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Molecular and Crystal Structure of Azobenzene-Containing Amphiphile, $C_3AzoC_5N^+Br^-$

Guiqing Xu, Kenji Okuyama,* and Masatsugu Shimomura
Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184

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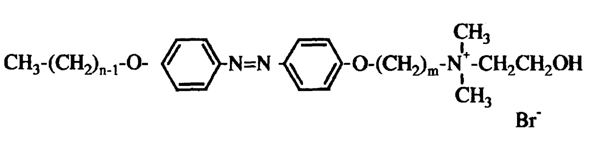
An azobenzene-containing odd-number amphiphile, $C_3AzoC_5N^+Br^-$, was crystallized by the vapor-diffusion method. The crystal is monoclinic with the space group $P2_1$, $a=25.866(3)$, $b=7.3560(9)$, $c=6.4833(7)$ Å, $\beta=96.255(9)°$, and $Z=2$. The structure was solved by the direct method and refined by the full-matrix least-squares method: $R=0.03$ for 2116 observed reflections ($2\theta<130°$, Cu $K\alpha$, $\lambda=1.5418$ Å). The molecules are arranged in an antiparallel fashion and interdigitated mutually. The azobenzene chromophores are aligned at the center part of the hydrophobic layer (the H-aggregation state) and inclined about 65° to each other. In the hydrophilic layer, detailed structures are different from those of even-number compounds with the H-aggregation state, resulting in an odd-even effect on their transition temperature.

The fundamental structure of biological membranes is a lipid bimolecular layer.[1] Initially, the bimolecular layer was thought to be constructed only from natural lipid molecules. However, about 15 years ago, it was found that even the totally synthetic lipid could construct a bilayer structure.[2] After this finding, many kinds of artificial lipids have been synthesized and many have been shown to be bilayer-forming. Bilayer-forming lipids have been proved very effective in orientating functional groups. For example, amphiphiles $C_nAzoC_mN^+Br^-$ (Fig. 1) show two typical aggregation states of the azobenzene chromophores, depending on the number of carbon atoms in the spacer (m) and tail (n) parts,[3] or on heat treatments.[4] These are the side-by-side arrangement (H-aggregate) of chromophores and the head-to-tail arrangement (J-aggregate). The former was found for compounds with the relationship of $m-n=2$[5] and latter for $C_nAzoC_5N^+Br^-$ ($n=6$—12).[6—9] On the other hand, by heating, the H-aggregate changes to the J′-aggregate which is similar to the J-aggregate.[4] Interestingly, the odd-even effect on phase transition temperatures (T_c) from the H-aggregate to the J′-aggregate was observed depending on the odd-number or even-number of carbon atoms in the spacer (m) and tail (n) parts.[9] That is, transition temperatures of odd-number compounds were higher than those of even-number compounds, by about 40 degrees (Fig. 2). In the J′-aggregation state, the structures between odd- and even-number compounds seem to be similar to each other from the linear relationship between long periods and the number of carbon atoms.[9] On the other hand, in the H-aggregation state, an odd-even effect of long periods was observed.[9] Therefore, the odd-even effect on the transition temperature may be attributed to the structural differences at lower temperatures (H-aggregate) and the structural similarities at higher temperatures (J′-aggregate). In the H-aggregation state, the crystal structures of even-number compounds, $C_6AzoC_8N^+Br^-$ and $C_8AzoC_{10}N^+Br^-$, have been reported.[5] They exhibit very similar molecular arrangements to each other. In this paper, the crystal structure of an odd-number compound, $C_3AzoC_5N^+Br^-$, which shows the H-aggregation state of azobenzene chromophores judging from its hypsochromic shift,[9] was studied for further understanding the relationship between their structures and an odd-even effect on their transition temperatures.

Experimental and Structure Determination

The $C_3AzoC_5N^+Br^-$ (5 mg) was dissolved in a mixture



$$CH_3\text{-}(CH_2)_{n-1}\text{-}O\text{-}C_6H_4\text{-}N{=}N\text{-}C_6H_4\text{-}O\text{-}(CH_2)_m\text{-}\overset{CH_3}{\underset{CH_3}{N^+}}\text{-}CH_2CH_2OH \quad Br^-$$

$C_nAzoC_mN^+Br^-$

Fig. 1. Chemical formula of azobenzene-containing amphiphiles (abbreviated as $C_nAzoC_mN^+Br^-$).

