X-RAY CRYSTALLOGRAPHIC STUDY OF ALKYLAMMONIUM ANTHRACENE-9-CARBOXYLATES AS A MODEL FOR FIBROUS STRUCTURE OF BINARY ANTHRACENE SALT GELS

Tahahiro Tani[1], Kazuki Sada[2],*, Masatsugu Ayabe[3], Yuya Iwashita[4], Takanori Kishida[5], Michihiro Shirakawa[6], Norifumi Fujita[7] and Seiji Shinkai[8],*

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 6-10-1 Hakozaki Higashi-ku Fukuoka 812-8581, Japan; e-mail: [1] *tanitcm@mbox.nc.kyushu-u.ac.jp,* [2] *sadatcm@mbox.nc.kyushu-u.ac.jp,* [3] *ayabe@mbox.nc.kyushu-u.ac.jp,* [4] *yuyatcm@mbox.nc.kyushu-u.ac.jp,* [5] *qchantcm@mbox.nc.kyushu-u.ac.jp,* [6] *3000htcm@mbox.nc.kyushu-u.ac.jp,* [7] *nfjttcm@mbox.nc.kyushu-u.ac.jp,* [8] *seijitcm@mbox.nc.kyushu-u.ac.jp*

Dedicated to Professor Ivan Stibor on the occasion of his 60th birthday in recognition of his outstanding contributions to supramolecular chemistry.

Crystal structure of hexylammonium anthracene-9-carboxylate was investigated. The salt was arranged by a one-dimensional hydrogen bond network to form a columnar structure in the crystalline state. This columnar structure should be the model of fibrous assemblies in the organogels of anthracene-9-carboxylate alkylammonium salts having a long alkyl chain.
Keywords: Crystal structure determination; Gels; Supramolecular chemistry; Aggregation; Ion pairs; Anthracenes; Alkylammonium salts; Molecular column; Crystal engineering; Organogelators.

Organogelators have received considerable interest as new supramolecular assemblies and functional materials[1]. They are low-molecular-weight organic compounds that form physical gels in various organic solvents by self-assembly. One-dimensional fibrous or two-dimensional layer aggregates have been found in the gel fibers, and the solvents being solidified by interweaving or crosslinking of these nanostructures. Molecular structures of organogelators mostly possess two functional groups; one is to arrange the molecules along one- or two-dimensional directions by non-covalent bonds, and the other is a solvatophilic group miscible with the solvents to suppress crystallization. For example, one-dimensional hydrogen-bonding

groups such as in ureas and amides have been used for the former purpose, and long alkyl chains have been used for the latter[2,3]. Although the X-ray crystallographic structures are not necessarily correlated with the aggregate structures formed in hydrogen-bond independent organogels (e.g., cholesterol-based gels)[4], it is assumed that the two structures are more or less similar in hydrogen-bond-dependent systems. Therefore, X-ray crystallographic study of a model compound with shorter alkyl chains often gives the structure model of the molecular assembly in the gel fiber[2,3,5].

Recently, we demonstrated that photoresponsive organogels can be readily obtained from the primary alkylammonium anthracene-9-carboxylate salts (1_n)[6]. Of the ten salts (1_4–1_{12}, 1_{16}) shown in Fig. 1, 1_8, 1_9, and 1_{10} in cyclohexane afford gels. SEM observations showed a fibrillar morphology in the gel phase. When the cyclohexane gel of 1_{10} was photo-irradiated ($\lambda > 300$ nm), the UV-VIS absorption bands decreased and simultaneously the gel changed into the sol. Warming the sol to the boiling point of cyclohexane, followed by cooling to 15 °C, regenerated the gel phase by conversion of the photodimer to the monomer. However, details of ionic and hydrogen bonding interactions in the gel fibers still remain unclear. In this report, we describe the crystal structure of 1_6 as a structure model for the fibrous aggregates in the anthracene salt gels. Moreover, they imply a few new facts to rationalize the photoreactivity of the anthracene moieties in the gel phase.

