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X-Ray Analysis of the Domain Structure of the 1:1 Complex of Carbazole–TCNQ

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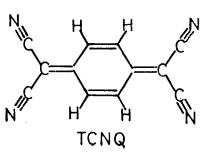
The crystal structure of the 1:1 complex of carbazole–TCNQ was investigated by X-ray diffraction. Analysis of sharp spots and diffuse streaks in the diffraction patterns revealed that the crystal is composed of an ordered domain and a disordered one. The ordered domain is made up from two types of ordered molecular arrangements, whereas the disordered one consists of a one-dimensionally disordered structure. The structures of the two ordered domains are closely related with each other. They both contain mixed stack columns of alternating carbazole and TCNQ usually observed in charge transfer (CT) complexes. The existence of various types of domain structures as shown by diffraction patterns of many crystals grown from acetone, acetonitrile and tetrahydrofuran solutions can be interpreted in terms of the combinations of ordered and disordered domains. No CT band appears in the visible absorption spectra of the acetone solution of carbazole–TCNQ, whereas the spectra of the powdered crystals show a CT band at about 18000 cm^{-1}. The calculation of SCF-MO-CI of the system of the carbazole–TCNQ pair indicates a weak CT interaction.

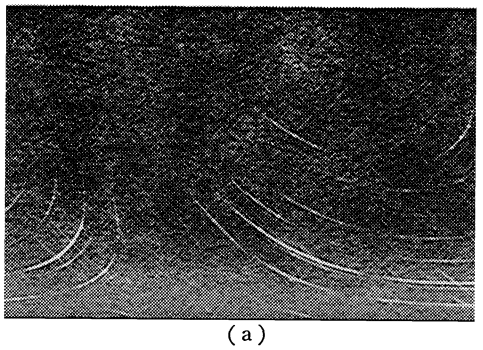
Charge transfer (CT) complexes containing carbazole, a weak electron donor, do not seem to have been investigated much, no structural study ever having been reported. The crystal structure of the 1: 1 complex of carbazole and 7,7,8,8-tetracyanoquinodimethane (TCNQ) has been determined. The domain structure



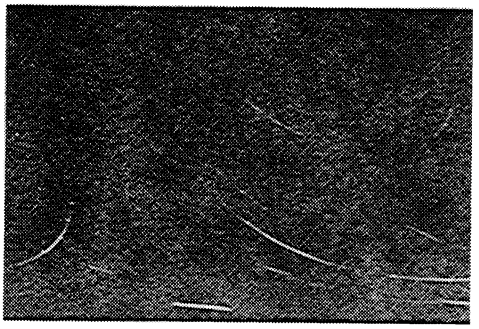
of carbazole–TCNQ, the analysis of diffuse streaks and the spectroscopic study are reported in this paper.

Experimental

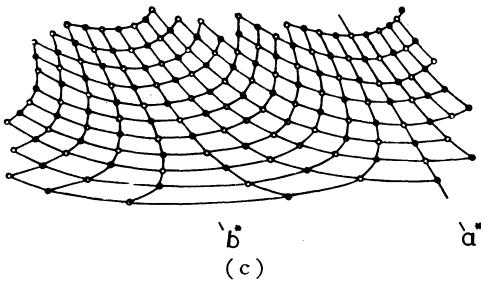
The crystals of carbazole–TCNQ were grown by a diffusion method, acetone solution of both compoments being used. The crystal is hardly soluble and black, needle-like crystals could be easily obtained after a few days. Elemental analysis shows that the crystal is the 1:1 complex of carbazole–TCNQ. Found: C, 77.9; N, 18.9; H, 3.3%. Calcd for carbazole–TCNQ (1:1): C, 77.6; N, 18.9; H, 3.5%.



(a)



(b)



(c)

Fig. 1. Weissenberg photographs.
(a) (ξ, η, 1/2), (b) (ξ, η, 3/2), (c) Distribution of sharp spots observed in the photographs (a) and (b). The open circles and filled circles represent the two different groups IIIa and IIIb in Table 2.