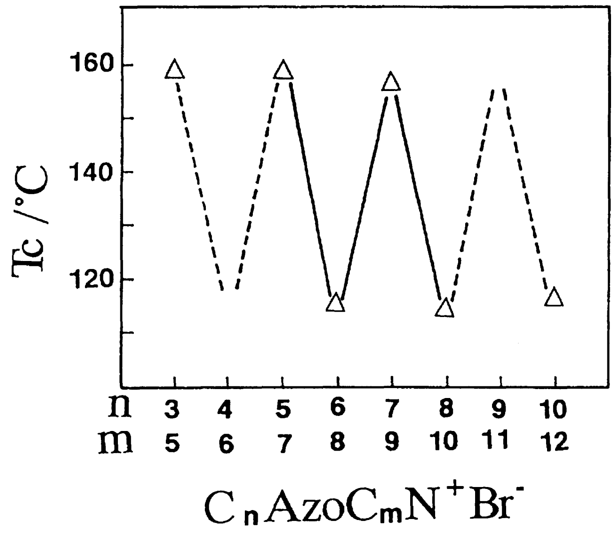


Fig. 2. Phase transition temperatures of $C_nAzoC_mN^+Br^-$ ($m-n=2$) from H-aggregates to J′-aggregates.

(10 ml) of nitrobenzene and ethanol (nitrobenzene/ethanol=1/1 by volume) in a small beaker. This was kept in a larger beaker with water and the larger beaker was sealed up. Single crystals were obtained by vapor diffusion of nitrobenzene and ethanol into water at room temperature in about four months. The size of the crystal used for intensity measurement was about 0.4 mm×0.3 mm×0.3 mm.

The lattice parameters and diffraction intensities were measured on a Rigaku four-circle diffractometer (RASA-5RII) with graphite monochromatized Cu $K\alpha$ radiation (λ=1.5418 Å). The lattice parameters were refined by the least-squares fit for 25 reflections in the 2θ range of 57—61°. By using the ω-scan mode with a scan rate of $4^\circ\ \mathrm{min}^{-1}$, intensities of 2116 reflections with $|F_o| \geq 3\sigma|F_o|$ were measured up to 130° in 2θ. The scan width was $\Delta\omega=(1.50+0.14\tan\theta)^\circ$. Three reflections monitored every 100 reflections showed no significant intensity deterioration during the data collection. Corrections were made for the Lorentz and polarization factors, but not for absorption. The density was measured by the flotation method in a solution of hexane and tetrachloromethane.

Crystal Data: 4-Propoxy-4′-[5-(*N*,*N*-dimethyl-2-hydroxyethylamino)-pentyloxy]-azobenzene bromide (abbreviated as $C_3AzoC_5N^+Br^-$); $C_{24}H_{36}N_3O_3Br$; F.W.=494.5; monoclinic; space group $P2_1$; $Z=2$; $a=25.866(3)$, $b=7.3560(9)$, $c=6.4833(7)$ Å; $\beta=96.255(9)^\circ$; $V=1226.2(2)$ Å^3; $D_x=1.339$ and $D_m=1.34\ \mathrm{g\,cm^{-3}}$.

The structure was solved by the direct method using the program SAPI-85.[10] All the non-hydrogen atoms were found on the E-map. After several refinement cycles of full-matrix least-squares, positions of hydrogen atoms were obtained from the difference Fourier map. The final refinement with anisotropic parameters for non-hydrogen atoms and isotropic ones for hydrogen atoms gave $R=0.030$ and $R_w=0.032$. The quantity minimized in the refinement was $\Sigma w(|F_o|-|F_c|)^2$, where $w=[\sigma^2(F_o)+(0.021\cdot F_o)^2]^{-1}$. The final atomic parameters for non-hydrogen atoms are given in Table 1.[11]

The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[12] Calculations were carried out on an A-70 minicomputer with the aid of the CRYSTAN program in RASA-5RII system (Rigaku Denki).

