Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006.

To cite this article: G. Xu , K. Okuyama , M. Ozawa & M. Shimomura (1993): The Odd-Even Effect on Bilayer Structures of $C_nAzoC_mN^+Br^-$, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 237:1, 207-215

To link to this article: http://dx.doi.org/10.1080/10587259308030136

Mol. Cryst. Liq. Cryst., 1993, Vol. 237, pp. 207–215
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Printed in the United States of America

The Odd-Even Effect on Bilayer Structures of $C_nAzoC_mN^+Br^-$

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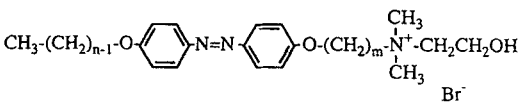
(Received July 24, 1992; in final form September 4, 1992)

The phase transition behavior of totally synthetic bilayer-forming amphiphiles, $C_nAzoC_mN^+Br^-$, with various chain lengths of the spacer (m) and tail (n) parts, has been investigated by the differential scanning calorimetry, X-ray diffraction, and absorption spectroscopic methods. The compounds which have the relationship of $m - n = 2$ showed similar aggregation states, the so-called H-aggregation state. However, there are some structural differences between the odd and the even number compounds in the hydrophilic region. These structural differences made big differences in the transition temperatures (Tc), enthalpy (ΔH) and entropy (ΔS) at Tc between the odd and even number compounds. On the other hand, the $C_nAzoC_5N^+Br^-$ ($n = 6 \sim 12$) showed very similar molecular aggregation states, the so-called J-aggregation state. Their transition temperatures showed no such tendency. They had similar values of about 130°C. However, very small odd-even effects of the ΔH and ΔS at Tc were observed. These were attributed to the slight differences of the molecular areas between the odd and even number compounds of $C_nAzoC_5N^+Br^-$.

Keywords: the odd-even effect, phase transition, H-aggregate J-aggregate, bilayer structure

INTRODUCTION

Biological membranes are organized assemblies consisting mainly of lipids and proteins. Their fundamental structure is the lipid bilayer known as the fluid mosaic model.[1] Lipids are amphiphilic molecules, usually composed of the hydrophobic alkyl chain part and the hydrophilic phospholyl part. A totally artificial lipid, dioctadecyldimethylammonium bromide ($2C_{18}N^+2C_2Br^-$) was synthesized as a biological membrane model. This synthetic lipid showed multilamellar structures similar to those of biological lipids by an electron microscopic observation.[2] Since then, a large variety of synthetic amphiphiles containing single,[3] double,[2] and triple[4] alkyl chains in a hydrophobic tail part has been extensively studied and various methods[5–7] for immobilizing the aqueous bilayer as highly oriented solid films have been developed to constitute a new functional molecular architecture system. In the case of single-chain amphiphiles with azobenzene chromophore ($C_nAzoC_mN^+Br^-$), a series of compounds has been synthesized by changing carbon atoms in the spacer (m) and tail (n) parts.[3] Their structures and physical properties have been intensively studied by X-ray diffraction, spectroscopic method, and thermal analysis.



CnAzoCmN$^+$Br$^-$

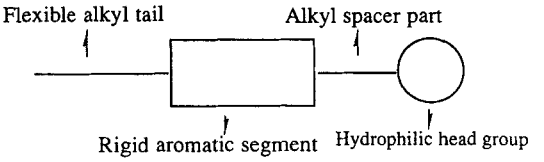


FIGURE 1 Chemical formula and its schematic illustration for single-chain azobenzene-containing amphiphiles (abbreviated as $C_nAzoC_mN^+Br^-$). n and m represent the number of carbon atoms in the alkyl tail and spacer parts, respectively.