Weissenberg photographs are shown in Fig. 1. Oscillation photographs of axes c and a show sharp layer lines and intermediate layer lines with diffuse streaks. Disregarding the layer lines accompanying diffuse streaks, all the spots can be indexed with respect to the orthorhombic unit cell with dimensions listed in Table 1. The diffuse streaks occur parallel to b^*. Distributions of the diffuse streaks are summarized in Table 2. In the half-integral layer lines, the sharp spots appear along the diffuse streaks at intervals of b^*. Closer examination revealed that these spots deviate slightly up and below alternately with respect to the streaks.

Table 1. Crystallographic data of the average structure of carbazole–TCNQ

Carbazole–TCNQ	Formula $C_{12}H_9N \cdot C_{12}H_4N_4$
Orthorhombic	Space group Immm
$a=10.751\pm0.010$ Å	F.W.$=371.4$ g/cm^3
$b=12.944\pm0.020$	d_m $=1.340$ g/cm^3 (flotation method)
$c=3.339\pm0.015$	d_x $=1.328$ g/cm^3
$U=464.6$ Å^3	Z $=1$

Table 2. Summary of reflections
The Miller indices refer to the unit cell listed in Table 1. h, k, l, n and m indicate integral number; η may take non-integral values.

	a^*	b^*	c^*		
I	h	k	l	$h+k+l=2n$	sharp spots
II	$h/2$	η	l	$h=2n+1$, $l=2m+1$	streaks
IIIa	$h'/2$	k	$l'^*/2$	$h'=2n'+1$, $(h'+l')/2$ $+k=2m'$, $l'=2n''+1$	sharp spots
IIIb	$h'/2$	k	$l'/2$	$h'=2n'+1$, $(h'+l')/2$ $+k=2m'+1$, $l'=2n''+1$	sharp spots

a) h', l', n', n'', and m' indicate that they differ slightly from integer, *viz.*, the spots of groups IIIa and IIIb deviate slightly from the center of the streaks (group II).

The intensity data were collected with multiple-film equi-inclination Weissenberg photographs with Cu$K\alpha$ radiation. The intensities were estimated visually with a standard film strip and converted into $|F(hkl)|$ by applying the Lorentz-polarization and shape corrections.

Results and Discussion

Determination of the Average Structure. If the half-integral layer lines with diffuse streaks are neglected, the unit cell (Table 1) is of the average structure of a disordered crystal. In view of the planar structures of the component molecules, the space group Immm was assumed. The body centered lattice containing only one formula unit indicates that each lattice point is occupied by carbazole and TCNQ with equal prob-

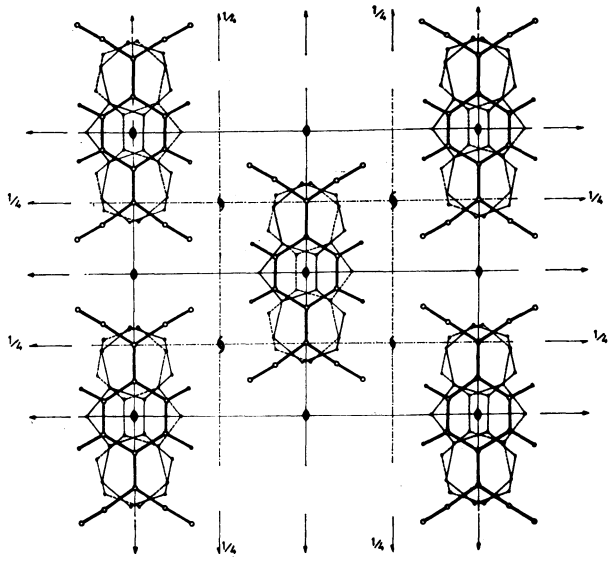


Fig. 2. Projection of the average structure along the c axis.

