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Crystal and Molecular Structures of 2-Dodecyl-7,7,8,8-tetracyanoquinodimethane

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To develop a possible structural model for molecular arrangement in Langmuir–Blodgett (LB) films of 2-alkyl-7,7,8,8-tetracyanoquinodimethane (alkyl-TCNQ) the molecular and crystal structures of 2-dodecyl-7,7,8,8-tetracyanoquinodimethane (dodecyl-TCNQ) have been determined by X-ray single-crystal analysis. The compound crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$. The molecule consists of the planar TCNQ moiety and the dodecyl chain having all-*trans* conformation. In the crystals the TCNQ fragments make a stacking structure in a head-to-head manner across the centers of symmetry to form a double layer of TCNQ groups. The dodecyl chains protrude oppositely from the TCNQ layers and are assembled to form a close-packed layer, being interdigitated with each other. In this way, the TCNQ moieties and the dodecyl groups form layers alternately. This molecular arrangement in the crystal provides new insight into the structure of the LB films of alkyl-TCNQ.

In recent years, Langmuir–Blodgett (LB) films containing a tetracyanoquinodimethane (TCNQ) or its related chromophore have been investigated extensively because some of them show fairly high conductivity.[1,2] To explore the mechanism of conductivity that the LB films show and to design a new LB film with a TCNQ chromophore or its derivative that yields higher conductivity, it is of importance to study the structure and morphology of LB films of 2-alkyl-7,7,8,8-tetracyanoquinodimethane (alkyl-TCNQ; Fig. 1) and charge-transfer (CT) LB films having a TCNQ chromophore as an acceptor. We have been investigating them by use of infrared and ultraviolet-visible spectroscopy and atomic force microscopy (AFM).[3–14]

Our studies on the LB films of alkyl-TCNQ have provided the following conclusions about their structure and morphology. (i) The LB films of octadecyl-TCNQ consist of numerous platelet microcrystal domains, which have a layered assembly formed by bimolecular layers with a thickness of 3.7 nm.[7,8] Octadecyl-TCNQ molecules are arranged periodically with a period of 0.85 nm inside the domains.[7,8] The domains in the first layer (4.3 nm) are thicker than those in the layers above the fist layer (3.7 nm). (ii) The hydrocarbon chains in the LB films of dodecyl-, pentadecyl-, and octadecyl-TCNQ are tilted with respect to the surface normal.[3,4] The TCNQ planes and their long axes are also inclined with respect to the surface normal in the LB films.[3,4] (iii) The LB films of alkyl-TCNQ show the order-disorder transition.[5] The order–disorder transition in a multi-layer LB film of octadecyl-TCNQ with the longer even-numbered hydrocarbon chain occurs at a temperature higher than that in the corresponding LB film of dodecyl-TCNQ with the shorter even-numbered hydrocarbon chain.[5] The LB film of pentadecyl-TCNQ with the odd-numbered hydrocarbon chain shows a transition temperature similar to the film of dodecyl-TCNQ.[5] (iv) The time-dependent structural changes are observed for one-layer LB films of dodecyl- and pentadecyl-TCNQ but not for that of octadecyl-TCNQ. The alkyl chain becomes more tilted with respect to the surface normal during the time course and the TCNQ plane becomes closer to perpendicular with respect to the substrate surface.[13]

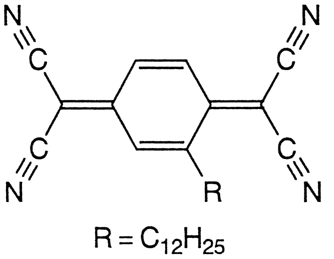

Fig. 1. Chemical structure of 2-dodecyl-7,7,8,8-tetracyanoquinodimethane.

