

Molecular and Crystal Structure of Azobenzene-Containing Amphiphile, C₆AzoC₁₀N⁺Br[−]

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A totally synthetic azobenzene-containing amphiphile C₃₂H₅₂N₃O₃Br (C₆AzoC₁₀N⁺Br[−]) was crystallized from its solution in trichloromethane and ethanol. The crystal is triclinic with space group $P\bar{1}$; $Z=2$; $a=24.317(5)$, $b=8.632(1)$, and $c=8.043(2)$ Å; and $\alpha=91.41(2)$, $\beta=80.62(2)$, and $\gamma=99.01(1)^\circ$. The structure was solved by the direct method and refined by the full-matrix least-squares method: $R=0.038$ for 4305 observed reflections ($2\theta < 120^\circ$, Cu $K\alpha$, $\lambda=1.5418$ Å). Two molecules in a unit cell are related by a center of symmetry and pack tail-to-tail in a bilayer structure. The plane of the azobenzene chromophore is almost perpendicular to the layer surface and is overlapped with that of the azobenzene chromophore along its long axis with a separation of 3.55 Å. Different from other homologous compounds, this molecule bends almost 90° at the neck of the hydrophilic head group.

Totally synthetic azobenzene-containing amphiphiles with a single alkyl chain, C_{*n*}AzoC_{*m*}N⁺Br[−], show several types of azobenzene chromophore aggregation states, depending on the number of carbon atoms in the tail part (*n*) and the spacer part (*m*).¹⁾ The J-like aggregation between adjacent chromophores was found in single crystals, casted films, and aqueous dispersions of C_{*n*}AzoC₅N⁺Br[−] (*n*=6, 8, 10, and 12). Their detailed crystal structures were determined by X-ray single crystal structure analyses and bore out the J-like aggregation of azobenzene chromophores at an atomic level.^{2–4)} Compared with C_{*n*}AzoC₅N⁺Br[−], the

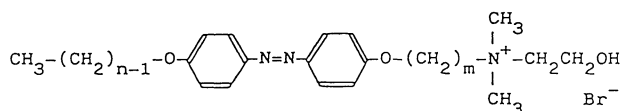
title amphiphile, C₆AzoC₁₀N⁺Br[−], shows several different properties, such as thermal properties, spectroscopic properties, and shapes of single crystals.

In this paper, we discuss the detailed molecular and crystal structure of this compound for understanding the relationship between its structure and physical properties.

Experimental and Structure Determination

4-(Hexyloxy)-4'-[ω-(dimethylethanolammonio)-decyloxy]-azobenzenebromide (abbreviated as C₆AzoC₁₀N⁺Br[−]) (30 mg) was dissolved in a solution (3 ml) of trichloromethane and ethanol (trichloromethane/ethanol=1/5 by volume). Yellow, plate-like crystals with dimensions of 0.5×0.2×0.1 mm³ were obtained by keeping the solution at room temperature for about a week. The density was measured by the flotation method in a solution of hexane and tetrachloromethane.

Lattice parameters and diffraction intensities were



Scheme 1.

