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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G. Xu [a], K. Okuyama [a] & M. Shimomura [a]

[a] Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo, 184

Version of record first published: 24 Sep 2006.

To cite this article: G. Xu , K. Okuyama & M. Shimomura (1992): Crystal Structures of H-Aggregate of Azobenzene-Containing Amphiphiles, $C_6AzoC_8N^+$ Br^- and $C_8AzoC_{10}N^+$ Br^- , Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 213:1, 105-115

To link to this article: http://dx.doi.org/10.1080/10587259208028722

Mol. Cryst. Liq. Cryst., 1992, Vol. 213, pp. 105–115
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Printed in the United States of America

Crystal Structures of H-Aggregate of Azobenzene-Containing Amphiphiles, $C_6AzoC_8N^+Br^-$ and $C_8AzoC_{10}N^+Br^-$

G. XU, K. OKUYAMA and M. SHIMOMURA

Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184

(Received June 10, 1991; in final form August 26, 1991)

The molecular and packing structures of H-aggregates of azobenzene-containing amphiphiles, $C_6AzoC_8N^+Br^-$ and $C_8AzoC_{10}N^+Br^-$, have been determined by X-ray single crystal analyses. Both crystals belong to the monoclinic system with the space group $P2_1$ and $Z = 2$. The unit cell dimensions of the former crystal are $a = 34.04(7)$, $b = 7.468(2)$, $c = 5.967(1)$ Å, $\beta = 94.67(3)°$. Those of the latter are $a = 38.81(2)$, $b = 7.451(1)$, $c = 5.936(1)$ Å, $\beta = 97.56(3)°$. Molecular and crystal structures of these two compounds are quite similar. Molecules are packed laterally to form a monolayer structure. Therefore, two hydrophobic chains are arranged in the antiparallel fashion and interdigitated mutually. Contrary to the expectation for the H-aggregates, a fairly large inclination angle (ca. 65°) was observed between the planes of the neighboring azobenzene chromophores.

INTRODUCTION

Recently, bilayer-forming synthetic amphiphiles have attracted much attention because of the variety of their structural characteristics, such as molecular orientation and phase transition. Among them, the structure and physical properties of the single-chain azobenzene-containing amphiphiles, $C_nAzoC_mN^+Br^-$, have been studied in detail by means of X-ray diffraction, the spectroscopic method, and thermal analyses. These amphiphiles show different aggregation states of azobenzene chromophores, depending on the number of carbon atoms in the spacer (m) and tail (n) part. Various aggregation states of chromophores have been studied by an absorption spectra and classified into four types, dimeric type, monomeric type, H-aggregate and J-aggregate.[1] Because of their chromophore orientations, the latter two aggregates are particularly interesting. For instance, in the typical J-aggregate, such as casted film of $C_nAzoC_5N^+Br^-$ ($n = 6 \sim 12$), the absorption maximum (λ_{max}) is located at about 375 nm. Their crystal structures were determined in detail by X-ray analyses,[2–4] which showed the adjacent azobenzene chromophores were aligned in head-to-tail fashion.

On the other hand, for the typical H-aggregate, such as casted films of $C_6AzoC_8N^+Br^-$ and $C_8AzoC_{10}N^+Br^-$, the value of λ_{max} is 300 nm. According to the absorption spectroscopy, H-aggregate implies the parallel orientation of chro-

TABLE I

Crystal data and details of experiment and analysis

Compound	$C_6AzoC_8N^+Br^-$	$C_8AzoC_{10}N^+Br^-$
Formula weight	578.7	634.7
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$
a/Å	34.04(7)	38.81(2)
b/Å	7.468(2)	7.451(1)
c/Å	5.967(1)	5.936(1)
β/°	94.67(3)	97.56(3)
Cell Volume/Å^3	1512.1(7)	1707(1)
Z	2	2
Dx/g cm^{-3}	1.271	1.235
Dm/g cm^{-3}	1.27	1.23
Radiation	CuKα	CuKα
μ (calcd)/cm^{-1}	19.56	17.73
F(000)	616	680
Crystal size/mm^3	0.5 × 0.2 × 0.01	0.3 × 0.2 × 0.01
Scan mode	ω	2θ − ω
Scan speed/° (in ω) min^{-1}	6	4
Scan width/° (in ω)	1.30 + 0.14 tanθ	1.80 + 0.14 tanθ
2θ range/°	2.5–120.0	2.2–110.0
No. of observed unique reflections	2377	1952
No. of reflections for *R*	2152	1566
R	0.08	0.14
Rw	0.07	0.13