These previous studies have provided new insight into the molecular structure, orientation, aggregation, and morphology of the LB films of alkyl-TCNQ. However, these investigations cannot offer detailed information about the molecular structure and intermolecular interaction of alkyl-TCNQ in the LB films. The purposes of the present X-ray crystallographic study of dodecyl-TCNQ are to elucidate its crystal and molecular structures and to develop a possible structural model for the molecular arrangements in the LB films of alkyl-TCNQ. The present study may give knowledge about the stacking of TCNQ chromospheres, hydrophobic interaction and packing of the alkyl chains, and layer structure of alkyl-TCNQ molecules. Relatively few amphiphilic molecules with a chromophoric group have been subjected to an X-ray crystallographic study. Thus, the present study may be important also from the point of the studies of crystal structure of functional dye molecules with

Table 1. Crystal Data of Dodecyl-TCNQ

Formula	$C_{24}H_{28}N_4$
Formula weight	372.513(5)
Crystal system	Triclinic
Space group	$P\bar{1}$
Cell dimension	
a/Å	4.708(3)
b/Å	8.147(2)
c/Å	29.202(7)
α/°	91.01(2)
β/°	93.65(4)
γ/°	97.72(4)
V/Å^3	1107.3(9)
Z	2
Dx/g cm^{-3}	1.117(1)
D_m/g cm^{-3}	1.114[a)]
μ(Mo-$K\alpha$)/cm^{-1}	0.313

a) By floating method with Nal aq.

Table 2. Final Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factor, Beq[a)] for the Non-Hydrogen Atoms. Standard Deviations of the Least Significant Figures are given in Parentheses

Atom	x	y	z	Beq/Å^2
N9	0.6266(10)	0.9044(6)	0.2429(2)	8.3(2)
N10	1.2590(10)	1.1252(5)	0.1606(1)	8.1(2)
N11	0.6728(10)	0.0250(5)	0.0739(2)	8.4(2)
N12	1.3204(10)	0.3191(5)	−0.0048(1)	8.3(2)
C1	0.9605(8)	0.7093(5)	0.1528(1)	4.0(1)
C2	0.7929(8)	0.5478(5)	0.1603(1)	4.0(1)
C3	0.8090(9)	0.4205(5)	0.1304(1)	4.4(1)
C4	0.9899(8)	0.4349(5)	0.0925(1)	4.1(1)
C5	1.1651(9)	0.5918(5)	0.0871(1)	4.8(1)
C6	1.1520(9)	0.7202(5)	0.1154(1)	4.6(1)
C7	0.9491(9)	0.8497(5)	0.1780(1)	4.7(1)
C8	0.9914(9)	0.3023(5)	0.0632(1)	4.9(1)
C9	0.7665(9)	0.8724(5)	0.2144(2)	5.5(1)
C10	1.1208(9)	1.0023(5)	0.1683(2)	5.5(1)
C11	0.8148(10)	0.1462(6)	0.0681(2)	5.9(2)
C12	1.1709(10)	0.3100(5)	0.0249(2)	5.7(2)
C1′	0.6152(8)	0.5155(5)	0.2014(1)	4.4(1)
C2′	0.8019(9)	0.4811(5)	0.2441(1)	4.8(1)
C3′	0.6277(9)	0.4446(5)	0.2857(1)	5.2(1)
C4′	0.8119(9)	0.3988(6)	0.3273(1)	5.7(2)
C5′	0.6429(9)	0.3696(6)	0.3700(1)	5.3(1)
C6′	0.8273(9)	0.3250(6)	0.4115(1)	5.3(1)
C7′	0.6611(9)	0.2961(6)	0.4542(1)	5.3(1)
C8′	0.8443(9)	0.2503(5)	0.4956(1)	5.1(1)
C9′	0.6770(9)	0.2204(6)	0.5383(1)	5.3(1)
C10′	0.8573(9)	0.1731(6)	0.5797(1)	5.3(1)
C11′	0.6919(10)	0.1431(6)	0.6223(2)	6.3(2)
C12′	0.8765(12)	0.0971(7)	0.6635(2)	7.6(2)

a) Beq is defined as

$$\mathrm{Beq} = \frac{4}{3}\sum_{i}\sum_{j}\beta_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$$

where β_{ij}'s are the anisotropic temperature factors and $\mathbf{a}_i$'s are the unit cell vectors.

long alkyl chains.