Table 1. Fractional Coordinates and Equivalent Isotropic Temperature Factor for Non-Hydrogen Atoms of C₆AzoC₁₀N⁺Br[−] with Estimated Standard Deviations in Parentheses
 $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+2(B_{12}ab+B_{23}bc+B_{31}ca))$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} /Å ²	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} /Å ²
Br	0.90450(2)	0.17892(3)	0.41310(3)	4.73(2)	C(14)	0.7369(1)	−1.2428(4)	1.2603(4)	4.84(10)
O(1)	1.0123(1)	−0.2066(3)	−0.0595(3)	7.05(10)	C(15)	0.7364(1)	−1.4968(3)	1.3821(4)	4.25(9)
O(2)	0.76664(9)	−1.3649(2)	1.3028(3)	5.13(7)	C(16)	0.7679(1)	−1.6134(4)	1.4109(4)	4.54(10)
O(3)	0.57875(9)	−2.5666(3)	1.9741(3)	6.15(8)	C(17)	0.7424(1)	−1.7493(3)	1.4923(4)	4.41(10)
N(1)	0.95978(9)	−0.2780(3)	0.3007(3)	3.88(7)	C(18)	0.6787(1)	−1.5192(4)	1.4345(4)	4.93(11)
N(2)	0.6536(1)	−1.9116(3)	1.6309(3)	4.87(9)	C(19)	0.6534(1)	−1.6588(4)	1.5164(4)	5.09(11)
N(3)	0.6842(1)	−2.0107(3)	1.6570(3)	4.78(8)	C(20)	0.6845(1)	−1.7728(3)	1.5459(4)	4.27(9)
C(1)	1.0420(2)	−0.1563(5)	0.0765(6)	5.71(13)	C(21)	0.6548(1)	−2.1503(3)	1.7385(4)	4.35(10)
C(2)	1.0027(1)	−0.1372(4)	0.2381(4)	4.76(10)	C(22)	0.6879(1)	−2.2545(4)	1.7797(4)	4.92(10)
C(3)	0.9121(2)	−0.2922(6)	0.2022(4)	9.73(24)	C(23)	0.6649(1)	−2.3956(4)	1.8591(4)	4.87(10)
C(4)	0.9886(2)	−0.4203(4)	0.2913(4)	6.75(15)	C(24)	0.5963(1)	−2.1879(4)	1.7761(4)	5.19(11)
C(5)	0.9369(1)	−0.2451(3)	0.4844(4)	4.02(9)	C(25)	0.5728(1)	−2.3278(4)	1.8548(4)	5.54(12)
C(6)	0.8871(1)	−0.3638(4)	0.5616(4)	4.46(10)	C(26)	0.6069(1)	−2.4318(4)	1.8971(4)	4.64(10)
C(7)	0.8681(1)	−0.3237(4)	0.7458(4)	4.99(11)	C(27)	0.6105(1)	−2.6778(4)	2.0256(4)	5.52(12)
C(8)	0.8173(1)	−0.4435(4)	0.8240(4)	5.33(12)	C(28)	0.5683(2)	−2.8086(4)	2.1149(5)	6.38(14)
C(9)	0.8328(1)	−0.6006(4)	0.8672(4)	4.94(11)	C(29)	0.5961(2)	−2.9380(4)	2.1723(4)	5.85(13)
C(10)	0.7822(1)	−0.7145(4)	0.9545(4)	4.66(10)	C(30)	0.5523(2)	−3.0736(4)	2.2539(5)	6.84(15)
C(11)	0.8018(1)	−0.8614(4)	1.0122(4)	4.90(11)	C(31)	0.5789(2)	−3.2044(4)	2.3102(5)	6.92(15)
C(12)	0.7558(1)	−0.9817(4)	1.1051(4)	4.49(10)	C(32)	0.5369(2)	−3.3432(5)	2.3824(6)	9.16(22)
C(13)	0.7806(1)	−1.1147(4)	1.1735(4)	4.88(10)					

measured on a Rigaku four circle diffractometer (RASA-5R11) with graphite monochromatized Cu K α radiation ($\lambda=1.5418$ Å). The lattice parameters were refined by the least-squares fit using 21 reflections ($40.0^\circ \leq 2\theta \leq 60.0^\circ$). By using the ω - 2θ scan mode with a scan rate of 6° min^{-1} , intensities of 4725 reflections were measured up to 120° in 2θ . The scan width was $\Delta\omega=(1.3+0.14 \tan \theta)^\circ$. Three reflections monitored every 100 reflections showed no

significant intensity deterioration. Corrections were made for the Lorentz and polarization factors, but not for absorption effect. A total of 4305 reflections with $|F_o| > 3\sigma(F)$ was used for the calculation.

Crystal Data: $\text{C}_{32}\text{H}_{52}\text{N}_3\text{O}_3\text{Br}$; F.W.=606.7; triclinic; space group $P\bar{1}$; $Z=2$; $a=24.317(5)$, $b=8.632(1)$, and $c=8.043(2)$ Å; $\alpha=91.41(2)$, $\beta=80.62(2)$, and $\gamma=99.01(1)^\circ$; $\mu(\text{calcd})=17.5 \text{ cm}^{-1}$; $V=1645.2(6) \text{ Å}^3$; $D_x=1.225$ and $D_m=1.23 \text{ g cm}^{-3}$.