mophore. This H-aggregate was changed to the J-aggregate by heating above its transition temperature (*Tc*). This transition was found to be a crystal/crystal transition by taking X-ray diffraction patterns of powder specimens below and above this temperature.[5] In the case of a powder/water mixture of this compound, the X-ray diffraction pattern taken below *Tc* showed the same Debye-rings as those from the powder. Above *Tc*, however, a halo was observed in the wide angle region. This halo is attributable to the liquid-crystal state of alkyl chains. Therefore, the transition of the powder/water mixture was a crystal/liquid-crystal transition. In spite of these interesting physical properties, no detailed structural information from X-ray single crystal analyses has been available for the H-aggregate, so far. The reason for this is based on the difficulty of growing single crystals suitable for X-ray diffractions. Although, we already succeeded in growing single crystals of $C_6AzoC_8N^+Br^-$ and $C_8AzoC_{10}N^+Br^-$, these were very thin and far from ideal crystals for X-ray work. In spite of many trials of crystallization, no better crystal was obtained. Therefore, we performed structure analyses by using these thin crystals. In this paper, we discuss the detailed structures of these compounds for better understanding of the stereochemical characteristics of the H-aggregate.

EXPERIMENTAL

Crystal Data

The $C_6AzoC_8N^+Br^-$ (15 mg) was dissolved in a solution of ethanol (6 ml) and nitrobenzene (3.5 ml). Yellow, thin plate-like crystals were grown from the solution

TABLE II

Fractional coordinates and equivalent isotropic temperature factors for non-hydrogen atoms of $C_6AzoC_8N^+Br^-$ with estimated standard deviations in parentheses
$Beq = (4/3) \times \{B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + 2(B_{12}ab + B_{23}bc + B_{31}ca)\}$

Atom	x	y	z	Beq/Å²
Br	0.57445(4)	0.1370(5)	0.1705(2)	5.60(7)
O(1)	0.4839(3)	0.1362(28)	0.9552(14)	5.9(3)
O(2)	0.1583(2)	0.1592(24)	1.4310(13)	5.0(3)
O(3)	−0.1591(2)	0.1026(15)	2.0669(15)	4.2(3)
N(1)	0.4284(2)	0.1310(28)	0.4702(17)	4.4(3)
N(2)	0.0029(3)	0.1180(32)	1.6558(20)	5.0(4)
N(3)	−0.0040(3)	0.1594(27)	1.8483(18)	4.2(3)
C(1)	0.4886(4)	0.2094(29)	0.7396(27)	9.5(9)
C(2)	0.4713(3)	0.0889(27)	0.5579(24)	7.0(7)
C(3)	0.4234(6)	−0.0298(39)	0.3376(41)	5.3(8)
C(4)	0.4168(7)	0.2989(32)	0.3280(31)	5.7(8)
C(5)	0.4039(2)	0.1414(32)	0.6752(19)	4.3(4)
C(6)	0.3597(3)	0.1042(29)	0.6161(24)	5.7(5)
C(7)	0.3380(3)	0.1611(31)	0.8210(24)	5.5(5)
C(8)	0.2944(3)	0.1022(28)	0.7961(21)	5.4(6)
C(9)	0.2730(3)	0.1680(28)	0.9986(21)	3.7(4)
C(10)	0.2304(4)	0.1105(45)	0.9952(24)	5.6(5)
C(11)	0.2121(3)	0.1431(49)	1.2084(24)	5.9(5)
C(12)	0.1699(3)	0.0935(22)	1.2187(18)	4.7(6)
C(13)	0.1200(2)	0.1439(17)	1.4766(13)	4.1(3)
C(14)	0.1104(2)	0.2223(17)	1.6774(13)	4.1(4)
C(15)	0.0719(2)	0.2122(17)	1.7409(13)	4.1(4)
C(16)	0.0910(2)	0.0555(17)	1.3394(13)	4.2(4)
C(17)	0.0525(2)	0.0454(17)	1.4030(13)	4.2(4)
C(18)	0.0430(2)	0.1238(17)	1.6038(13)	3.7(3)
C(19)	−0.0432(2)	0.1352(16)	1.8966(14)	3.7(3)
C(20)	−0.0526(2)	0.2176(16)	2.0950(14)	4.0(4)
C(21)	−0.0913(2)	0.2134(16)	2.1561(14)	4.4(4)
C(22)	−0.0724(2)	0.0487(16)	1.7593(14)	4.4(4)
C(23)	−0.1111(2)	0.0445(16)	1.8204(14)	3.7(4)
C(24)	−0.1206(2)	0.1269(16)	2.0188(14)	4.5(4)
C(25)	−0.1712(3)	0.1769(23)	2.2719(22)	4.2(5)
C(26)	−0.2127(3)	0.1015(21)	2.2987(27)	5.4(6)
C(27)	−0.2310(3)	0.1817(20)	2.5025(25)	5.6(7)
C(28)	−0.2734(4)	0.1118(35)	2.5171(31)	7.6(8)
C(29)	−0.2938(4)	0.1907(27)	2.7093(28)	5.8(6)
C(30)	−0.3339(5)	0.1148(55)	2.7377(34)	8.5(7)

by the solvent-evaporation method for about two months at room temperature. Single crystals of $C_8AzoC_{10}N^+Br^-$ were obtained from a trichloromethane-ethanol (9:1 by v/v) solution by a similar method. The densities of these crystals were measured by a flotation method in a hexane and tetrachloromethane solution.