Experimental

The sample of dodecyl-TCNQ was obtained from Hayashibara Biochemical Laboratories, Inc. Kankoh-Shikiso Institute, and was used without further purification. The columnar yellow single-crystals were obtained from a bromoform solution by slow evaporation of the solvent.

Preliminary crystallographic data were obtained from oscillation and Weissenberg photographs. The density of the crystal was measured by the flotation method. The unit cell parameters were determined by a least-squares fit of 2θ values of 22 reflections in the range of $18° < 2\theta < 24°$ by use of Mo $K\alpha$ radiation. The intensity data were collected on a computer-controlled four-circle diffractometer over the range of $3° < 2\theta < 45°$ by using the ω–2θ scan technique. The intensities were corrected for the Lorentz and polarization effects, but not for absorption. A total of 2893 independent reflections was measured, of which 1670 reflections with $|F_o| > 3\sigma(|F_o|)$ were considered observed and used for the structure determination.

The structure was solved by the direct method using the program MULTAN78[15] and refined by the least-squares method. Anisotropic thermal vibrations were assumed for the non-hydrogen atoms. All the hydrogen atoms were found from a difference Fourier map and were refined isotropically. The final $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - F_c|)^2/\Sigma w(|F_o|^2)]^{1/2}$ values were 7.9 and 8.2%, respectively.

Results and Discussion

Molecular Structure. The crystallographic data and the outline of the structure determination are summarized in Table 1. Final atomic parameters are listed in Table 2. The bond lengths and angles are given in Table 3. The hydrogen-atom parameters, the anisotropic thermal parameters for the non-hydrogen atoms, and a table of observed and calculated structure factors can be obtained on request from the authors with an asterisk.

Figure 2 illustrates the molecular structure of dodecyl-TCNQ with the atomic labeling. Notably, the alkyl chain assumes a *trans*-zigzag structure. The angle between the long axis of the chain and the normal of the TCNQ plane is 50°, and that between the normal and the C(2)–C(1′) line is 84°. The TCNQ chromophore is nearly planar but bends slightly. The CN groups are out of the plane of the six-membered ring; the largest deviation of 0.373(9) Å from the plane occurs at the N(9) atom, which is close to the alkyl chain. In the alkyl tail, the average C–C bond length of 1.523(6) Å is slightly shorter than the normal C(sp3)–C(sp3) length of 1.541 Å, and the average C–C–C angle of 113.1(3)° is somewhat larger than the normal C(sp3)–C(sp3)–C(sp3) angle of 109.5°. These average length and angle are within the range of those found for other amphiphilic compounds having a long hydrocarbon chain.[16,17]

In the TCNQ moiety, the angles of C(2)–C(1)–C(7) and C(1)–C(7)–C(9) are larger than those of C(3)–C(4)–C(8) and C(4)–(8)–C(11), respectively. The angle C(1)–C(2)–C(1′) is wider than that of C(3)–C(2)–C(1′). Moreover, the angle of C(9)–C(7)–C(10) is appreciably smaller than that of C(11)–C(8)–C(12). These variations in the bond angles may be due to a repulsive interaction between the C(1′)H_2 group and the