RESULTS AND DISCUSSION

As described earlier, anthracene-9-carboxylate salts were prepared by mixing two components in THF and purified by reprecipitation[6]. The resulting 1:1 salts were recrystallized from various organic solvents to prepare single crystals. The single crystal of 1_6 suitable for X-ray structure analysis was grown from solutions in toluene. The other salts gave only fine needles which did not have sufficient size for X-ray crystallographic studies.
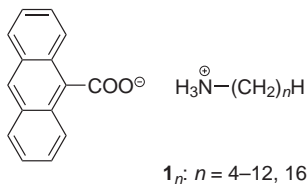

1_n: $n = 4$–12, 16

FIG. 1
Anthracene salts

X-ray crystallographic parameters are summarized in Table I, and the ORTEP drawing of the salt is shown in Fig. 2. The asymmetric unit of $\mathbf{1}_6$ contains two independent ion pairs. All the conformations of the carboxylate anions are quite similar, and the dihedral angles between the aromatic plane and the carboxylate plane are 68 and 65°. This indicates that the carboxylate groups are directed nearly perpendicular to the aromatic planes due to steric repulsion between the carboxylate oxygen atoms and the hydrogen atoms of the anthracene ring. On the other hand, the conformations of alkyl chains in the alkylammonium cations are also similar to each other. The characteristic bent molecular shapes are attributed to *gauche* conformations at the C(α)–C(β) bond. The dihedral angles of N–C(α)–C(β)–C(γ) are 59 and 68°. The other conformations are all *trans*, giving straight structures toward the terminal methyl group.
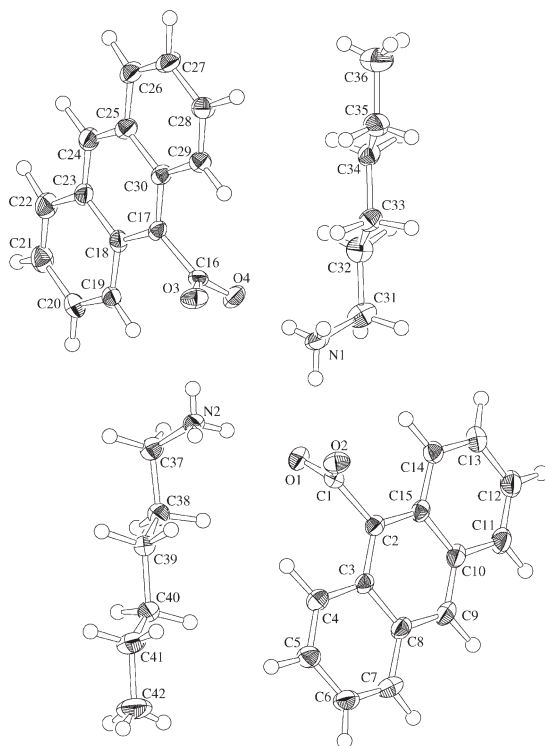

Fig. 2
ORTEP drawing (50% probabilities) of $\mathbf{1}_6$

The most striking structure feature of the crystal structure of 1_6 is a one-dimensional columnar structure. One of the columns is marked by the dotted line in Fig. 3. In the column, the ion pairs are associated in an infinite one-dimensional structure by hydrogen bonding, as shown in Fig. 4. Two pairs of the alkylammonium cations and carboxylate anions form a cyclic 2+2 hydrogen bond network by using two of the three N^+H's of the primary ammonium cations and two oxygen atoms of the carboxylate anions. This cyclic dimer is the unit structure of the column. The dimers are stacked by the two hydrogen bonds from the remaining protons of the cations to the carboxylate anions of the neighboring dimer to form the one-dimensional hydrogen bond network. This provides the columnar structure of 1_6 in the crystalline state. In the hydrogen bond network, the primary ammonium groups act as hydrogen bond donors providing all the three protons and

TABLE I
X-ray crystallographic parameters of 1_6

Parameter	1_6
Formula	$C_{42}H_{50}N_2O_4$
Formula weight	646.87
Crystal system	orthorhombic
Space group	*Pna2*$_1$
a, Å	8.9929(6)
b, Å	18.889(1)
c, Å	21.498(2)
V, Å^3	3651.8(5)
Z	4
D_c, g cm^{-3}	1.18
Number of reflections	3401
R_1, wR_2	0.037/0.101[a]
GOF	0.77
$2\theta_{max}$, °	136.42
Observed reflections	3401
Parameters	434
Temperature, °C	–150
Residual electron densities, e Å^{-3}	0.69, –0.34

[a] $wR_2 = [\Sigma\, w(F_o^2 - F_c^2)^2/\Sigma\, wF_o^2]^{1/2}$ (for all data).

the carboxylate anions accept three protons from three different ammoni-
um cations. The hydrogen bond ability between the ion-pairs is common
for the primary alkylammonium carboxylate salts[7,8], but this kind of hydro-
gen bond network has been never reported.