Lattice parameters and diffraction intensities were measured on a four circle diffractometer (RASA-5RII, Rigaku Co.) with graphite monochromatized CuKα radiation (λ = 1.5418 Å). The lattice parameters were refined by the least-squares fit using 25 reflections in the 2θ range of 38–42° for $C_6AzoC_8N^+Br^-$ and 19 reflections in the 2θ range of 42–52° for $C_8AzoC_{10}N^+Br^-$. Crystal data and experimental details are listed in Table I. Three standard reflections, which were measured every 100 reflections, indicated no crystal decay in both cases. All in-

TABLE III

Fractional coordinates and isotropic temperature factors for non-hydrogen atoms of $C_8AzoC_{10}N^+Br^-$ with estimated standard deviations in parentheses

Atom	x	y	z	Biso/Å^2
Br	0.93448(6)	0.0006(6)	0.8072(3)	3.80(5)
O(1)	0.0132(4)	0.0122(40)	3.0525(20)	2.7(4)
O(2)	0.3605(4)	0.0392(21)	2.5176(22)	3.5(4)
O(3)	0.6404(4)	−0.0003(54)	1.9837(24)	4.4(4)
N(1)	0.0632(4)	0.0064(37)	3.5453(25)	3.1(4)
N(2)	0.4973(5)	0.0008(52)	2.3461(20)	3.6(4)
N(3)	0.5031(4)	0.0395(24)	2.1509(35)	1.7(4)
C(1)	0.0087(6)	−0.0672(33)	3.2650(28)	4.5(8)
C(2)	0.0260(5)	0.0531(41)	3.4480(41)	4.2(7)
C(3)	0.0681(10)	−0.1755(54)	3.6709(63)	4.0(8)
C(4)	0.0744(10)	0.1594(31)	3.7138(46)	2.3(7)
C(5)	0.0853(5)	−0.0042(64)	3.3547(29)	3.4(5)
C(6)	0.1235(8)	−0.0332(51)	3.4336(37)	3.0(6)
C(7)	0.1435(5)	0.0288(49)	3.2394(35)	3.8(6)
C(8)	0.1823(6)	−0.0228(53)	3.2757(38)	4.0(6)
C(9)	0.2023(6)	0.0405(52)	3.0823(31)	3.2(6)
C(10)	0.2405(7)	−0.0142(73)	3.1128(42)	5.1(6)
C(11)	0.2592(5)	0.0547(45)	2.9153(34)	2.8(6)
C(12)	0.2957(6)	−0.0286(38)	2.9326(34)	3.7(6)
C(13)	0.3133(5)	0.0351(51)	2.7287(34)	2.9(6)
C(14)	0.3498(6)	−0.0269(48)	2.7232(32)	4.5(7)
C(15)	0.3942(3)	0.0121(27)	2.4803(24)	3.0(5)
C(16)	0.4028(3)	0.0917(27)	2.2823(24)	3.4(7)
C(17)	0.4369(3)	0.0850(27)	2.2328(24)	2.2(6)
C(18)	0.4198(3)	−0.0742(27)	2.6288(24)	2.7(6)
C(19)	0.4539(3)	−0.0809(27)	2.5794(24)	3.5(7)
C(20)	0.4625(3)	−0.0014(27)	2.3814(24)	2.7(5)
C(21)	0.5380(3)	0.0122(26)	2.1138(23)	2.2(4)
C(22)	0.5470(3)	0.0905(26)	1.9161(23)	2.9(6)
C(23)	0.5812(3)	0.0815(26)	1.8687(23)	2.6(6)
C(24)	0.5632(3)	−0.0751(26)	2.2639(23)	2.8(7)
C(25)	0.5974(3)	−0.0841(26)	2.2164(23)	2.3(6)
C(26)	0.6064(3)	−0.0058(26)	2.0188(23)	3.1(5)
C(27)	0.6503(6)	0.0542(39)	1.7743(40)	2.7(6)
C(28)	0.6862(6)	−0.0321(35)	1.7704(35)	3.3(6)
C(29)	0.7047(5)	0.0485(41)	1.5791(35)	3.9(7)
C(30)	0.7414(5)	−0.0295(44)	1.5784(37)	4.3(7)
C(31)	0.7605(6)	0.0564(58)	1.3937(41)	4.2(7)
C(32)	0.7973(8)	−0.0159(75)	1.4022(42)	5.2(6)
C(33)	0.8167(6)	0.0644(44)	1.2206(42)	4.1(7)
C(34)	0.8530(7)	−0.0177(70)	1.2145(42)	7.1(7)

tensities were corrected for the Lorentz and polarization effects but not for absorption and extinction.