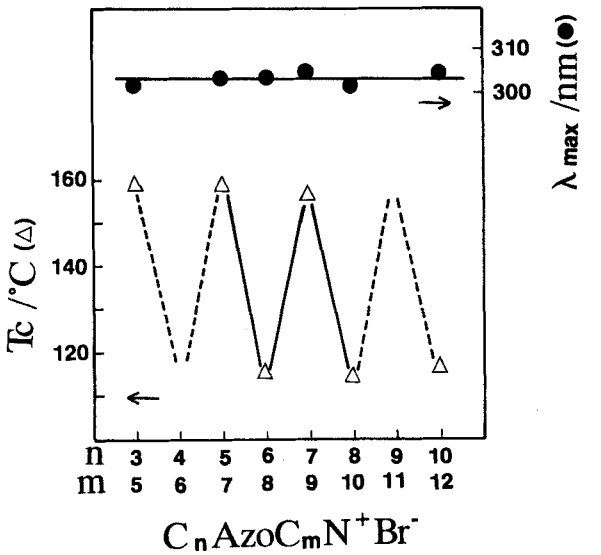


FIGURE 2 Transition temperatures Tc (Δ) and absorption spectra λ_{max} (●) of $C_nAzoC_mN^+Br^-$ with m − n = 2.

The isolated azobenzene chromophores such as azobenzene amphiphiles dissolved in organic solvents have an absorption maximum (λ_{max}) at 355 nm. The absorption maxima of molecular aggregates such as vesicles in aqueous solution, casted films, and single crystals, show shift to some extent from the above λ_{max} of the isolated chromophore. For example, λ_{max} of casted films of $C_nAzoC_mN^+Br^-$ with m − n = 2 and $C_nAzoC_5N^+Br^-$ (n = 6 ~ 12) are located at about 300 nm and 375 nm, respectively. The former hypsochromic shift is explained by the side-by-side arrangement (H-aggregate) of azobenzene chromophores[8] and the latter bathochromic shift is explained by the head-to-tail arrangement (J-aggregate).[10–12] By heating, the H- and J-type aggregation compounds showed the phase transition

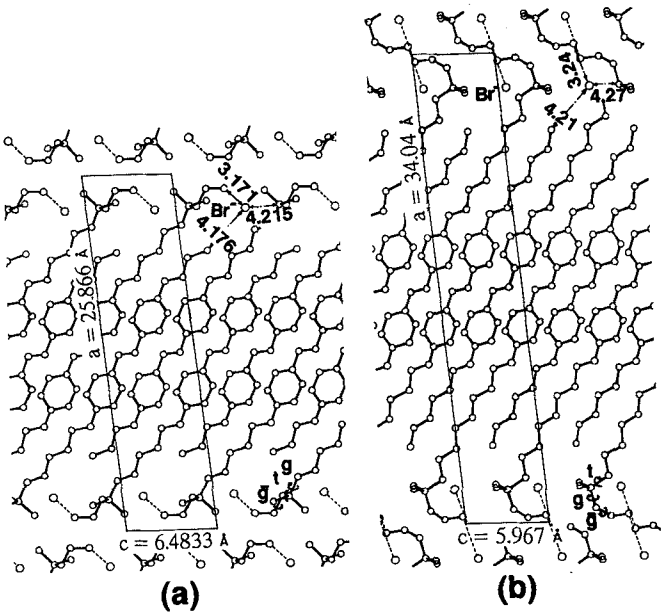


FIGURE 3 The packing structures of H-crystals, $C_3AzoC_5N^+Br^-$ (a) and $C_6AzoC_8N^+Br^-$ (b). Some short distances are shown in Å.

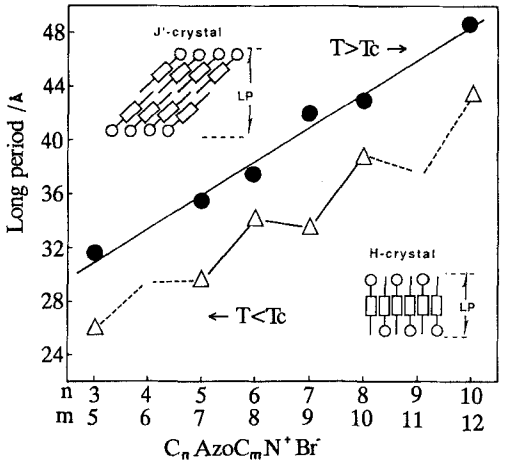


FIGURE 4 Long periods (/Å) of H- (Δ) and J'-crystals (•) for $C_nAzoC_mN^+Br^-$ with m − n = 2.