   To assemble into three-dimensional crystals, further association of the
hydrogen-bonded columns is required. Since all the hydrogen bond donors
and acceptors are used for formation of the columnar structure, bundles of
the columns are attributed to weaker intermoleucular interactions, such as
van der Waals forces between the alkyl chains and π–π interactions between
the aromatic moieties. In the column, the alkyl chains of the cations are
closely packed, but the anthracene moieties are arranged in a herring-bone
fashion[9], as shown in Fig. 4d. The distances between the aromatic moieties
in the column are 9.0 Å, which is much larger than the distance suitable for
π–π stacking. Therefore, there is no π–π stacking within the column, but
they are used for association of the columns to arrange them into the
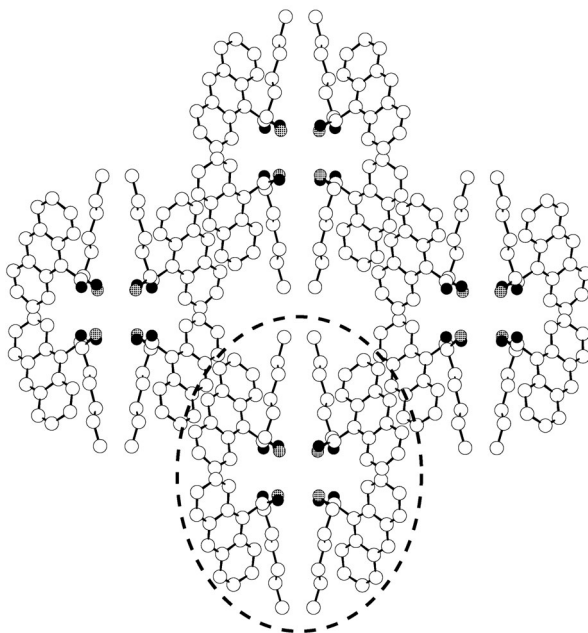two-dimensional directions (Fig. 3). The alkyl group of the ammonium

FIG. 3
Crystal packing diagram of 1_6 viewed down from the crystallographic a-axis and c-axis. The
open, filled, and dotted circles represent carbon, oxygen, and nitrogen atoms, respectively.
The hydrogen atoms are omitted for clarity. The dotted lines show a single column

cation extends to the void space between the columns, which accommodate the hexyl groups. Therefore, in the crystalline state of 1_6, the one-dimensional hydrogen bond between the ion-pairs constructs the columnar structures, and the π–π stacking between the anthracene moieties connects them to form three-dimensional crystal structures.