Structure Determination and Refinement

The structures of both crystals were solved by a direct method using the program SAPI-85[6] which provided the non-hydrogen atom positions. After the refinement calculations with isotropic thermal factors, the benzene ring was fairly deviated from the standard hexagon. Therefore, the benzene ring was fixed to the regular

TABLE IV

Bond lengths (Å) of the $C_6AzoC_8N^+Br^-$ with e.s.d.'s in parentheses

O(1) — C(1)	1.42(2)	C(16) — C(17)	1.40(1)
C(1) — C(2)	1.49(3)	C(17) — C(18)	1.40(1)
C(2) — N(1)	1.54(4)	C(18) — N(2)	1.42(1)
C(3) — N(1)	1.44(3)	N(2) — N(3)	1.23(2)
C(4) — N(1)	1.55(3)	C(19) — N(3)	1.40(2)
C(5) — N(1)	1.54(3)	C(19) — C(20)	1.39(1)
C(5) — C(6)	1.54(4)	C(20) — C(21)	1.40(2)
C(6) — C(7)	1.54(3)	C(21) — C(24)	1.40(2)
C(7) — C(8)	1.54(3)	C(19) — C(22)	1.39(1)
C(8) — C(9)	1.54(2)	C(22) — C(23)	1.40(2)
C(9) — C(10)	1.51(3)	C(23) — C(24)	1.40(1)
C(10) — C(11)	1.48(2)	C(24) — O(3)	1.38(2)
C(11) — C(12)	1.49(2)	C(25) — O(3)	1.43(2)
C(12) — O(2)	1.44(2)	C(25) — C(26)	1.54(2)
C(13) — O(2)	1.36(2)	C(26) — C(27)	1.53(2)
C(13) — C(14)	1.40(1)	C(27) — C(28)	1.54(3)
C(14) — C(15)	1.40(1)	C(28) — C(29)	1.51(3)
C(15) — C(18)	1.39(1)	C(29) — C(30)	1.50(4)
C(13) — C(16)	1.40(1)		

Bond angles(°) of the $C_6AzoC_8N^-Br^-$ with e.s.d.'s in parentheses

O(1) — C(1) — C(2)	111(2)	C(13) — C(16) — C(17)	120.1(9)
C(1) — C(2) — N(1)	115(2)	C(16) — C(17) — C(18)	120.0(9)
C(2) — N(1) — C(3)	95(2)	C(15) — C(18) — N(2)	122(1)
C(2) — N(1) — C(4)	123(2)	C(17) — C(18) — N(2)	117.9(9)
C(2) — N(1) — C(5)	107(1)	C(18) — N(2) — N(3)	117(1)
C(3) — N(1) — C(4)	111(2)	N(2) — N(3) — C(19)	115(1)
C(3) — N(1) — C(5)	116(2)	N(3) — C(19) — C(20)	114(1)
C(4) — N(1) — C(5)	105(2)	N(3) — C(19) — C(22)	125.8(9)
N(1) — C(5) — C(6)	113(1)	C(19) — C(20) — C(21)	119.9(9)
C(5) — C(6) — C(7)	107(1)	C(20) — C(21) — C(24)	120.1(9)
C(6) — C(7) — C(8)	111(2)	C(21) — C(24) — C(23)	120(1)
C(7) — C(8) — C(9)	110(1)	C(20) — C(19) — C(22)	120.1(9)
C(8) — C(9) — C(10)	114(2)	C(19) — C(22) — C(23)	120.0(9)
C(9) — C(10) — C(11)	114(2)	C(22) — C(23) — C(24)	120(1)
C(10) — C(11) — C(12)	118(2)	C(21) — C(24) — O(3)	125.8(9)
C(11) — C(12) — O(2)	107(1)	C(23) — C(24) — O(3)	114(1)
C(12) — O(2) — C(13)	119(1)	C(24) — O(3) — C(25)	118(1)
O(2) — C(13) — C(14)	116(1)	O(3) — C(25) — C(26)	106(1)
O(2) — C(13) — C(16)	124.5(9)	C(25) — C(26) — C(27)	112(1)
C(13) — C(14) — C(15)	120.0(9)	C(26) — C(27) — C(28)	111(1)
C(14) — C(15) — C(18)	120.0(8)	C(27) — C(28) — C(29)	114(2)
C(14) — C(13) — C(16)	120(1)	C(28) — C(29) — C(30)	115(2)
C(15) — C(18) — C(17)	120.1(8)		

Bond lengths (Å) of the $C_8AzoC_{10}N^+Br^-$ with e.s.d.'s in parentheses

O(1) — C(1)	1.42(2)	C(18) — C(19)	1.39(2)
C(1) — C(2)	1.50(3)	C(19) — C(20)	1.40(2)
C(2) — N(1)	1.52(3)	C(20) — N(2)	1.39(3)
C(3) — N(1)	1.55(5)	N(2) — N(3)	1.24(3)
C(4) — N(1)	1.54(3)	C(21) — N(3)	1.42(3)
C(5) — N(1)	1.51(2)	C(21) — C(22)	1.40(2)
C(5) — C(6)	1.51(4)	C(22) — C(23)	1.39(2)
C(6) — C(7)	1.54(4)	C(23) — C(26)	1.39(2)
C(7) — C(8)	1.54(4)	C(21) — C(24)	1.39(2)
C(8) — C(9)	1.54(3)	C(24) — C(25)	1.39(2)
C(9) — C(10)	1.52(4)	C(25) — C(26)	1.40(2)
C(10) — C(11)	1.54(4)	C(26) — O(3)	1.36(3)