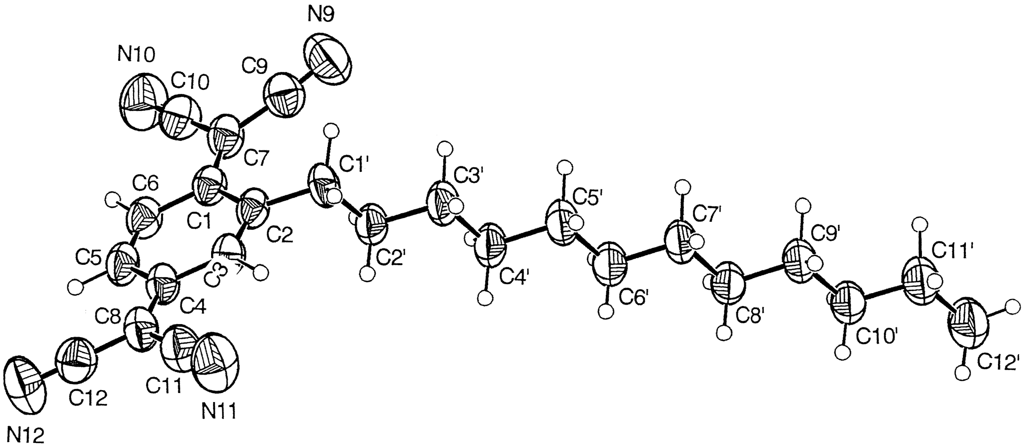

Fig. 2. ORTEP drawing of the molecular structure of dodecyl-TCNQ. Thermal ellipsoids are scaled to include 50% probablity level except for the hydrogen atoms, which are represented by spheres of a fixed radius.

Table 3. Bond Distances and Angles with Estimated Standard Deviations in Parentheses

Bond	Distance (Å)	Bond	Angle (°)
N9–C9	1.141(7)	C2–C1–C6	117.6(3)
N10–C10	1.153(6)	C2–C1–C7	124.8(4)
N11–C11	1.138(6)	C6–C1–C7	117.6(3)
N12–C12	1.149(6)	C1–C2–C3	118.7(4)
C1–C2	1.468(5)	C1–C2–C1′	122.5(3)
C1–C6	1.457(6)	C3–C2–C1′	118.7(3)
C1–C7	1.358(6)	C2–C3–C4	123.0(3)
C2–C3	1.356(6)	C3–C4–C5	117.5(3)
C2–C1′	1.514(6)	C3–C4–C8	119.9(3)
C3–C4	1.437(6)	C5–C4–C8	122.6(4)
C4–C5	1.442(5)	C4–C5–C6	121.2(4)
C4–C8	1.366(6)	C1–C6–C5	121.8(4)
C5–C6	1.331(6)	C1–C7–C9	127.8(4)
C7–C9	1.434(6)	C1–C7–C10	121.1(4)
C7–C10	1.432(6)	C9–C7–C10	111.0(4)
C8–C11	1.437(6)	C4–C8–C11	122.8(4)
C8–C12	1.440(6)	C4–C8–C12	122.0(4)
C1′–C2′	1.531(6)	C11–C8–C12	115.2(4)
C2′–C3′	1.520(6)	N9–C9–C7	174.3(5)
C3′–C4′	1.530(6)	N10–C10–C7	179.9(5)
C4′–C5′	1.527(6)	N11–C11–C8	176.9(5)
C5′–C6′	1.523(6)	N12–C12–C8	177.9(5)
C6′–C7′	1.518(6)	C2–C1′–C2′	111.4(3)
C7′–C8′	1.521(6)	C1′–C2′–C3′	112.5(3)
C8′–C9′	1.522(6)	C2′–C3′–C4′	112.3(4)
C9′–C10′	1.520(6)	C3′–C4′–C5′	112.9(4)
C10′–C11′	1.515(6)	C4′–C5′–C6′	112.8(4)
C11′–C12′	1.521(7)	C5′–C6′–C7′	113.2(4)
		C6′–C7′–C8′	113.3(4)
		C7′–C8′–C9′	113.2(4)
		C8′–C9′–C10′	113.7(4)
		C9′–C10′–C11′	113.9(4)
		C10′–C11′–C12′	113.1(4)

C(9)–N(9) group, the C(1′)···C(9) being 2.908(7) Å. The other bond lengths and angles in the TCNQ chromophore are very close to those in TCNQ itself.[18]

Crystal Structure. Figure 3a and 3b show the crystal structure viewed along the *a*- and *b*-axis, respectively. The TCNQ groups form a head-to-head arrangement across the centers of symmetry in the *ab* plane. The dodecyl groups, which are almost parallel to the (011) plane and protrude oppositely from the TCNQ array, interpenetrate to each other to form a close-packed arrangement shown schematically in Fig. 4. A similar stacking of hydrocarbon chain is found in an azobenzene-containing amphiphile, C_3H_7–O–Azo–O–$(CH_2)_5$–$N^+(CH_3)_2(CH_2)_2OH$, where Azo indicates the azobenzene group.[19]