Results and Discussion

Molecular Structure. The molecular structure with 50% probability plots for thermal ellipsoids and its atomic numbering scheme are shown in Fig. 3. All the bond lengths and angles (Table 2) are compatible with those found in other homologous compounds.[5—8] Alkyl chains in the spacer and tail parts have a *trans*-zigzag conformation. The azobenzene moiety showed a planar conformation (Table 3). However, the planarity of the azobenzene moiety in the H-aggregation state is not so strict compared with those for the homologous compounds in the J-aggregation state (Table 3).

Table 1. Fractional Coordinates and Equivalent Isotropic Temperature Factors for Non-Hydrogen Atoms of $C_3AzoC_5N^+Br^-$ with Estimated Standard Deviations in Parentheses

$$B_{eq} = (4/3)\left\{B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + 2\,(B_{12}ab + B_{23}bc + B_{31}ca)\right\}$$

Atom	x	y	z	$B_{eq}/\text{Å}^2$
Br	0.90125(2)	0.38109(0)	0.76386(6)	5.14(1)
O(1)	0.9582(1)	1.0589(6)	1.5547(5)	5.76(9)
O(2)	0.70080(7)	0.8874(7)	0.2599(3)	4.13(6)
O(3)	0.29876(9)	0.8263(4)	−0.7675(4)	4.13(7)
N(1)	0.9093(1)	0.8454(5)	1.1469(4)	3.38(8)
N(2)	0.5019(1)	0.8307(4)	−0.1609(5)	3.47(7)
N(3)	0.4971(1)	0.8841(7)	−0.3442(4)	3.65(6)
C(1)	0.9549(2)	1.1102(8)	1.3444(7)	5.03(13)
C(2)	0.9066(2)	1.0410(7)	1.2163(8)	4.22(12)
C(3)	0.9204(2)	0.7190(8)	1.3262(9)	4.91(13)
C(4)	0.9501(2)	0.8235(9)	1.0016(7)	5.03(13)
C(5)	0.8567(1)	0.7882(6)	1.0380(6)	3.61(9)
C(6)	0.8389(1)	0.8824(9)	0.8361(5)	3.92(8)
C(7)	0.7850(2)	0.8122(8)	0.7557(6)	4.27(10)
C(8)	0.7653(2)	0.8935(10)	0.5470(6)	4.28(9)
C(9)	0.7117(2)	0.8236(7)	0.4693(6)	4.18(10)
C(10)	0.6510(1)	0.8670(8)	0.1632(5)	3.28(7)
C(11)	0.6426(1)	0.9438(6)	−0.0339(6)	3.63(9)
C(12)	0.5943(1)	0.9354(5)	−0.1448(5)	3.51(9)
C(13)	0.6110(2)	0.7824(6)	0.2494(6)	3.75(9)
C(14)	0.5619(2)	0.7756(6)	0.1388(6)	3.81(10)
C(15)	0.5535(1)	0.8488(5)	−0.0587(5)	3.26(9)
C(16)	0.4454(1)	0.8650(7)	−0.4465(5)	3.18(7)
C(17)	0.4372(2)	0.9403(6)	−0.6425(6)	3.89(9)
C(18)	0.3881(1)	0.9338(6)	−0.7560(6)	3.66(9)
C(19)	0.4047(2)	0.7797(6)	−0.3618(6)	3.69(9)
C(20)	0.3568(1)	0.7717(6)	−0.4726(6)	3.69(9)
C(21)	0.3480(1)	0.8478(6)	−0.6707(5)	3.43(10)
C(22)	0.2880(1)	0.8921(9)	−0.9762(6)	4.02(9)
C(23)	0.2343(2)	0.8236(8)	−1.0585(7)	4.80(12)
C(24)	0.2173(2)	0.9001(12)	−1.2727(8)	5.52(13)

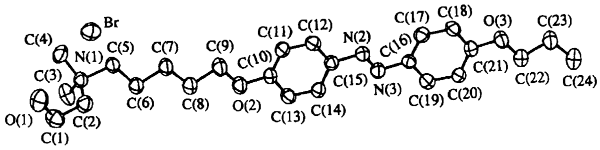


Fig. 3. Molecular structure and atomic numbering scheme for $C_3AzoC_5N^+Br^-$. Thermal ellipsoids are drawn at the 50% probability level (ORTEP[13]) drawing).