TABLE IV (*continued*)

Bond lengths (Å) of the $C_8AzoC_{10}N^+Br^-$ with e.s.d.'s in parentheses

C(11) — C(12)	1.54(4)	C(27) — O(3)	1.41(3)
C(12) — C(13)	1.54(3)	C(27) — C(28)	1.54(4)
C(13) — C(14)	1.49(4)	C(28) — C(29)	1.54(3)
C(14) — O(2)	1.43(3)	C(29) — C(30)	1.54(4)
C(15) — O(2)	1.37(2)	C(30) — C(31)	1.54(4)
C(15) — C(16)	1.40(2)	C(31) — C(32)	1.52(5)
C(16) — C(17)	1.39(2)	C(32) — C(33)	1.52(4)
C(17) — C(20)	1.40(2)	C(33) — C(34)	1.54(5)
C(15) — C(18)	1.40(2)		

Bond angles (°) of the $C_8AzoC_{10}N^+Br^-$ with e.s.d.'s in parentheses

O(1) — C(1) — C(2)	107(2)	C(15) — C(18) — C(19)	120(1)
C(1) — C(2) — N(1)	117(2)	C(18) — C(19) — C(20)	120(2)
C(2) — N(1) — C(3)	116(2)	C(17) — C(20) — N(2)	122(2)
C(2) — N(1) — C(4)	104(2)	C(19) — C(20) — N(2)	118(2)
C(2) — N(1) — C(5)	109(2)	C(20) — N(2) — N(3)	116(2)
C(3) — N(1) — C(4)	109(2)	N(2) — N(3) — C(21)	114(2)
C(3) — N(1) — C(5)	106(3)	N(3) — C(21) — C(22)	115(2)
C(4) — N(1) — C(5)	113(2)	N(3) — C(21) — C(24)	125(1)
N(1) — C(5) — C(6)	114(2)	C(21) — C(22) — C(23)	120(2)
C(5) — C(6) — C(7)	107(2)	C(22) — C(23) — C(26)	120(1)
C(6) — C(7) — C(8)	114(2)	C(22) — C(21) — C(24)	120(2)
C(7) — C(8) — C(9)	113(2)	C(21) — C(24) — C(25)	120(1)
C(8) — C(9) — C(10)	114(2)	C(24) — C(25) — C(26)	120(2)
C(9) — C(10) — C(11)	112(2)	C(23) — C(26) — C(25)	120(2)
C(10) — C(11) — C(12)	110(2)	C(23) — C(26) — O(3)	120(2)
C(11) — C(12) — C(13)	109(2)	C(25) — C(26) — O(3)	120(2)
C(12) — C(13) — C(14)	116(2)	C(26) — O(3) — C(27)	122(2)
C(13) — C(14) — O(2)	107(2)	O(3) — C(27) — C(28)	104(2)
C(14) — O(2) — C(15)	119(2)	C(27) — C(28) — C(29)	111(2)
O(2) — C(15) — C(16)	114(1)	C(28) — C(29) — C(30)	112(2)
O(2) — C(15) — C(18)	126(1)	C(29) — C(30) — C(31)	112(2)
C(15) — C(16) — C(17)	120(1)	C(30) — C(31) — C(32)	112(3)
C(16) — C(15) — C(18)	120(1)	C(31) — C(32) — C(33)	113(3)
C(16) — C(17) — C(20)	120(1)	C(32) — C(33) — C(34)	114(3)
C(17) — C(20) — C(19)	120(1)		

hexagon with a C—C bond length of 1.395 Å and C—C—C bond angles of 120°. These calculations were carried out by the constrained least-squares method with the SHELX76[7] program. The quantity minimized in the refinement was $\Sigma w(|Fo| - |Fc|)^2$, where $w = 1/(\sigma^2(Fo) + (pFo)^2)$, $p = 0.006$ for $C_6AzoC_8N^+Br^-$ and $p = 0.030$ for the other. In both refinements, the reflections with $Fo < 3\sigma(Fo)$ were excluded from the reflection data. The final R value of $C_6AzoC_8N^+Br^-$ was 0.077 ($Rw = 0.070$) for all non-hydrogen atoms with anisotropic temperature factors and 37 hydrogen atoms with isotropic temperature factors. That of $C_8AzoC_{10}N^+Br^-$ was 0.139 ($Rw = 0.129$) for all non-hydrogen atoms with isotropic temperature factors.