TABLE 3. FINAL ATOMIC PARAMETERS ($\times 10^4$) AND THEIR ESTIMATED STANDARED DEVIATIONS

The B_{ij}'s are defined by:

$$\exp\left[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)\right].$$

	x	y	z	B_{11}	B_{22}	B_{12}	B_{13}	B_{23}	B_{23}
				Carbazole					
C1	701(29)	0	0	129(48)	344(57)	170(159)	0	0	0
C2	1263(21)	1006(22)	0	128(34)	248(33)	1938(351)	−7(29)	0	0
C3	2412(27)	971(19)	0	270(41)	152(23)	1811(325)	−59(29)	0	0
C4	3106(42)	0	0	106(45)	204(43)	4315(937)	0	0	0
N1	0	1358(43)	0	192(73)	180(57)	70(280)	0	0	0
				TCNQ					
C5	622(17)	925(15)	0	138(32)	91(15)	2273(327)	−38(17)	0	0
C6	1258(30)	0	0	124(44)	111(26)	3541(754)	0	0	0
C7	2565(35)	0	0	275(56)	95(21)	457(226)	0	0	0
C8	3301(18)	878(13)	0	146(26)	77(12)	925(185)	16(17)	0	0
N2	3841(18)	1654(13)	0	193(14)	104(14)	2325(293)	24(18)	0	0

TABLE 4. OBSERVED AND CALCULATED STRUTURE FACTORS

The reflections belong to those of group I (Table 2).