Crystal Structure. The molecular arrangement viewed along the c and b axes is shown in Figs. 4 and 5-(a). The crystal structure can be seen as an alternation of the hydrophobic and hydrophilic layers stacked in the a direction. In the hydrophobic layer, neighboring molecules are arranged in the antiparallel fashion and interdigitated mutually. The azobenzene chromophores are aligned at the center of the hydrophobic layer (the H-aggregation state) and inclined about 65° to each other. In the hydrophilic layer, the nitrogen cations and bromide anions are almost located on the same plane parallel to the layer surface. One hydrophilic layer contains such two planes formed by nitrogen cations and bromide anions. The bromide anion is linked to the hy-

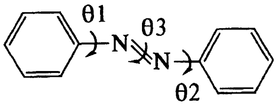
Table 2. Bond Lengths (l) and Bond Angles (θ) with Estimated Standard Deviations in Parentheses

Bond length	l/Å	Bond length	l/Å
O(1)–C(1)	1.408(6)	C(13)–C(14)	1.390(6)
C(1)–C(2)	1.509(8)	C(14)–C(15)	1.384(5)
C(2)–N(1)	1.512(6)	C(15)–N(2)	1.431(5)
C(3)–N(1)	1.492(6)	N(2)–N(3)	1.245(4)
C(4)–N(1)	1.498(6)	C(16)–N(3)	1.431(4)
C(5)–N(1)	1.524(6)	C(16)–C(17)	1.382(5)
C(5)–C(6)	1.508(6)	C(16)–C(19)	1.389(6)
C(6)–C(7)	1.525(7)	C(17)–C(18)	1.397(6)
C(7)–C(8)	1.516(6)	C(18)–C(21)	1.380(5)
C(8)–C(9)	1.513(7)	C(19)–C(20)	1.366(6)
C(9)–O(2)	1.435(5)	C(20)–C(21)	1.397(5)
C(10)–O(2)	1.378(4)	C(21)–O(3)	1.367(4)
C(10)–C(11)	1.392(5)	C(22)–O(3)	1.435(5)
C(10)–C(13)	1.377(6)	C(22)–C(23)	1.518(6)
C(11)–C(12)	1.373(6)	C(23)–C(24)	1.518(7)
C(12)–C(15)	1.399(6)		
Bond angle	θ/°	Bond angle	θ/°
O(1)–C(1)–C(2)	113.6(5)	C(13)–C(14)–C(15)	120.4(4)
C(1)–C(2)–N(1)	115.0(4)	C(11)–C(10)–C(13)	120.4(3)
C(2)–N(1)–C(3)	111.8(4)	C(12)–C(15)–N(2)	124.3(3)
C(2)–N(1)–C(4)	110.4(4)	C(14)–C(15)–N(2)	115.9(3)
C(2)–N(1)–C(5)	109.5(4)	C(15)–N(2)–N(3)	113.8(3)
C(3)–N(1)–C(4)	109.6(4)	N(2)–N(3)–C(16)	113.7(3)
C(3)–N(1)–C(5)	105.9(4)	N(3)–C(16)–C(17)	115.5(3)
C(4)–N(1)–C(5)	109.5(3)	N(3)–C(16)–C(19)	124.7(3)
N(1)–C(5)–C(6)	116.6(4)	C(16)–C(17)–C(18)	120.8(4)
C(5)–C(6)–C(7)	108.8(4)	C(17)–C(18)–C(21)	118.9(4)
C(6)–C(7)–C(8)	112.1(4)	C(18)–C(21)–C(20)	119.9(3)
C(7)–C(8)–C(9)	111.7(4)	C(16)–C(19)–C(20)	119.7(4)
C(8)–C(9)–O(2)	106.4(4)	C(19)–C(20)–C(21)	120.9(4)
C(9)–O(2)–C(10)	118.2(3)	C(17)–C(16)–C(19)	119.8(3)
O(2)–C(10)–C(11)	114.8(4)	C(18)–C(21)–O(3)	124.9(3)
O(2)–C(10)–C(13)	124.8(3)	C(20)–C(21)–O(3)	115.2(3)
C(10)–C(11)–C(12)	120.3(4)	C(21)–O(3)–C(22)	118.0(3)
C(11)–C(12)–C(15)	119.6(3)	O(3)–C(22)–C(23)	107.2(4)
C(12)–C(15)–C(14)	119.8(4)	C(22)–C(23)–C(24)	111.1(4)
C(10)–C(13)–C(14)	119.4(4)		