Atomic scattering factors were taken from International Tables for X-ray Crystallography, Vol. IV.[8] Computations were done on an A-70 minicomputer with the aid of the CRYSTAN program in the RASA-5RII system (Rigaku Co.) and on an ACOS 1000 computer at the Information Processing Center, Tokyo University of Agriculture and Technology.

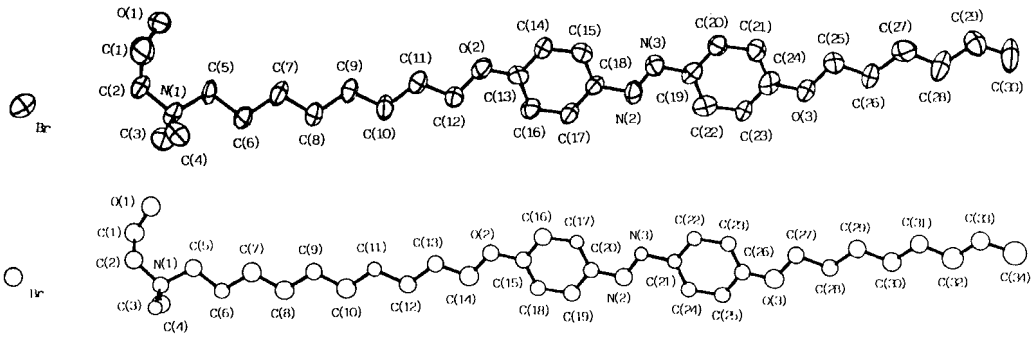


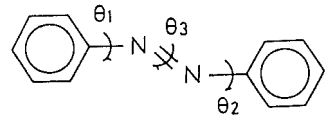
FIGURE 1 (a) Molecular structure and atomic numbering scheme of $C_6AzoC_8N^+Br^-$ with 50% probability plots for thermal ellipsoids (ORTEP[9] drawing). (b) Molecular structure and atomic numbering scheme of $C_8AzoC_{10}N^+Br^-$ with 50% probability plots for isotropic thermal spheres (ORTEP[9]).

TABLE V

Torsion angles for $C_nAzoC_mN^+Br^-$

Compound	Torsion angles[a]		
	θ1/°	θ2/°	θ3/°
$C_6AzoC_8N^+Br^-$	168	−167	−174
$C_8AzoC_{10}N^+Br^-$	166	−167	−170
$C_6AzoC_5N^+Br^{-4}$	−178	179	180
$C_8AzoC_5N^+Br^{-4}$	−178	179	180
$C_{10}AzoC_5N^+Br^{-4}$	−177	180	−179
$C_{12}AzoC_5N^+Br^{-4}$	−178	179	180

[a] Torsion angles are defined as follows:



RESULTS AND DISCUSSION

Molecular Conformation

The final atomic parameters for non-hydrogen atoms are given in Tables II and III.* The molecular structure and the atom numbering scheme are given in Figure 1. The numbering system is similar to those for J-aggregates reported previously.[2-4] Bond lengths and bond angles are given in Table IV.

Molecular structures of both compounds are very similar to each other. The average C—C single bond length and C—C—C bond angle are 1.52(3) Å and 113(2)° in the case of $C_6AzoC_8N^+Br^-$, and 1.53(4) Å and 112(2)° in the other

*Tables of observed and calculated structure amplitudes and anisotropic temperature parameters for non-hydrogen atoms are available from the authors on request.