from H- to J'-crystal and from J- to J'-crystal, respectively. Here, the J'-crystal showed the X-ray diffraction pattern similar to those from the J-crystal. However, the absorption maxima of the J'-crystal (λ_{max} = 360 nm) was considerably different from that of the J-crystal (λ_{max} = 375 nm). Furthermore, odd-even effects of the alkyl chain length were observed for thermal behaviors such as transition temperature Tc, enthalpy difference ΔH, and entropy difference ΔS.

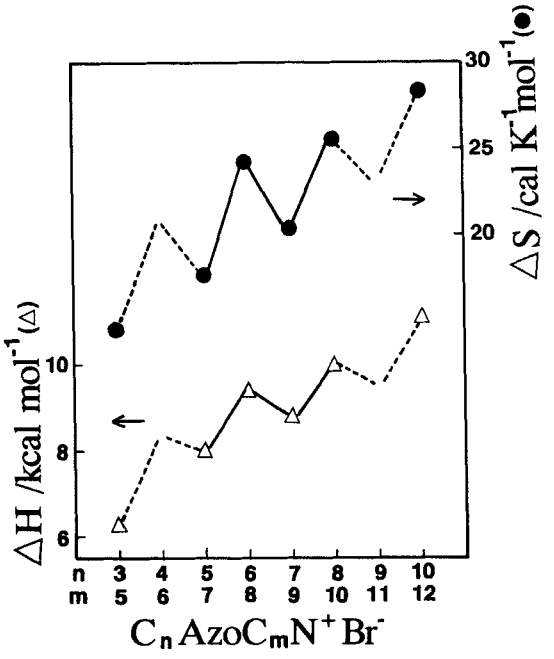


FIGURE 5 Enthalpy differences ΔH (Δ) and entropy differences ΔS (●) at Tc for various compounds of $C_nAzoC_mN^+Br^-$ with m − n = 2.

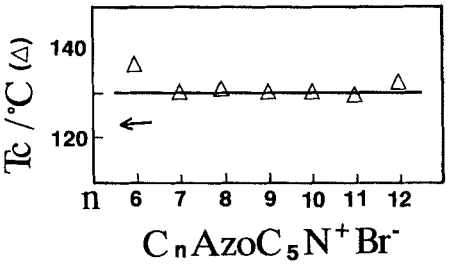


FIGURE 6 Transition temperatures Tc of $C_nAzoC_5N^+Br^-$ (n = 6 ~ 12).

In this paper, we will discuss these odd-even effects on thermal behaviors based on their crystal structures for two aggregation states.

EXPERIMENTAL

The chemical formula of the p-ω-N,N-dimethyl-*N*-hydroxy-ethylammonioalkyloxy-p′-alkyloxyazobenzenebromide (abbreviated as $C_nAzoC_mN^+Br^-$) is shown in Figure 1. General procedures for the preparation of the $C_nAzoC_mN^+Br^-$ with various chain lengths of the spacer (m) and tail (n) parts were described previously.[3] For X-ray and thermal analyses, samples were ground to fine powder by using an agate mortar and pestle.

TABLE I

Crystal data of $C_nAzoC_5N^+Br^-$ (n = 6 ~ 12)

n	$C_nAzoC_5N^+Br^-$ 6	7	8	9	10	11	12
Crystal system	triclinic						
Space group	$P\bar{1}$						
Z	2						
a/Å	27.446(9)	28.570(7)	30.098(6)	31.125(7)	32.33(5)	33.136(2)	34.243(6)
b/Å	8.592(1)	8.576(3)	8.553(2)	8.568(4)	8.54(2)	8.536(1)	8.525(1)
c/Å	6.112(1)	6.147(1)	6.084(1)	6.123(2)	6.08(1)	6.0834(6)	6.073(1)
α /°	106.91(2)	73.43(1)	72.99(1)	73.20(2)	106.96(8)	73.675(7)	73.45(1)
β /°	87.05(2)	89.49(2)	92.57(2)	94.41(3)	86.6(1)	94.43(1)	88.03(1)
γ /°	93.18(4)	89.17(3)	95.64(2)	97.17(3)	88.3(1)	90.20(1)	93.32(1)
Cell volume/Å^3	1375.8(5)	1443.4(7)	1490.3(5)	1549.4(7)	1601(4)	1646.1(3)	1694.1(4)