Table 3. Dihedral Angles for $C_nAzoC_mN^+Br^-$

	Dihedral angle[a]		
Compound	$\theta1$/°	$\theta2$/°	$\theta3$/°
H-crystals			
$C_3AzoC_5N^+Br^-$	−174.2(6)	173.4(7)	179.7(4)
$C_6AzoC_8N^+Br^-$ 5)	168(3)	−167(3)	−174(2)
$C_8AzoC_{10}N^+Br^-$ 5)	166(3)	−167(3)	−170(3)
J-Crystals			
$C_6AzoC_5N^+Br^-$ 8)	−178(1)	178(2)	−179.8(8)
$C_7AzoC_5N^+Br^-$	−179(2)	179(2)	180(1)
$C_8AzoC_5N^+Br^-$ 6)	−178(1)	179(1)	−179.8(8)
$C_9AzoC_5N^+Br^-$	−178(4)	−178(4)	180(3)
$C_{10}AzoC_5N^+Br^-$ 6)	−177(7)	180(8)	−179(7)
$C_{11}AzoC_5N^+Br^-$	−178.1(8)	178.9(8)	179.8(9)
$C_{12}AzoC_5N^+Br^-$ 7)	−178(2)	179(2)	179.8(9)

a) Dihedral angels are defined as follows:



droxyl group of the same unit cell by a hydrogen bond (3.171(4) Å, ∠OHBr$^-$=161(5)°).

The distance between the methyl moiety at the hydrophobic chain and the bromide anion is 4.176(6) Å, which is very close to the van der Waals distance between these atoms (3.85 Å). This suggests that further interdigitation by the longer alkyl chain in the tail part is impossible because of the short interaction between the methyl moiety and the bromide anion. Therefore, the difference in the number of carbon atoms between the spacer (m) and tail (n) part is a very important factor for the packing of the H-aggregation state. That is, the difference ($m-n$) in the number of carbon atoms must be larger than or equal to 2 when the aggregation mode is H (Figs. 4 and 5).

Odd–Even Effects. Since the molecular and crystal structures of even-number compounds, $C_6AzoC_8N^+Br^-$ and $C_8AzoC_{10}N^+Br^-$,[5] have a very similar molecular arrangements to each other, only the packing structure of $C_6AzoC_8N^+Br^-$ is compared with that of the odd-number compound, $C_3AzoC_5N^+Br^-$ (Fig. 5). In the hydrophobic layer, molecular arrangements of both odd- and even-number compounds are similar to each other. However, different types of the chain conformation were observed in the hydrophilic layer. In the even-number compound, the conformation at the

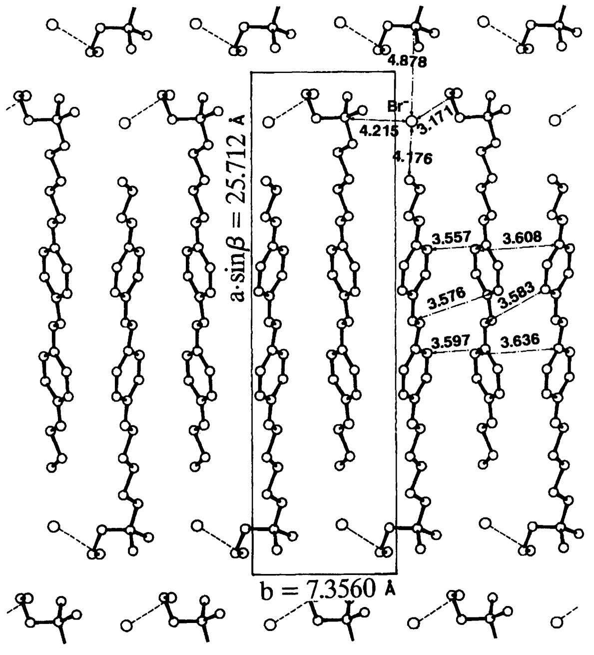


Fig. 4. Packing of $C_3AzoC_5N^+Br^-$ projected along the c axis. Hydrogen bonds between bromide anions and hydroxyl groups are indicated by broken lines. Some short interatomic distances (l/Å) are shown (ORTEP[13]).

