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Effects of Polysubstitution on Mesomorphic Properties: Methyl Derivatives of 4- Alkanoyloxy-4′-ethoxy- and 4-(4-Alkoxybenzoyloxy)-4′-ethoxyazobenzenes

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Effects of Polysubstitution on Mesomorphic Properties: Methyl Derivatives of 4-Alkanoyloxy-4′-ethoxy- and 4-(4-Alkoxybenzoyloxy)-4′-ethoxyazobenzenes

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The effects of methyl substituents placed in the 2- and/or 3-positions of 4-alkanoyloxy-4′-ethoxyazobenzenes upon the nematic-isotropic transition temperature have been examined. While the 2- and 3-methyl derivatives exhibit transition temperatures lower by 50–55°C than the parent compound, the 2,3-dimethyl derivative exhibits a temperature higher by 20–30°C than either the 2- or 3-methyl derivative. Furthermore, the mesomorphic behavior of a complete set of mono-, di-, tri-, and tetramethyl derivatives have been recorded employing 4-[4-(decyloxy)benzoyloxy]- and 4-[4-(dodecyloxy)benzoyloxy]-4′-ethoxyazobenzenes as the parent compounds in order to demonstrate the effects of methyl groups added to the central part of the three-ring system.

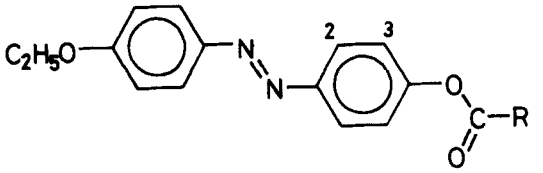
Keywords: liquid crystals, nematic, lateral methyl groups

INTRODUCTION

As reported in our previous papers,[1,2] the effects of mono-, di-, and trichloro substitution of the terminal phenyl ring upon the thermal stability of the nematic phase of N-[4-(4-methoxybenzoyloxy)benzylidene]aniline and its related compounds are not always additive. A chloro group introduced to the 2- or 3-position reduces drastically the nematic-isotropic transition temperature irrespective of the presence of a substituent at the 4-position, whereas the introduction of chloro groups to both the 2- and 3-positions gives rise to an enhancement of the mesomorphic behavior compared to either the 2- or 3-chloro derivative. As a result, the nematic-isotropic transition temperature in these chloro derivatives decreases in the following order: 4-Cl, 2,4-Cl_2, 2,3,4-Cl_3, 3,4-Cl_2, unsubstituted, 2,3-Cl_2, 2-Cl or 3-Cl. Moreover, we showed that methyl substitution exerts effects closely similar to those described above.

In this paper, we report an extension of our studies to 4-alkanoyloxy- and 4-(4-alkoxybenzoyloxy)-4′-ethoxyazobenzenes (1 and 2, respectively) using methyl substituent(s). The lateral substituents in compounds 1 are located at the terminal

ring, but those in compounds 2 are at the central one of the three-ring system. The mesomorphic properties of the unsubstituted compounds 1 have been known by the work of Van Hecke and his collaborators.[3]



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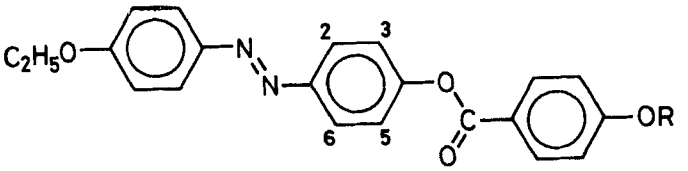

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EXPERIMENTAL

4-Ethoxy-4′-hydroxyazobenzene and its methyl derivatives were prepared by the coupling of diazotized *p*-phenetidine with phenol and methylated phenols. The esterification with alkanoic acid or 4-alkoxybenzoic acid by the procedure of Hassner and Alexanian yielded the desired compounds.[4] For example, Found: C, 75.05; H, 8.34; N, 5.02%. Calcd for $C_2H_5O\,C_6H_4$—N=N—$C_6\,(CH_3)_4\,O_2C\,C_6H_4\,OC_{10}H_{21}$: C, 75.24; H, 8.30; N, 5.01%. The 4-alkoxybenzoic acids were synthesized using the method described by Jones or the method newly developed by us.[5,6]