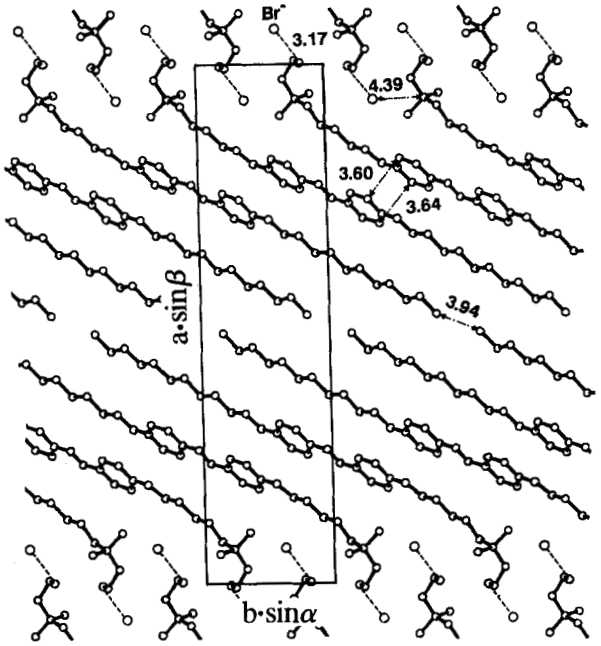


FIGURE 7 The packing structure of $C_{11}AzoC_5N^+Br^-$ as a typical example of J-crystal. Some short distances are shown in Å.

Thermal behaviors of the samples were observed by a differential scanning calorimetry (DSC 8230, Rigaku) with a heating rate of 10°C min^{-1}. Transition temperatures (Tc) were determined by extrapolation of the DSC curves to the onset of thermal activity. X-ray diffraction patterns from powder samples below and above Tc were taken by an imaging plate (DIP-100, MAC Science) with mono-

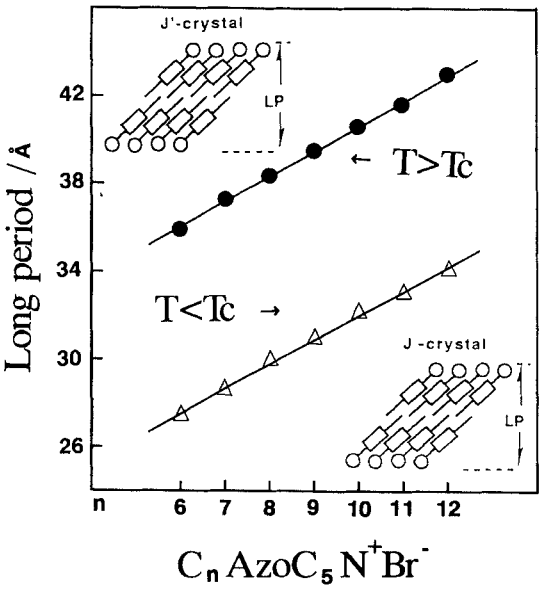


FIGURE 8 Long periods (/Å) of J- (Δ) and J'-crystals (•) for $C_nAzoC_5N^+Br^-$ (n = 6 ~ 12).

chromatized CuKα radiation (Rota Flex RU-200, Rigaku). Absorption spectra were obtained with a spectrophotometer (UV-160, Shimazu).