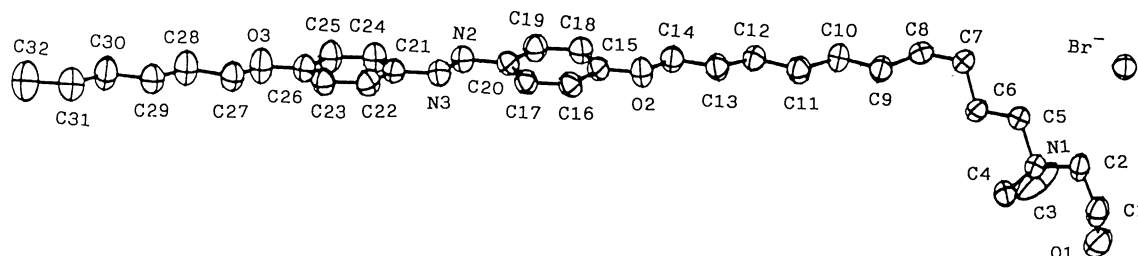


Fig. 1. Molecular structure and atomic numbering scheme for $\text{C}_6\text{AzoC}_{10}\text{N}^+\text{Br}^-$. Thermal ellipsoids are drawn at the 50% probability level (ORTEP¹¹) drawing).

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

Bond distances	<i>l</i> /Å		<i>l</i> /Å		<i>l</i> /Å
O1–C1	1.429(2)	C13–C14	1.506(4)	C22–C23	1.383(4)
C1–C2	1.504(3)	C14–O2	1.445(4)	C23–C26	1.381(4)
C2–N1	1.510(3)	C15–O2	1.365(3)	C24–C25	1.374(4)
C3–N1	1.496(5)	C15–C16	1.401(5)	C25–C26	1.395(5)
C4–N1	1.500(4)	C15–C18	1.384(4)	C26–O3	1.362(4)
C5–N1	1.528(3)	C16–C17	1.366(4)	C27–O3	1.430(4)
C5–C6	1.517(4)	C17–C20	1.389(4)	C27–C28	1.510(4)
C6–C7	1.527(4)	C18–C19	1.392(4)	C28–C29	1.509(5)
C7–C8	1.539(4)	C19–C20	1.377(5)	C29–C30	1.534(5)
C8–C9	1.526(5)	C20–N2	1.434(4)	C30–C31	1.499(6)
C9–C10	1.533(4)	N2–N3	1.259(4)	C31–C32	1.507(5)
C10–C11	1.530(5)	C21–N3	1.417(4)		
C11–C12	1.513(4)	C21–C22	1.376(5)		
C12–C13	1.532(5)	C21–C24	1.393(4)		
Bond angles	<i>θ</i> /°			<i>θ</i> /°	
O1–C1–C2	112.3(2)	C16–C15–C18		120.0(3)	
C1–C2–N1	117.0(2)	C15–C18–C19		118.3(3)	
C2–N1–C3	109.0(3)	C18–C19–C20		121.7(3)	
C2–N1–C4	109.1(2)	C19–C20–N2		116.5(3)	
C2–N1–C5	106.7(2)	C17–C20–N2		124.0(3)	
C3–N1–C4	113.9(3)	C20–N2–N3		113.8(3)	
C3–N1–C5	108.3(2)	N2–N3–C21		115.1(3)	
C4–N1–C5	109.6(2)	N3–C21–C22		115.9(3)	
N1–C5–C6	114.2(2)	N3–C21–C24		124.8(3)	
C5–C6–C7	110.5(2)	C21–C22–C23		122.0(3)	
C6–C7–C8	110.5(2)	C22–C23–C26		118.4(3)	
C7–C8–C9	113.9(3)	C23–C26–C25		120.2(3)	
C8–C9–C10	113.0(3)	C22–C21–C24		119.3(3)	
C9–C10–C11	110.2(3)	C21–C24–C25		119.3(3)	
C10–C11–C12	115.4(3)	C24–C25–C26		120.8(3)	
C11–C12–C13	111.1(3)	C23–C26–O3		124.4(3)	
C12–C13–C14	113.8(3)	C25–C26–O3		115.4(3)	
C13–C14–O2	107.0(3)	C26–O3–C27		118.9(2)	
C14–O2–C15	118.9(2)	O3–C27–C28		106.7(3)	
O2–C15–C16	115.6(3)	C27–C28–C29		112.6(3)	
O2–C15–C18	124.4(3)	C28–C29–C30		111.6(3)	
C15–C16–C17	120.9(3)	C29–C30–C31		112.6(3)	
C16–C17–C20	119.6(3)	C30–C31–C32		113.8(3)	
C17–C20–C19	119.6(3)				