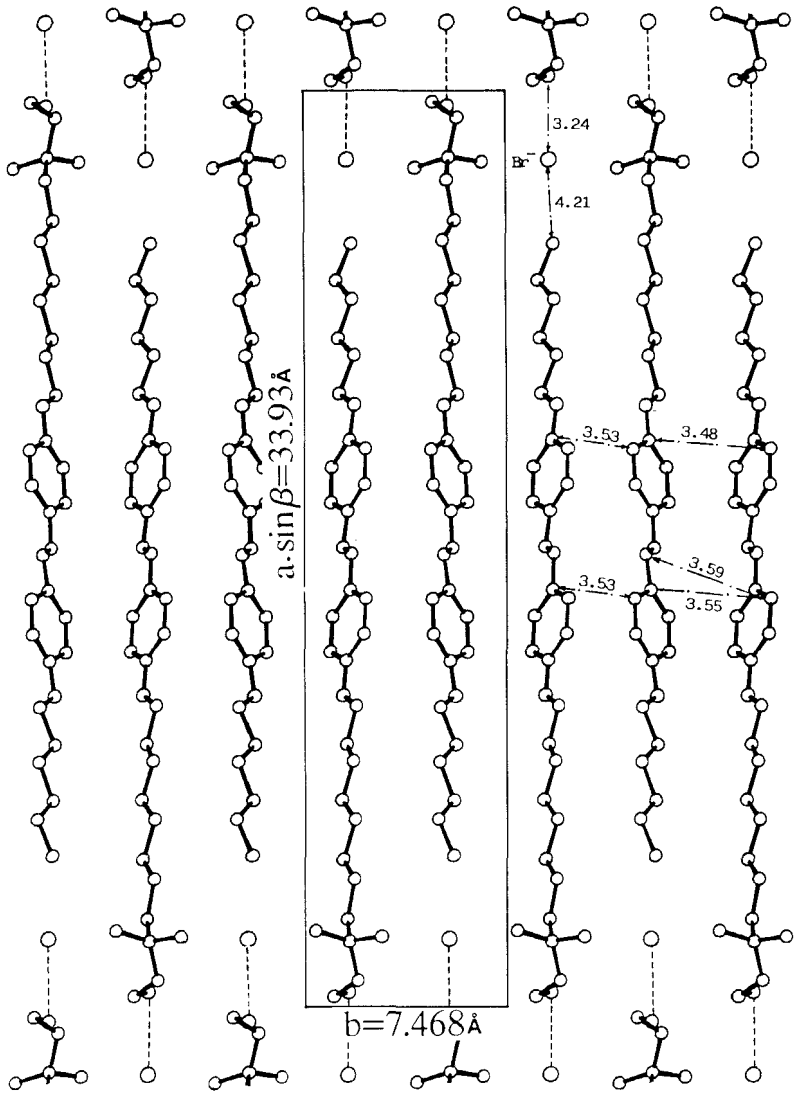


FIGURE 2 Packing of $C_6AzoC_8N^+Br^-$ projected along the *c*-axis. Hydrogen bonds between bromide anions and hydroxyl groups are indicated by broken lines. Some short interatomic distances (/Å) are shown (ORTEP[9]).

case. These values are in good agreement with those of the J-aggregate, $C_nAzoC_5N^+Br^-$ ($n = 6 \sim 12$).[2-4]

Table V shows the values of two torsional angles (θ_1 and θ_2) between the nitrogen atom and the carbon atom in a benzene ring, and that of one torsional angle (θ_3) between the nitrogen atoms at the azo moiety in $C_nAzoC_mN^+Br^-$. In all the cases of J-aggregates, the deviation from the planar conformation is less than 3°, while in the present compounds the deviation is more than 9°. Therefore, the planarity of the molecules in H-aggregates seems to be inferior to that in J-aggregates.

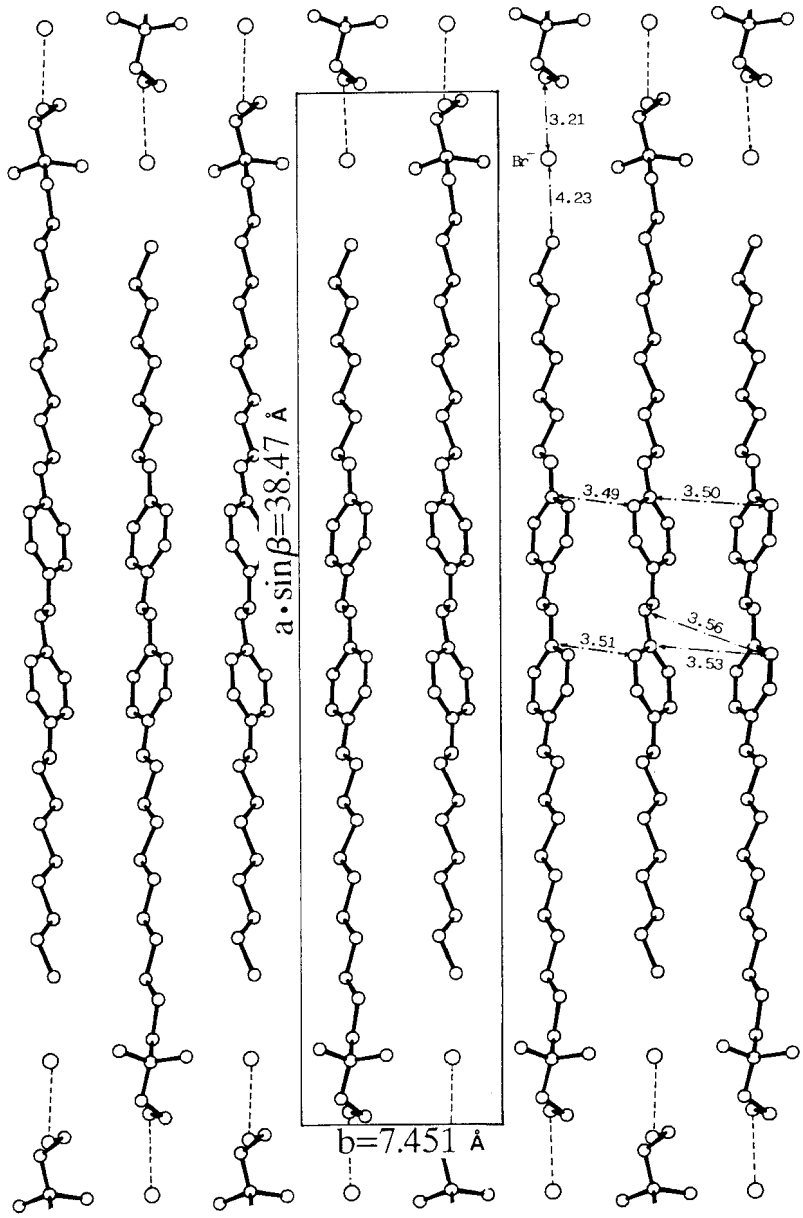


FIGURE 3 Packing of $C_8AzoC_{10}N^+Br^-$ projected along the *c*-axis (ORTEP[9]).

