h** were carried out in the same way. Spectral data and the phase transition temperatures are summarized in Table I. The results of elementary analyses, were according to calculated data.

Step d. A mixture of 10.68 g (0.02 mole) of 1,2-bis(4′-butoxybenzeneazobenzene-4)ethane, 200 cm^3 benzene and 250 cm^3 peracetic acid solution, obtained from 1050 cm^3 acetic anhydride and 240 cm^3 30% H_2O_2, was heated under reflux at 60° for 5 hours until the solution turned yellow. Next the solution was poured into water, the benzene layer was separated, washed with 5% sodium hydroxide solution and water, and dried over anhydrous magnesium sulfate. After evaporating benzene, the solid residue was recrystallized from a 1:1 chloroform ethanol mixture. 10.5 g (90% yield) of pale yellow 1,2-bis-(4′-butoxybenzeneazoxybenzene-4)ethane crystals (compound **6a**) were obtained. The phase transition temperatures were *K* 137° *S* 290° *N* 330° *I* with decomposition; IR(KBr pellet)1160 cm^{-1} band, Ar—N= bond; 915 cm^{-1} band, =N → O bond. The UV-VIS spectrum: $\lambda_{\max}$ 352 nm (π-π^* band). Anal. calcd. for:

$C_{34}H_{38}N_4O_5$:			
	C = 72.08%,	H = 6.71%,	N = 9.89%;
Found:	C = 71.96%,	H = 6.78%,	N = 9.72%.

The remaining bis-azoxycompounds **6c**, **6d** and **6f** were obtained in an analogous way.

The melting and phase transition temperatures were determined using a VEB Analytic (Dresden) model PHMK microscope with polarization plates and heated stage. The tested compound was placed between thin glass plates. The phase transition temperatures were also determined using the Du Pont 910 scanning calorimeter. The measurements were carried out in nitrogen atmosphere, and aluminium oxide was used as the reference system. The calorimeter was calibrated using metallic indium and tin, and 4,4′-diheptyloxyazoxybenzene. The heating rate in the range of phase transitions (±15 deg.) was one deg/min. The IR absorption spectra were registered by means of the Specord 71 spectrophotometer, and the UV-VIS ones by means of the Beckman Acta VII in a chloroform solution for concentrations of 10^{-3} mole/litre.

The phases were identified by the miscibility method. For this purpose was used 2-(4-*n*-octylphenyl)-5-(octyloxyphenyl)pyrimidyne that has the phases S_C and S_A in the required temperature range.[27]

References

1. G. Oesterhelt, P. Marugg, R. Rueher and A. Germann, *J. Chromatogr.*, **234**, 99 (1982).
2. G. M. Janini, G. M. Muschik and C. M. Hanlon, *Mol. Cryst. Liq. Cryst.*, **53**, 15 (1979)
3. G. M. Janini, R. I. Sato and G. M. Muschik, *Anal. Chem.*, **52**, 2417 (1980).
4. Z. Witkiewicz and A. Wacławczyk, *J. Chromatogr.*, **173**, 43 (1979).
5. Z. Witkiewicz, Z. Suprynowicz and R. Dąbrowski, *J. Chromatogr.*, **175**, 37 (1979).
6. M. Ciosek, Z. Witkiewicz and R. Dąbrowski, *Chem. Anal.*, **25**, 567 (1980).
7. K. Kubica and Z. Witkiewicz, *J. Chromatogr.*, **241**, 33 (1982).
8. W. R. Young, I. Haller and D. C. Green, *J. Org. Chem.*, **37**, 3707 (1972).
9. M. J. S. Dewar and A. C. Griffin, *J. Am. Chem. Soc.*, **97**, 6662 (1975).
10. A. C. Griffin and D. L. Wertz, *Mol. Cryst. Liq. Cryst.*, **44**, 267 (1978).
11. J. P. Ven Meter and B. H. Klanderman, *Mol. Cryst. Liq. Cryst.*, **22**, 285 (1973).
12. J. C. Dubois and A. Bequin, *Mol. Cryst. Liq. Cryst.*, **47**, 193 (1978).
13. Nguyen Huu Tinh, A. Zann and J. C. Dubois, *Mol. Cryst. Liq. Cryst.*, **53**, 29 (1979).
14. "Mesomorphic Order in Polymers and Polimerization in Liquid Crystalline Media" A. Blumstein (Ed) Am. Chem. Soc. Symposium Series 74 Washington 1978.
15. N. A. Plate and V. P. Shibaev, Comb-Like Polymers and Liquid Crystals, *Khimiya*, Moskov 1980.
16. A. Ziółek, Z. Witkiewicz and R. Dąbrowski, *J. Chromatogr.*, 1984.
17. A. Ziółek, Z. Witkiewicz and R. Dąbrowski, *J. Chromatogr.*, 1984.
18. J. Dziaduszek, T. Szczuciński, A. Wacławczyk and Z. Witkiewicz, *Biul. Wojsk. Akad. Tech.*, **28**, Nr 6, 73 (1979).
19. M. Calvin and R. E. Buckles, *J. Am. Chem. Soc.*, **62**, 3324 (1940).
20. O. Fischer and E. Hepp, *Chem. Ber.*, **26**, 2231 (1893).
21. G. Adamska, R. Dąbrowski and J. Dziaduszek, *Mol. Cryst. Liq. Cryst.*, **76**, 93 (1981).
22. R. Dąbrowski, G. Adamska, Z. Stolarz, A. Konarzewski and W. Wacławek, *Polish J. Chem.*, **54**, 1233 (1980).

23. V. N. Tsvetkov, Advances in Liquid Crystals Research and Applications, L. Bata (Ed.), Pergamon Press, Akademioi Kiado, Budapest 1979, Vol. 2, p. 813.
24. H. Kelker and R. Hatz, *Ber. Bunsen-Ges.*, **78**, 821 (1974).
25. L. Skulski, G. C. Palmer and M. Calvin, *Roczniki Chemii*, **38**, 789 (1964).
26. A. Wulf, *J. Chem. Phys.*, **64**, 104 (1976).
27. S. Diele, D. Demus, A. Echtermeyer, U. Preukschas and H. Sackmann, *Acta Phys. Pol.*, **A55**, 125 (1979).