Microscopic observations and calorimetric measurements were made as described in our previous paper.[1]

RESULTS AND DISCUSSION

The transition temperatures and the associated enthalpy and entropy changes are listed in Table I for 4-alkanoyloxy-4′-ethoxyazobenzenes and their mono- and dimethyl derivatives. Here, nematic and isotropic liquid phases are denoted by N and I respectively. Because the N-I transition is monotropic in some instances, melting point t_m represents the crystal-nematic phase or crystal-isotropic liquid transition temperature. The parent compounds are known to exhibit considerable polymorphism in the solid state.[3] The data cited from the work by Van Hecke and others are for the most stable crystal forms. As is shown in Figure 1, the N-I transition temperature decreases with the increase of the alkyl chain length showing an odd-even alternation; namely, from 129°C of the hexanoyloxy homologue to 106°C of the tetradecanoyloxy homologue.

When a single methyl group is placed in the 2-position, the N-I transition temperature is lowered by about 55°C and the transition in the four homologues becomes monotropic though the melting point is also depressed by the substitution.

TABLE I

Transition temperatures and enthalpy and entropy changes of the methyl derivatives of compound 1

Substituent(s)	t_m/°C	t_{NI}/°C	ΔH_m/ kJmol^{-1}	ΔH_{NI}/ kJmol^{-1}	ΔS_{NI}/ JK^{-1}mol^{-1}
			$n = 5$[a]		
None[b]	72	129	30	1.1	2.7
2-Methyl	55	70	39	0.9	2.6
3-Methyl	76	78	40	0.8	2.3
2,3-Dimethyl	76	101	31	0.6	1.6
			$n = 6$[a]		
None[b]	66	119	23	0.9	2.3
2-Methyl	69	(62)[c]	45	0.7	2.1
3-Methyl	69	(67)[c]	38	0.6	1.8
2,3-Dimethyl	76	89	32	0.4	1.1
			$n = 7$[a]		
None[b]	86	120	48	1.1	2.8
2-Methyl	51	67	38	0.9	2.7
3-Methyl	62	72	39	0.8	2.3
2,3-Dimethyl	73	92	45	0.6	1.6
			$n = 8$[a]		
None[b]	72	115	28	0.9	2.3
2-Methyl	54	60	40	0.7	2.1
3-Methyl	50	66	43	0.6	1.8
2,3-Dimethyl	69	85	32	0.4	1.1
			$n = 9$[a]		
None[b]	76	113	—	1.1	2.8
2-Methyl	62	63	51	1.0	3.0
3-Methyl	51	66	48	0.9	2.7
2,3-Dimethyl	71	85	43	0.7	2.0
			$n = 10$[a]		
None[a]	79	109	32	1.0	2.6
2-Methyl	62	63	46	1.0	3.0
3-Methyl	55	64	52	0.8	2.4
2,3-Dimethyl	68	81	44	0.6	1.7
			$n = 11$[a]		
None[b]	81	109	39	1.2	3.1
2-Methyl	63	(61)[c]	58	1.2	3.6
3-Methyl	50	67	49	1.0	2.9
2,3-Dimethyl	67	82	39	0.7	2.0
			$n = 12$[a]		
None[b]	83	107	42	1.2	3.2
2-Methyl	60	(58)[c]	64	1.0	3.0
3-Methyl	52	64	49	0.8	2.4
2,3-Dimethyl	67	77	45	0.8	2.3
			$n = 13$[a]		
None[b]	85	106	43	1.3	3.4
2-Methyl	66	(64)[c]	66	1.3	3.9
3-Methyl	50	64	42	1.0	3.0
2,3-Dimethyl	79	79	45	0.9	2.6

[a]The number of carbon atoms in the alkyl group R.
[b]Taken from Reference 3.
[c]The transition is monotropic.