The columnar structures of 1_6 in the crystalline state remind of fibrous aggregates in the cyclohexane gels of the longer alkyl salts such as 1_8, 1_9, and 1_{10}. We believe that the same one-dimensional hydrogen bond network is present in the gel fibers. The longer alkyl chains cannot be accommodated in the space between the columns any longer. This leads to
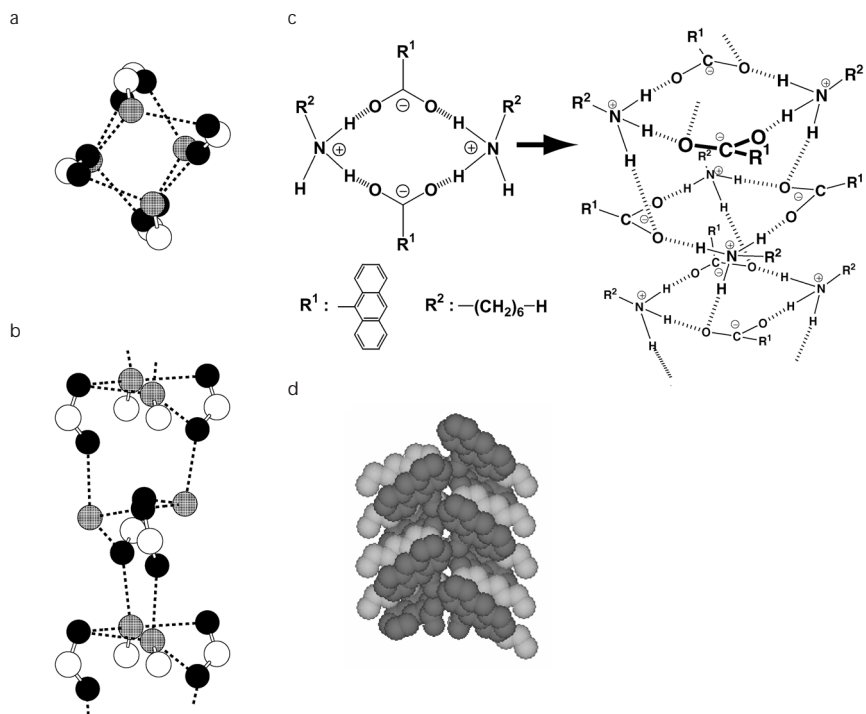

Fig. 4

The one-dimensional hydrogen bond network of the column of 1_6. a The top view and b the front view. The open, filled, and dotted circles represent carbon, oxygen, and nitrogen atoms, respectively. The hydrogen atoms are omitted for clarity. c Schematic representation of formation of the hydrogen bond network from the 2+2 cyclic dimer to the one-dimensional hydrogen bond network, and d the space filling model of the column viewed from the side. Light and dark grey molecules represent alkylammonium cations and anthracene-9-carboxylate anions, respectively

loose bundles of the columns and suppresses the formation of the two-dimensional ordered structure of the columns. As a result, these salts form the organogels in cyclohexane. Moreover, the crystal structure gives an insight into the photoreactivity in the gel phase. In the columnar structures, the anthracene moieties are arranged in a *face-to-face* manner suitable for photodimerization, as shown in Fig. 5. However, the intermolecular distances between C(9) and C(10) of the anthracene rings in the stacked pairs are ca. 5.0–5.9 Å due to the offset along the longer molecular axis of the anthracene ring. They are slightly longer than the distances of photodimerization in the crystalline state[10,11]. Loose packing by the elongation of the alkyl groups provides void space between the columns, increasing the mobility of the anthracene moieties in the gel fibers. The increased mobility and strong π–π interaction of the anthracene moieties in cyclohexane enables to react more efficiently in the gel fiber. Therefore, the columnar structure should be the model of fibrous assemblies in the organogels of alkylammonium anthracene-9-carboxylates.

EXPERIMENTAL

Preparation of the Salts. General Procedure

An equimolar amount of anthracene-9-carboxylic acid and the corresponding aliphatic amine was dissolved in THF at room temperature. The solvent was removed on a rotary evaporator and then in vacuo. The white residue was purified by reprecipitation from a chloroform solution into hexane.
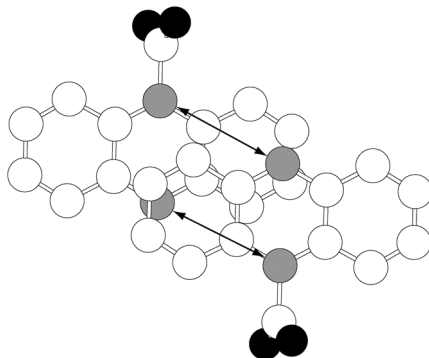

FIG. 5

Face-to-face arrangement of the anthracene moieties in the crystalline state of 1_6. The grey circles and the arrows represent presumable photodimerization sites. The open and filled circles represent carbon and oxygen atoms, respectively

X-ray Crystallographic Study

X-ray diffraction data were collected on a Rigaku R-AXIS RAPID diffractometer with a 2D area detector using graphite-monochromatized CuKα radiation (λ = 1.5418 Å) at –150 °C. Lattice parameters were obtained by least-squares analysis from reflections for three oscillation images. Direct methods (SIR92)[12] were used for the structure solution. All calculations were performed using the TEXSAN[13] crystallographic software package. The structure was refined by the full-matrix least-squares procedure using all reflections based on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were placed in idealized positions with isotropic displacement parameters relative to the connected non-hydrogen atoms, and were not refined. Absolute configuration was not determined reliably.