Crystal Structure of Dodecyl-TCNQ and Structure of the LB Films of Alkyl-TCNQ. It is of particular importance to investigate the detailed molecular arrangement and structure in the LB films of alkyl-TCNQ. However, there is no technique to determine the three-dimensional structure of alkyl-TCNQ molecules in the LB films. Thus far, we have employed AFM, infrared and ultraviolet-visible spectroscopy, and X-ray diffraction to investigate molecular structure, orientation and arrangement in the LB films of alkyl-TCNQ.[3–8,13,14] Such studies have revealed that the LB films of octadecyl-TCNQ are composed of numerous platelike microcrystal domains in which the TCNQ molecules form a bilayer structure with the interdigitated alkyl chains.

The present X-ray crystallographic study provides a strong base to explore the structure of the LB films of alkyl-TCNQ. Figure 5 illustrates a schematic drawing of the crystal structure of dodecyl-TCNQ. We infer that there is marked similarity between the crystal structure and the structure of the LB films. It is very likely that alkyl-TCNQ molecules achieve very close molecular structure and intermolecular interaction between the crystal and the LB films. However, there may be some minor structural differences between them. For example, the alkyl chain assumes *trans*-zigzag conformation in the crystal, but it takes a few gauche conformers in the LB films.[14] The interdigitated part of the alkyl chain contains only *trans* form but the non-interdigitated part includes some *gauche* forms.[14] In addition, it seems that the TCNQ chromophore forms a few kinds of aggregation forms as well as the monomeric form in the LB films[6] while in the crystal it assumes only one form.