RESULTS AND DISCUSSION

Phase Transition from H- to J'-Crystal

The compounds of $C_nAzoC_mN^+Br^-$ with m − n = 2 showed similar hypsochromic shifts at about 300 nm (Figure 2), which suggests that these compounds take similar H-aggregation states of azobenzene chromophores. These compounds showed crystal-to-crystal phase transitions at elevated temperatures. The phase transition behavior of $C_8AzoC_{10}N^+Br^-$ was investigated in detail.[13] In the case of $C_8AzoC_{10}N^+Br^-$, the H-crystal (λ_{max} = 300 nm) changes to the J'-crystal (λ_{max} = 360 nm) by heating above 115°C. A similar transition from H-crystal to J'-crystal was also observed for other compounds with m − n = 2. Interestingly, the transition temperatures, Tc, of these compounds changed by a considerable amount depending on the odd and the even number of m and n (Figure 2). That is, transition temperatures of odd-number compounds were higher than those of even-number compounds by about 40°C.

Crystal structures of the even-number compounds, $C_6AzoC_8N^+Br^-$ and $C_8AzoC_{10}N^+Br^-$, have been reported[8] (Figure 3(b)). They are very similar molecular aggregation states to each other both in the hydrophobic and hydrophilic layers. Recently, the crystal structure of the odd-number compound, $C_3AzoC_5N^+Br^-$, was analyzed.[9] The packing structure of this compound is shown in Figure 3(a). The structure of the hydrophobic layer is similar to those of the even-number

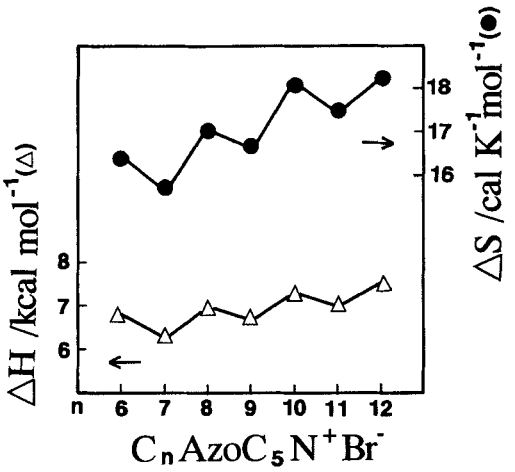


FIGURE 9 Enthalpy differences ΔH (Δ) and entropy differences ΔS (●) at Tc for various compounds of $C_nAzoC_5N^+Br^-$ (n = 6 ~ 12).

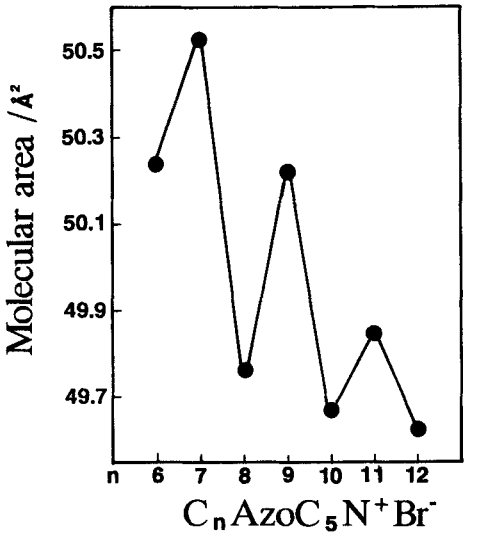


FIGURE 10 Molecular areas calculated from lattice constants of $C_nAzoC_5N^+Br^-$ (n = 6 ~ 12).

compounds (Figure 3(b)). That is, the hydrophobic chains are arranged in anti-parallel fashion and interdigitated mutually. Furthermore, the azobenzene chromophores are aligned in side-by-side fashion at the center part of the hydrophobic layer. On the other hand, two types of chain conformation were observed in the hydrophilic layer depending on the odd- or even-number compounds. In the case of odd-number compounds, the chain conformation at the end of the hydrophilic part is gauche, trans and gauche minus (Figure 3(a)), while it is trans, gauche and gauche minus in even-number compounds (Figure 3(b)). Moreover, the way of hydrogen bonding and ionic interaction are different between odd- and even-number compounds. These structural differences affect long periods as seen in Figure