CCDC 226409 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

REFERENCES

1. a) Terech P., Weiss R. G.: *Chem. Rev.* **1997**, *97*, 3133; b) van Esch J.-H., Feringa B. L.: *Angew. Chem., Int. Ed.* **2000**, *39*, 2263; c) Meléndez R. E., Carr A. J., Linton B. R., Hamilton A. D.: *Struct. Bonding (Berlin)* **2000**, *96*, 31.
2. a) Hanabusa K., Okui K., Koyama T., Shirai H.: *J. Chem. Soc., Chem. Commun.* **1992**, 1371; b) Hanabusa K., Yamada M., Kimura M., Shirai H.: *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1949; c) Hanabusa K., Shimura K., Hirose K., Kimura M., Shirai H.: *Chem. Lett.* **1996**, 885; d) Hanabusa K., Kawakami A., Kimura M., Shirai H.: *Chem. Lett.* **1997**, 191.
3. a) De Vries E. J., Kellogg R. M.: *J. Chem. Soc., Chem. Commun.* **1993**, 238; b) van Esch J., De Feyter S., Kellogg R. M., De Schryver F., Feringa B. L.: *Chem. Eur. J.* **1997**, *3*, 1238; c) van Esch J., Schoonbeek F., de Loos M., Kooijman H., Spek A. L., Kellogg R. M., Feringa B. L.: *Chem. Eur. J.* **1999**, *5*, 937; d) Schoonbeek F. S., van Esch J., Hulst R., Kellogg R. M., Feringa B. L.: *Chem. Eur. J.* **2000**, *6*, 2633.
4. a) Lin Y.-C., Kachar B., Weiss R. G.: *J. Am. Chem. Soc.* **1989**, *111*, 5542; b) Otsuni E., Kamaras P., Weiss R. G.: *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1324; c) Lu L., Cocker M., Bachman R. E., Weiss R. G.: *Langmuir* **2000**, *16*, 20.
5. a) Luboradzki R., Gronwald O., Ikeda M., Shinkai S., Reinhoudt D. N.: *Tetrahedron* **2000**, *56*, 9595; b) Gronwald O., Shinkai S.: *Chem. Eur. J.* **2001**, *7*, 4329; c) Shirakawa M., Kawano S.-I., Fujita N., Sada K., Shinkai S.: *J. Org. Chem.* **2003**, *68*, 5037.
6. Ayabe M., Kishida T., Fujita N., Sada K., Shinkai S.: *Org. Biomol. Chem.* **2003**, *1*, 2744.
7. Kinbara K., Hashimoto Y., Sukegawa M., Nohira H., Saigo K.: *J. Am. Chem. Soc.* **1996**, *118*, 3441.
8. a) Matsumoto A., Odani T., Chikada M., Sada K., Miyata M.: *J. Am. Chem. Soc.* **1999**, *121*, 11122; b) Nagahama S., Inoue K., Sada K., Miyata M., Matsumoto A.: *Cryst. Growth Design* **2003**, *3*, 247.

9. a) Gavezzotti A., Desiraju G. R.: *Acta Crystallogr., Sect. B: Struct. Sci.* **1988**, *44*, 427; b) Desiraju G. R., Gavezzotti A.: *J. Chem. Soc., Chem. Commun.* **1989**, 621; c) Desiraju G. R., Gavezzotti A.: *Acta Crystallogr., Sect. B: Struct. Sci.* **1989**, *45*, 473.

10. Ito Y., Olovsson G.: *J. Chem. Soc., Perkin Trans. 1* **1997**, 127.

11. Becker H.-D.: *Chem. Rev.* **1993**, *93*, 145.

12. Altomare A., Cascarano G., Giacovazzo C., Guagliardi A., Burla M., Polidori G., Camalli M.: *J. Appl. Crystallogr.* **1994**, *27*, 435.

13. *TEXSAN, X-ray Structure Analysis Package.* Molecular Structure Corporation, Woodlands (TX) 1985.