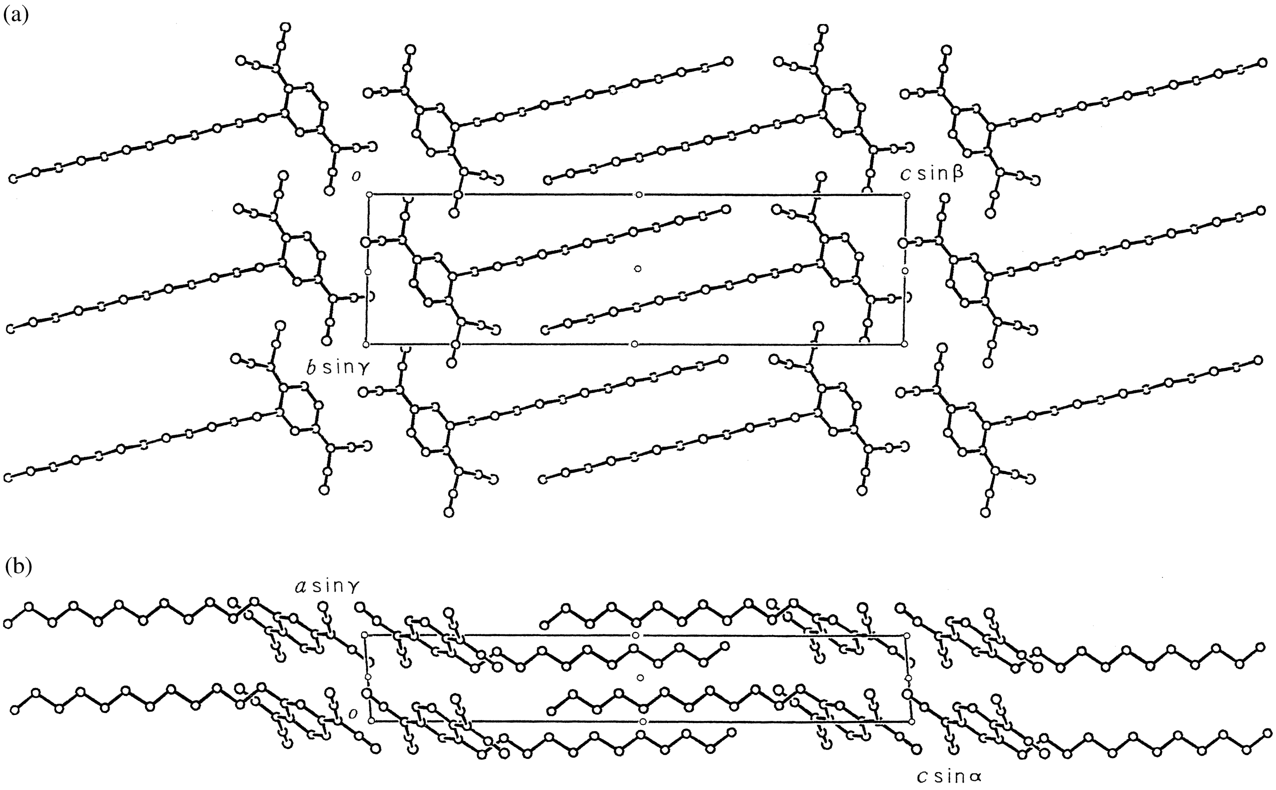

Fig. 3. Crystal structure of dodecyl-TCNQ: (a) viewed along the *a*-axis, (b) viewed along the *b*-axis. Small circles represent a center of symmetry.

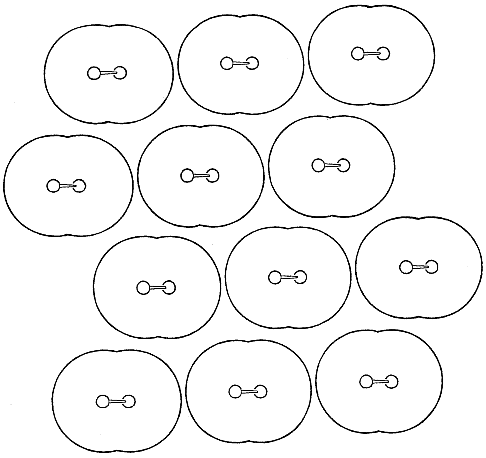

Fig. 4. Packing scheme of the dodecyl groups viewed parallel to the alkyl chain. The boundary lines are drawn at the van der Waals radius (2.0 Å) of the CH_2 group. The centers of the chains are separated by 4.3–4.9Å.

Conclusion

The present X-ray crystallographic study of dodecyl-TCNQ has revealed its crystal and molecular structure. The compound crystallizes in the triclinic space $P\bar{1}$ group with $Z = 2$. The TCNQ plane is nearly planar and the alkyl chain has *trans*-zigzag structure. In the crystal structure, the TCNQ chromophores form a head-to-head arrangement across the centers of symmetry in the *ab* plane. The dodecyl chains are almost parallel to the (011) plane and protrude oppositely from the TCNQ array, being interdigitated to each other. The TCNQ groups and dodecyl chains form the layer structure shown in Fig. 5.

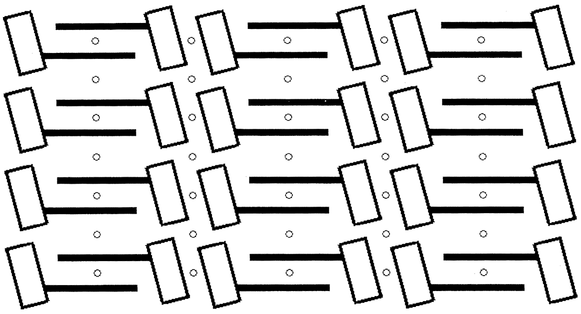

Fig. 5. Schematic drawing of the crystal structure. Note that the TCNQ groups make head-to-head contacts and the alkyl groups form the interpenetrated packing.

This sort of study is very useful for exploring the structure of LB films. Many more functional amphiphilic molecules with long alkyl chains must be subjected to X-ray crystallographic studies for structural characterization of various LB films.

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