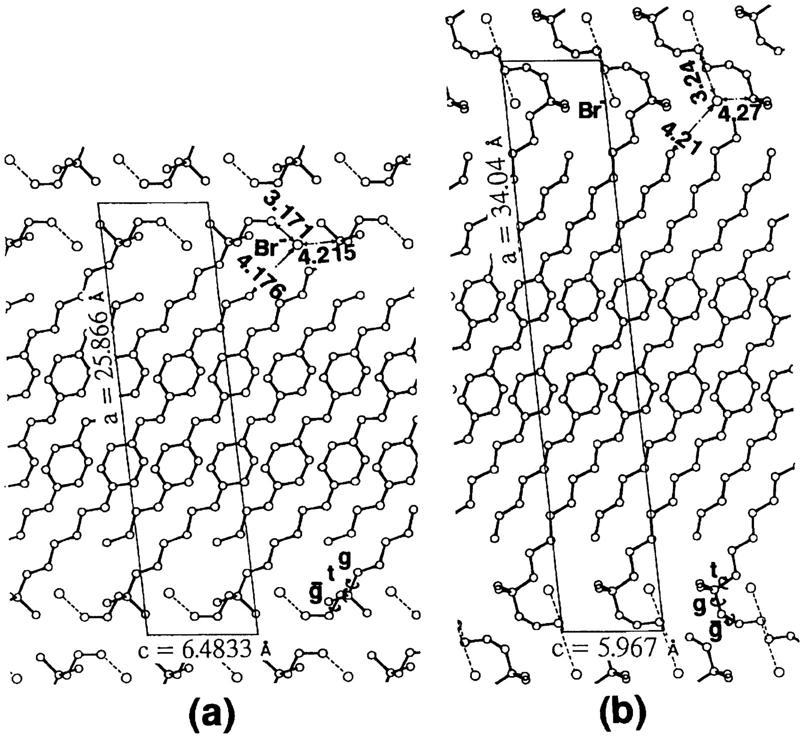


Fig. 5. Packing of (a) $C_3AzoC_5N^+Br^-$ and (b) $C_6AzoC_8N^+Br^-$ projected along the *b* axis (ORTEP[13]).

end of the hydrophilic part is *trans* (156(3)°), *gauche* (52(2)°), and −*gauche* (−94(3)°) (shown at the bottom right in Fig. 5(b)), while it is *gauche* (65.7(5)°), *trans* (174.6(5)°), and −*gauche* (−80.5(6)°) (shown at the bottom right in Fig. 5(a)) in the odd-number compound. Furthermore, the way of hydrogen bonding between the bromide anion and the hydroxyl group, the length of the hydrogen bond and the interaction between nitrogen cations and bromide anions are different. In the even-number compound, the bromide anion is linked to the terminal hydroxyl oxygen in the adjacent unit cell with a hydrogen bond length of 3.24(5) Å and the shortest ionic interaction between the nitrogen cation and the bromide anion is 4.27(2) Å. On the other hand, in the odd-number compound, the bromide anion is linked to the hydroxyl oxygen located in the same unit cell with a length of 3.171(4) Å and the shortest ionic interaction between the nitrogen cation and the bromide anion is 4.215(3) Å. Differences in the lattice dimensions of *c* (Fig. 5) and long periods[9] (*a*-dimensions) between odd-number and even-number compounds of $C_nAzoC_mN^+Br^-$ ($m-n=2$) in the H-aggregation state may be attributed to the above structural differences. On the other hand, the structures of the J′-aggregation state are similar to each other judging from the linear relationship of long periods and alkyl chain lengths.[9] Therefore, the observed odd-even effect of phase transition temperatures (Fig. 2) may be attributed to the above structural differences between odd- and even-number compounds in the H-aggregation state and the structural similarities in the J′-aggregation state.

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