H	K	L	FO	FC
0	2	0	119.5	116.2
0	6	0	2.7	6.6
0	10	0	20.0	18.7
0	16	0	3.4	2.6
1	3	0	30.2	29.4
1	7	0	3.0	2.2
1	11	0	1.0	0.6
2	2	0	42.1	33.3
2	6	0	3.5	4.1
2	10	0	6.6	5.1
2	14	0	1.1	1.5
3	1	0	45.8	39.6
3	5	0	10.5	7.0
3	9	0	1.7	2.8
3	15	0	2.7	2.1
4	2	0	3.3	2.7
4	6	0	7.1	8.5
4	12	0	3.5	3.9
5	3	0	35.9	34.2
5	7	0	9.2	7.8
5	11	0	2.8	4.2
6	2	0	2.6	3.8
6	6	0	3.3	2.0
6	12	0	1.8	0.9
7	3	0	2.7	5.2
7	7	0	4.8	3.7
8	2	0	4.1	5.6
8	6	0	8.0	7.5
9	5	0	1.4	2.9
10	6	0	1.4	4.1
10	10	0	3.3	2.0
12	0	0	1.3	1.6
0	3	1	9.0	9.1
0	7	1	2.4	3.6
0	11	1	16.0	16.3
0	15	1	3.4	2.3
1	2	1	32.1	34.4
1	6	1	12.0	13.2
1	10	1	5.5	5.2
2	3	1	13.0	16.6
2	11	1	3.3	3.6
3	0	1	41.1	39.8
3	4	1	10.3	13.1
3	8	1	2.2	3.3
4	1	1	13.3	15.1
0	4	0	54.7	53.6
0	8	0	6.4	8.1
0	12	0	16.1	14.9
1	1	0	68.7	58.7
1	5	0	25.0	26.0
1	9	0	13.3	13.9
2	0	0	39.8	34.0
2	4	0	11.5	9.7
2	8	0	3.0	3.8
2	12	0	1.9	2.9
2	16	0	1.3	0.1
3	3	0	14.5	15.3
3	7	0	2.9	2.3
3	11	0	2.1	5.7
4	0	0	44.5	40.2
4	4	0	8.6	9.6
4	8	0	5.2	5.1
5	1	0	31.8	31.6
5	5	0	5.5	7.3
5	9	0	4.5	6.9
6	0	0	12.3	9.9
6	4	0	2.1	3.0
6	8	0	1.8	1.4
7	1	0	1.4	4.3
7	5	0	6.9	7.8
7	11	0	1.5	2.3
8	4	0	1.2	3.1
9	3	0	1.2	2.2
10	2	0	1.9	1.6
10	8	0	1.5	0.9
11	1	0	1.9	5.7
0	1	1	172.3	175.7
0	5	1	20.7	23.6
0	9	1	10.1	10.6
0	13	1	4.7	5.5
1	0	1	32.4	35.6
1	4	1	1.6	3.0
1	8	1	6.8	9.4
2	1	1	17.3	21.8
2	9	1	4.6	4.6
2	15	1	1.0	0.6
3	2	1	5.4	5.4
3	6	1	2.6	2.0
3	14	1	1.1	0.2
4	3	1	8.9	11.7
4	5	1	2.1	2.6
4	11	1	2.1	2.4
5	2	1	26.3	28.3
5	6	1	9.5	11.1
5	12	1	1.2	2.6
6	3	1	1.0	3.2
6	9	1	1.3	0.0
7	4	1	3.4	5.5
7	8	1	1.5	1.1
8	1	1	1.0	0.3
8	5	1	4.2	3.1
9	0	1	1.3	2.0
10	1	1	0.9	1.8
11	0	1	1.3	5.0
12	1	1	0.8	0.6
0	2	2	29.9	29.3
0	6	2	3.5	2.8
0	10	2	10.6	8.6
1	1	2	15.6	14.6
1	5	2	5.7	4.5
1	9	2	4.8	4.6
2	0	2	6.0	6.6
2	4	2	2.4	3.5
2	10	2	2.8	3.4
3	1	2	9.7	14.6
3	5	2	2.8	5.3
4	0	2	7.8	5.3
4	4	2	1.0	2.5
4	8	2	1.6	3.2
5	1	2	10.0	9.3
5	5	2	1.5	2.3
5	9	2	2.0	2.2
6	0	2	3.5	2.9
6	4	2	1.2	4.9
6	8	2	1.0	0.1
7	5	2	2.8	2.5
8	2	2	1.5	2.8
8	6	2	3.3	3.6
11	1	2	1.2	2.1
0	5	3	4.8	3.3
0	11	3	5.8	4.0
1	2	3	4.7	4.2
1	6	3	1.6	1.3
0	0	4	14.0	13.2
1	1	4	3.9	4.1
4	9	1	2.9	4.6
5	0	1	14.9	17.5
5	4	1	8.1	10.0
5	10	1	4.0	5.2
6	1	1	4.6	5.9
6	5	1	2.8	4.1
7	0	1	1.5	5.5
7	6	1	4.5	4.8
7	10	1	1.3	1.7
8	3	1	1.4	5.9
8	7	1	3.1	5.2
9	6	1	1.1	2.2
10	3	1	1.1	0.1
10	9	1	1.9	1.8
0	0	2	83.1	80.4
0	4	2	11.8	13.8
0	8	2	4.0	4.4
0	12	2	8.8	6.9
1	3	2	4.6	6.5
1	7	2	0.7	1.9
1	11	2	1.1	0.6
2	2	2	6.5	8.9
2	8	2	1.6	1.0
2	12	2	1.4	2.2
3	3	2	2.3	5.4
3	7	2	1.6	1.6
4	2	2	1.1	2.0
4	6	2	0.5	0.4
4	12	2	2.0	1.4
5	3	2	9.9	11.5
5	7	2	2.8	4.2
5	11	2	2.3	2.3
6	2	2	1.8	3.5
6	6	2	5.1	2.8
7	3	2	1.1	0.0
7	7	2	2.5	1.6
8	4	2	1.3	1.3
10	2	2	1.2	1.2
0	1	3	29.2	24.6
0	9	3	3.8	3.6
1	0	3	8.0	7.7
1	4	3	1.4	0.2
1	10	3	1.7	0.0
0	2	4	6.9	6.0

ability. The average structure thus deduced was refined with the block-diagonal least-squares method. The final R-value was 0.15. The weighting scheme adopted was: $w=1$, for $|F_o|\geq 3.0$ and $w=0.2$ for $|F_o|<3.0$, for all the 179 observed reflections belonging to group I of the reflection (Table 2). The positional and thermal parameters are given in Table 3. The observed and calculated structure factors are compared in Table 4.