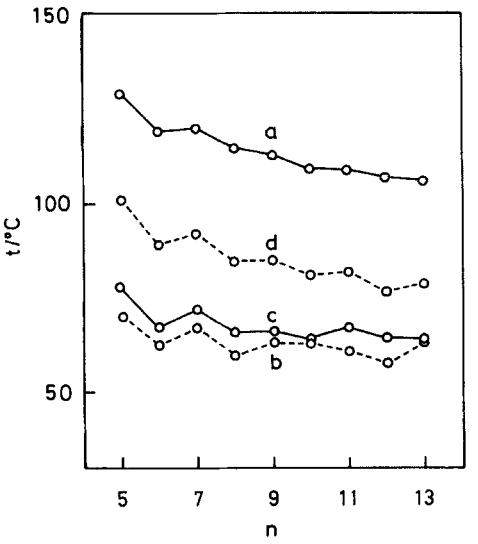

FIGURE 1 Plots of the N-I transition temperature of 4-alkanoyloxy-4′-ethoxyazobenzene against the number of carbon atoms in the alkyl group, (a) the unsubstituted compounds, (b) the 2-methyl derivatives, (c) the 3-methyl derivatives, and (d) the 2,3-dimethyl derivatives.

The present methyl derivatives exhibit also polymorphism; therefore, the highest melting points recorded are presented in the table. The N-I transition temperatures are reduced by a 3-methyl group by about 50°C, but the mesophases remain mostly enantiotropic. A decrease in the intermolecular cohesion due to the increased intermolecular separation by the substitution may account for these changes in the N-I transition temperature. The 3-substituent seems to be less exposed than the 2-substituent because of the presence of a long flexible alkanoyloxy group in the 4-position. The dependence of N-I transition temperature upon the alkyl chain length in these monomethyl derivatives is less significant than that in the parent compound; that is, the maximum variations are merely 12°C in the 2-methyl derivatives and 14°C in the 3-methyl derivatives (see Figure 1).

The introduction of an additional methyl group to the 3-position of the 2-methyl derivative or to the 2-position of the 3-methyl derivative raises the N-I transition temperature by 20 to 30°C. The plot of the resulting transition temperature against the alkyl chain length is essentially parallel to the similar plot for the parent compounds, the difference being found in the narrow range of 27 to 30°C. Because the second lateral substituent is, more or less, accommodated in the space produced by the introduction of the first one, the observed effects may be attributed to an increase in the cohesive forces due to the increased polarizability outweighing the decrease in the cohesive forces by the increased intermolecular separation.[7] The experimentally found enthalpy changes at the N-I transition are, however, smaller than the parent compound 1 in all cases of methyl substitution. Young and others noted a similar trend for their methylated phenyl benzoyloxybenzoates and suggested that this trend is in accord with the increased intermolecular separation due to lateral substitution or decreased molecular polarizability resulting from a steric loss of conjugation.[8] But it is apparent that the entropy changes for the 2,3-dimethyl

derivatives are so much smaller that the transition temperatures are raised above those of the monomethyl derivatives. It is also notable that the N-I transition enthalpy for the 2-methyl series increases with the alkyl chain length, but so does the transition entropy.

Table II summarizes the thermal behavior of sets of mono-, di-, tri- and tetramethyl derivatives of 4-[4-(decyloxy)benzoyloxy]- and 4-[4-(dodecyloxy)benzoyloxy]-4′-ethoxyazobezenes. Here, K stands for the crystalline phase and t_{KN} for the melting point. In order to support the tendencies found with these two sets, additional data for the octyloxy and tetradecyloxy homologues are included. The changes in the N-I transition temperature by methyl substitution are depicted by the diagrams shown in Figure 2. The addition of a 2- or 3-methyl group to the parent compound depresses the thermal stability of the nematic phase by about 42°C. The depression is larger in the 2-methyl derivative than in the 3-methyl

TABLE II

Transition temperatures and enthalpy and entropy changes of the methyl derivatives of compound 2