Molecular Packing

Molecular packing of both compounds in the *ab* plane are shown in Figures 2 and 3, together with some short interatomic distances between neighboring chains and hydrogen bonds between bromide anions and terminal hydroxyl oxygen atoms. Molecules pack laterally to form a monolayer structure, in contrast to the bilayer structure of the J-aggregates.[2–4] Therefore, two neighboring hydrophobic chains

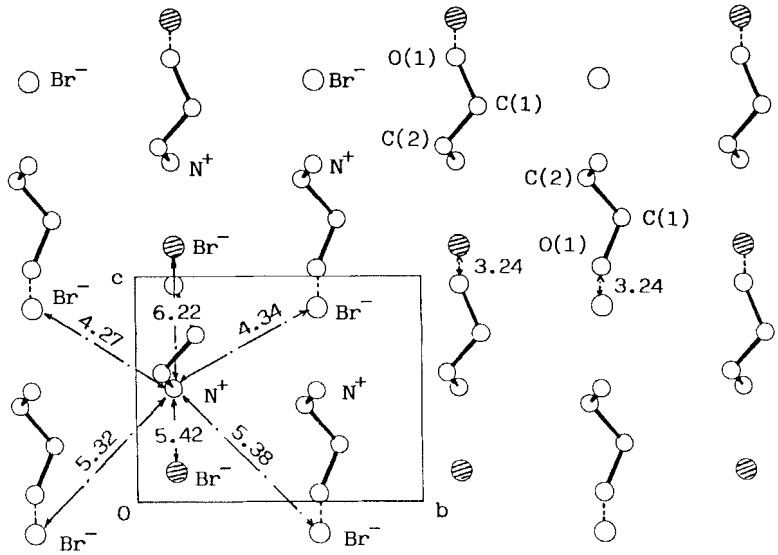


FIGURE 4 The arrangement of the hydrophilic portion of $C_6AzoC_8N^+Br^-$, viewed perpendicular to the layer interface (ORTEP[9]). Hydrogen bonds (broken lines) and the distances between nitrogen cation and bromide anions (above ○ and below ◍ the layer interface) are indicated. Contact distances are given in Å.

are arranged in antiparallel fashion and interdigitated mutually. The azobenzene chromophores are aligned at the center of the hydrophobic layer. The inclination angles of ca. 65° are observed between the planes of the neighboring azobenzene chromophores.

The methyl group at the end of the hydrophobic chain is in contact with the bromide anion with the length of 4.21 Å ($C_6AzoC_8N^+Br^-$) or 4.23 Å ($C_8AzoC_{10}N^+Br^-$). These distances are very close to, but somewhat larger than the van der Waals distance between CH_3 and Br^-(3.85 Å), which suggests that the further interdigitation of the hydrophobic chains is forbidden by the steric interaction between methyl groups and bromide anions. Therefore, the difference of the number of carbon atoms between spacer part (m) and tail part (n) becomes a very important factor for the packing in the H-aggregate crystals. Figures 2 and 3 show that the difference in the number of carbon (m-n) must be 2 when the aggregation mode is H.

The hydrophilic layer consists of ammonium cations, bromide anions and terminal hydroxyl groups in both sides of the monolayer. In both crystals, nitrogen cations and bromide anions have almost the same fractional coordinates (x) along the a direction, so they make a common plane parallel to the layer surface (Figures 2 and 3). Two such planes are accommodated in a hydrophilic layer. Further, both compounds have a very similar packing arrangement in the hydrophilic portion. As an example, the packing of the hydrophilic portion of $C_6AzoC_8N^+Br^-$ viewed perpendicular to the layer interface together with short interatomic distances are given in Figure 4. A nitrogen cation is surrounded by six bromide anions. Four of them are located at distances of 4.27–5.38 Å and on the same plane to which nitrogen cations belong. On the other hand, another two of them are located at

distances of 6.22 Å and 5.42 Å on the other plane in the same hydrophilic layer. The bromide anion is linked to the terminal hydroxyl group by a hydrogen bond. The hydrogen bond length and bond angle <OHBr$^-$ are 3.23 Å and 140°. These electrostatic interactions and hydrogen bonds stabilize the hydrophilic part and link the neighboring layers tightly. These packing structures in the hydrophilic part are very similar to those observed in J-aggregates.[2-4]

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