4. On the other hand, no significant difference was observed for the long periods of these compounds in the J′-crystal state (Figure 4), which suggests no structural difference in the J′-crystal state. From the above evidence, the odd-even effect on the transition temperatures (Figure 2) seems to be attributed to the structural differences in the H-crystal state and the structural similarities in the J′-crystal state. Furthermore, odd-even effects were found in enthalpy differences ΔH and entropy differences ΔS = ΔH/Tc between the H-crystal and J′-crystal structures at Tc (Figure 5). These are also attributed to the same reason.

Phase Transition from J- to J′-Crystal

Thermally-induced phase transitions were also found for compounds of C_n-$AzoC_5N^+Br^-$ (n = 6 ~ 12). X-ray diffraction patterns and the absorption spectra below and above the transition temperature (Tc) showed that this was the phase transition from J-crystal (λ_{max} = 375 nm) to J′-crystal (λ_{max} = 360 nm). In the contrast with the previous case, the transition temperatures from J- to J′-crystal showed similar values at about 130°C (Figure 6).

Crystal structures of the even number compounds, $C_nAzoC_5N^+Br^-$ (n = 6, 8, 10, and 12), have been reported.[10–12] Recently, structure analyses of the odd-number compounds, $C_nAzoC_5N^+Br^-$ (n = 7, 9, and 11) have been performed. Seven crystals with various tail lengths belonged to the same crystal system and only one significant difference for the dimension of the *a*-axis (Table I) was found. They have very similar molecular aggregation states in the hydrophobic and hydrophilic layers. As a typical example, the packing structure of $C_{11}AzoC_5N^+Br^-$ is shown in Figure 7. The molecules pack in a tail-to-tail fashion and incline about 30° to the bilayer surface.

Plots of long periods of the J- and J′-crystals as a function of the number of carbon atoms (n) in the tail part showed a linear and parallel relationship (Figure 8). These results indicate that the structures of $C_nAzoC_5N^+Br^-$ (n = 6 ~ 12) compounds in the J′-crystal state are similar to each other. Because of the structural similarity in the J-crystal state and that in the J′-crystal state, the phase transition temperatures from J- to J′-crystal showed no significant odd-even effect for $C_nAzoC_5N^+Br^-$ compounds.

On the other hand, very small differences in the enthalpy differences (ΔH) and entropy differences (ΔS) between the J- and J′-crystal structures at Tc were found between the odd- and the even-number compounds (Figure 9). According to the results of single-crystal analyses of the J-crystals, their molecular areas (= $bd \times \sin\alpha$) at the bilayer surface showed a very small odd-even effect depending on the number of carbon atoms (n) in the tail part (Figure 10). Small odd-even effects of the ΔH and ΔS at Tc may be attributed to the above subtle difference of the molecular areas.

CONCLUSION

By heating the compounds of $C_nAzoC_mN^+Br^-$ with m − n − 2, the phase transitions from H-crystal to J′-crystal were found by means of the X-ray diffraction,

thermal analysis and the spectroscopic method. Some structural differences in the H-crystal state between the odd- and the even-number compounds of C_n-$AzoC_mN^+Br^-$ ($m - n = 2$) were observed. On the other hand, from the linear relationship between the long period and carbon number of the spacer (m) and tail (n) parts, structures in the J′-crystal state seemed to be similar to each other. The odd-even effects on the transition temperatures (Tc), the enthalpy differences (ΔH) and the entropy differences (ΔS) at Tc were attributed to the structural differences at low temperature phase (H-crystals) and the structural similarity at high temperature phase (J′-crystals).

In the case of the $C_nAzoC_5N^+Br^-$ ($n = 6 \sim 12$), the phase transitions from J-crystal to J′-crystal were observed. Because of structural similarity of the J-crystals and that of the J′-crystals, the transition temperatures showed similar values at about 130°C. The subtle differences in the molecular areas of the J-crystals cause the very small odd-even effects of the ΔH and ΔS at Tc.

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