Substituent(s)	t_{KN}/°C	t_{NI}/°C	ΔH_{KN}/ kJmol^{-1}	ΔH_{NI}/ kJmol^{-1}	ΔS_{NI}/ JK^{-1}mol^{-1}
Octyloxy homologues (n = 8)[a]					
None	117	242	40	1.5	2.9
2-Methyl	92	195	42	1.6	3.4
3-Methyl	88	201	50	1.7	3.6
2,3-Dimethyl	104	219	39	1.5	3.0
Decyloxy homologues (n = 10)[a]					
None	108	228	37	1.3	2.6
2-Methyl	93	185	54	1.4	3.1
3-Methyl	92	186	51	1.5	3.3
2,3-Dimethyl	113	206	35	1.4	2.9
2,5-Dimethyl	105	141	70	2.1	5.1
2,6-Dimethyl	90	154	42	2.0	4.7
3,5-Dimethyl	96	146	45	2.0	4.8
2,3,5-Trimethyl	122	158	44	1.9	4.4
2,3,6-Trimethyl	117	172	61	2.0	4.5
2,3,5,6-Tetramethyl	152	185	53	1.7	3.7
Dodecyloxy homologues (n = 12)[a]					
None	102	217	50	1.3	2.7
2-Methyl	95	173	55	1.3	2.9
3-Methyl	87	177	37	1.4	3.1
2,3-Dimethyl	110	195	37	1.3	2.8
2,5-Dimethyl	102	132	63	1.8	4.4
2,6-Dimethyl	89	148	59	1.8	4.3
3,5-Dimethyl	88	135	52	2.0	4.9
2,3,5-Trimethyl	110	148	48	1.9	4.5
2,3,6-Trimethyl	101	161	53	1.8	4.1
2,3,5,6-Tetramethyl	147	170	55	1.6	3.6
Tetradecyloxy homologues (n = 14)[a]					
None	98	209	54	1.1	2.3
2-Methyl	97	164	53	1.2	2.7
3-Methyl	84	168	35	1.3	2.9
2,3-Dimethyl	98	187	48	1.2	2.6

[a]The number of carbon atoms in the alkyl group R.

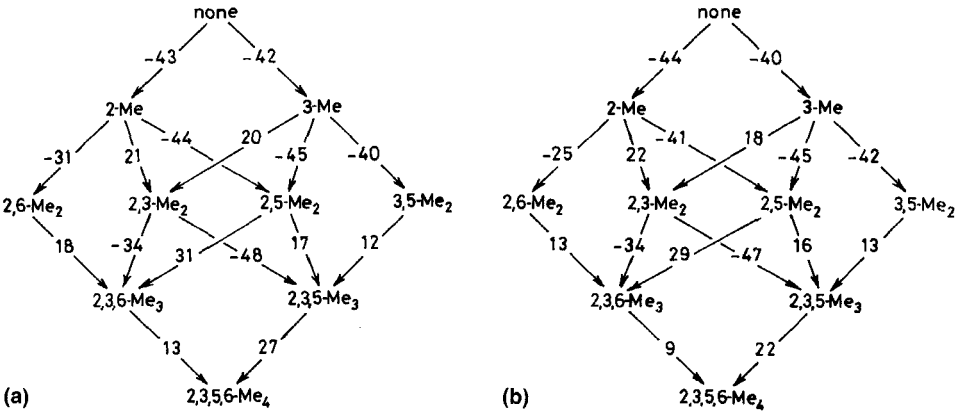

FIGURE 2 The change in the N-I transition temperatures (°C) by methyl substitution of (a) 4-[4-(decyloxy)benzoyloxy]- and (b) 4-[4-(dodecyloxy)benzoyloxy]-4′-ethoxyazobenzenes.

derivative (see also the octyloxy and tetradecyloxy homologues) in conformity with the observations made for the alkanoyloxy compounds; however, the magnitude is smaller by about 10°C, possibly because the substituents here are located at the middle part of a three-ring system.