The structure was solved by the direct method using the program SAPI-85.⁵⁾ All the non-hydrogen atoms were found on the E-map. After several cycles of full-matrix least-squares refinements, positions of hydrogen atoms were obtained from the D-Fourier map. The final refinement

with the anisotropic parameters for all non-hydrogen atoms and isotropic ones for 49 hydrogen atoms gave finally $R=0.038$ and $R_w=0.037$. The quantity minimized in the refinement was $\sum w(|F_o|-|F_c|)^2$ with $w=1/[\sigma^2(F_o)+(0.005 \times F_o)^2]$. The final atomic parameters for non-hydrogen atoms are

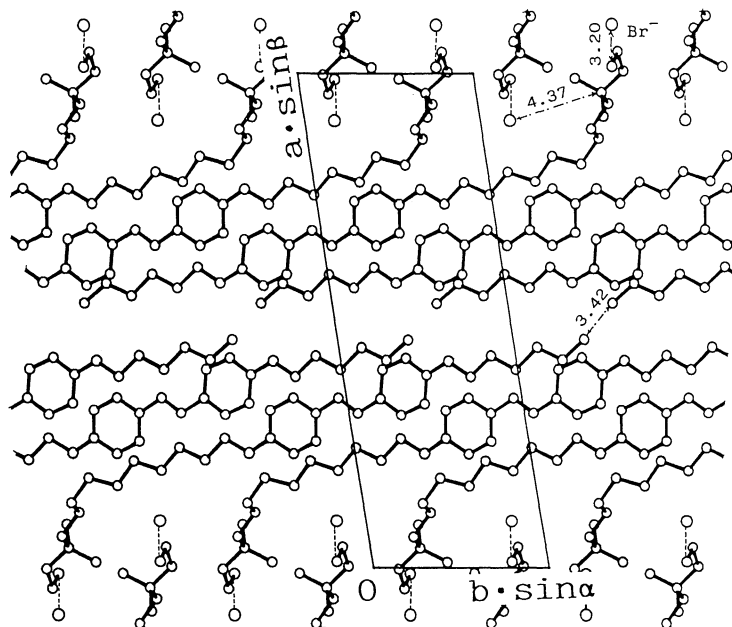


Fig. 2. Packing of $C_6AzoC_{10}N^+Br^-$ projected along the c axis. Hydrogen bonds between bromide anions and hydroxyl groups are indicated by broken lines. Some short interatomic distances (\AA) are shown (ORTEP¹¹⁾).