The clearing points of the dimethyl derivatives are in the following order: 2,3-Me_2 > 2,6-Me_2 > 3,5-Me_2 > 2,5-Me_2. In these compounds too, the nematic phase in the 2,3-dimethyl derivative is promoted by about 20°C compared with either the 2-methyl or 3-methyl derivative. On the other hand, the effects of the broadening of the molecular width on the N-I transition temperature arising from the second substituent are undoubtedly dominant in the 2,6-, 3,5-, and 2,5-dimethyl derivatives. Since the average decrease of the N-I transition temperature by the addition of a second lateral methyl group is about 39°C in these three dimethyl derivatives, the effects of methyl substitution can be said to be approximately additive, in agreement with the findings by Young and others.[8] They showed that placing two methyl groups on the same ring of phenyl 4-(benzoyloxy)benzoate molecule results in approximately twice the lowering of the N-I transition temperature against that obtained by substitution with a single methyl group. However, the extent of the depression in our compounds varies in a range of 25 to 45°C. While the azobenzene moiety is rigid, the twisting of the alkoxybenzoyl group may be enhanced by the introduction of two methyl groups into the 3- and 5-positions and gives rise to an additional depression of the clearing point. The reason why the 2,5-isomer has the lowest N-I transition temperature is not clear, since this mode of substitution seems to favor an effective packing of the molecules in the crystalline phase, as manifested in the second highest melting point among the dimethyl derivatives.

In conformity with the above-mentioned order of the clearing point of the dimethyl derivatives, the mesophase in the 2,3,6-trimethyl derivative is more stable by 13 to 14°C than that in the 2,3,5-isomer. The third methyl group introduced to the 2,5-, 2,6-, and 3,5-dimethyl derivatives is in a position to have a vicinal methyl group; therefore, it gives rise invariably to an enhancement of the mesophase, on the average, by 19°C. This change is in good agreement with that given by a similar

addition of a methyl group to the monomethyl derivatives. On the other hand, the methylation of the 2,3-dimethyl derivative results in the decrease of the N-I transition temperature by about 41°C. Here again, the depressive effects are approximately additive.

Because of an increase in the molecular polarizability by four substituents, not only the nematic phase but also the crystalline phase exhibited by the tetramethyl derivative are thermally more stable with respect to those exhibited by the trimethyl derivatives. In agreement with the changes given by the introduction of a vicinal methyl group to the mono- and dimethyl derivatives, the average stabilization is found to be about 18°C.

It is noteworthy that the enthalpy and entropy changes at the N-I transition temperature for all of the methylated compounds are larger than for the parent compound 2, in clear contrast to the case of compound 1. Young and others also observed the unusually large increase in the entropy change at the N-I transition by methyl substitution on the central ring of phenyl benzoyloxybenzoates. They proposed that methylation of the center of the molecule increases the coupling between orientational and translational degrees of freedom and concluded that the concept of increased intermolecular separation resulting from laterally-placed substituents is too simple.[8] The possibility of an enhanced short-range order was pointed out by them to be compatible with X-ray observations of the nematic phase of a diester, which was broadened by chlorination of the central ring.[9] The values of N-I transition entropy for the 2,5-, 2,6-, and 3,5-dimethyl derivatives are larger than for the monomethyl derivatives and also for the 2,3-isomer, while the increases in the enthalpy values are less pronounced. This arises from the relative elevation of transition temperature for the 2,3-isomer. A similar entropy factor is apparent in the case of the 2,3,5,6-tetramethyl derivative.

Summarizing the above results, one may conclude that the depressions of N-I transition temperature by methyl groups introduced to the central benzene ring of 4-(4-alkoxybenzoyloxy)-4′-ethoxyazobenzene are approximately as follows: the contribution per methyl group is about −40°C if a newly-substituted group finds no neighboring methyl group, and about +20°C if it does find one. Consequently, the clearing point of the tetramethyl derivative comes close to that of the monomethyl derivatives though the melting point of the former compound is considerably higher than that of the latter.

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