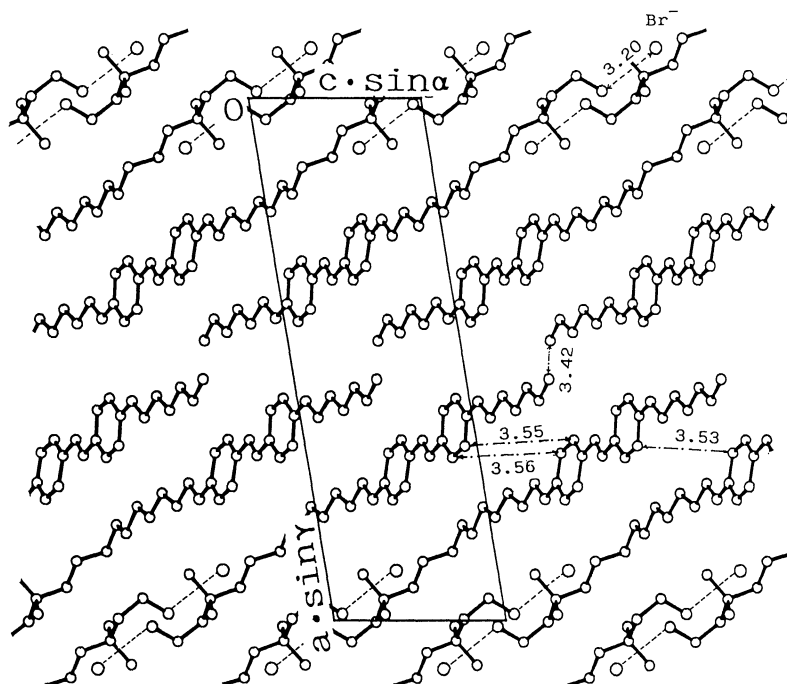


Fig. 3. Packing of $C_6AzoC_{10}N^+Br^-$ projected along the b axis (ORTEP¹¹⁾).

given in Table 1.⁶⁾

The atomic scattering factors were taken from International Tables for X-Ray Crystallography.⁷⁾ All calculations have been performed on an A-70 minicomputer with the aid of the CRYSTAN program in RASA5R-II system (Rigaku Denki).

Results and Discussion

Molecular Structure of $C_6\text{AzoC}_{10}\text{N}^+\text{Br}^-$. The molecular structure and the atom numbering scheme are given in Fig. 1. Bond distances and angles are shown in Table 2. The average C–C bond distance and C–C–C bond angle in the alkyl spacer and tail parts are 1.520(5) Å and 112.4(3)°, respectively. They are in good agreement with values previously found in other amphiphilic compounds with long hydrocarbon chains.^{2–4,8,9)}

The main difference in molecular conformation between $C_n\text{AzoC}_5\text{N}^+\text{Br}^-$ and $C_6\text{AzoC}_{10}\text{N}^+\text{Br}^-$ is the dihedral angle of C(6)–C(7)–C(8)–C(9). That is, in the former it is *trans*, while in the latter it is *gauche*, which makes the section ($70 \text{ Å}^2 = bc \sin \alpha$) of the hydrophilic part larger than that of $C_n\text{AzoC}_5\text{N}^+\text{Br}^-$ by about 20 Å^2 .

Crystal Structure of $C_6\text{AzoC}_{10}\text{N}^+\text{Br}^-$. The packing arrangement viewed along the *c*- and *b*-axis are shown in Figs. 2 and 3, respectively. The crystal structure can be considered as an alternation of the hydrophobic and hydrophilic layers stacked along the *a* axis. In the hydrophobic layer, two molecules are related by the inversion symmetry in the tail-to-tail fashion with the shortest distance of 3.42(1) Å. The alkyl chains and azobenzene moieties are stabilized by the van der Waals interaction. In the hydrophilic layer, the bromide anion is linked to the hydroxyl group of the adjacent molecule by a hydrogen bond with a distance of 3.200(2) Å. Through the hydrogen bonds between the bromide anions and hydroxyl groups, the hydrophilic head groups of amphiphiles are interdigitate mutually in adjacent bilayers. In addition to the electrostatic interaction between the cationic ammonium nitrogens and bromide anions, this interdigitated orientation stabilizes the crystal.

In the case of $C_n\text{AzoC}_5\text{N}^+\text{Br}^-$ crystals, the ammonium cations and bromide anions have almost the same values of x fractional coordinates,^{2–4)} so they make the

common plane parallel to the layer surface. In this crystal, however, the ammonium cation is separated from the bromide anion about 1.34 Å along the *a*-direction (Table 1).

The azobenzene chromophores in the $C_6\text{AzoC}_{10}\text{N}^+\text{Br}^-$ crystal show an absorption maximum (λ_{max}) at 365 nm. On the other hand, those in the typical J-aggregates, $C_n\text{AzoC}_5\text{N}^+\text{Br}^-$, show λ_{max} at 375 nm.¹⁰⁾ The difference in λ_{max} must be due to the difference of the chromophore orientations in the crystals. In the case of $C_6\text{AzoC}_{10}\text{N}^+\text{Br}^-$, the adjacent azobenzenes are overlapped with each other along their long axes with a separation of about 3.55 Å. On the other hand, in the case of $C_n\text{AzoC}_5\text{N}^+\text{Br}^-$, the adjacent azobenzenes are overlapped in a similar way, but the overlapped region is small and the interplanar spacing is large (about 3.62 Å).

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