The structure within one unit cell as viewed along axis c is shown in Fig. 2. Each lattice point is occupied by carbazole and TCNQ with equal probability. The site symmetry of the lattice point is mmm(D_{2h}), the apparent molecular structures of each component molecules thus being D_{2h}. The orientation of carbazole should be disordered since it has no such high symmetry. The molecule is assumed to take one of two alternative orientations with equal probability (Fig. 2). The bond lengths and angles are shown in Fig. 3. The mean bond lengths are: C–C (TCNQ), 1.37; C–N, 1.16; C–C (carbazole), 1.37; C–N, 1.43 Å. The standard deviations of each bond length and angle are about 0.05 Å and 4°, respectively.

Interpretation of Diffuse Streaks. Consider a lattice

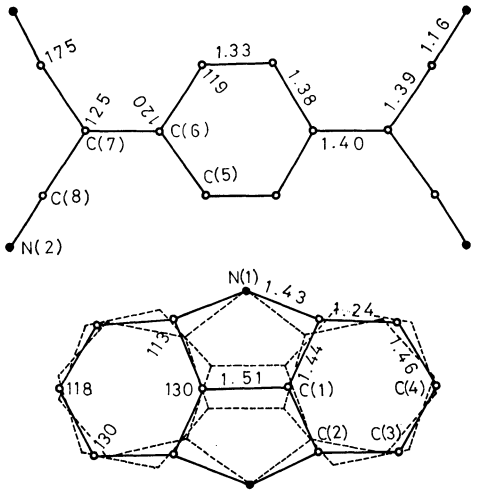
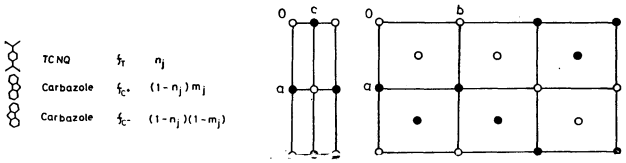


Fig. 3. Bond lengths (Å) and angles (°).
The broken line indicates the two alternative structure of carbazole.

having the same lattice constants as the average structure. Each lattice point can be occupied by TCNQ or carbazole, carbazole having two alternative orientations. Let us introduce $n_j,(1-n_j)m_j$ and $(1-n_j)(1-m_j)$ to represent the probability that j-th lattice point is occupied by T, C^+, and C^- respectively, where T denotes TCNQ and C^+ and C^- are the carbazole with the polar axis parallel to the $\boldsymbol{b}$ direction and $-\boldsymbol{b}$ direction, respectively (Fig. 4a).



4a 4b(i) 4b(ii)

Fig. 4. (a) The occupancy probabilities of the lattice points. (b) Schematic drawing of the arrangement of TCNQ and carbazole. (i) indicates that the molecular arrangement is ordered in the a—c layer and (ii) shows an example of the stacking disorder along the b-direction.
The open circles and filled circles represent carbazole and TCNQ molecules, respectively.

The structure factor of this lattice is given by

$$F(\boldsymbol{k}) = \sum_j (n_j f_T + (1-n_j)m_j f_{C^+} + (1-n_j)(1-m_j)f_{C^-}) \exp(i\boldsymbol{k}\cdot\boldsymbol{R}_j), \quad (1)$$

where f is the molecular structure factor, $\boldsymbol{R}_j$ is the lattice vector of j-th lattice point and $\boldsymbol{k}$ is the scattering vector. The corresponding intensity is given by

$$I(\boldsymbol{k}) = |\langle F(\boldsymbol{k})\rangle|^2$$

Neglecting the correlation between n_j and $m_{j'}$ (the correlation between the position of TCNQ and the orientation of carbazole), we have

$$I(\boldsymbol{k}) = |\sum_j(\langle n\rangle f_T + (1-\langle n\rangle)\langle m\rangle f_{C^+} + (1-\langle n\rangle)(1-\langle m\rangle)f_{C^-}) \times e^{i\boldsymbol{k}\cdot\boldsymbol{R}_j}|^2 + |(f_T - \langle m\rangle f_{C^+} - (1-\langle m\rangle)f_{C^-}|^2 \sum_{jj'}\chi^T(j,j') \times e^{i\boldsymbol{k}\cdot(\boldsymbol{R}_j-\boldsymbol{R}_{j'})} + |f_{C^+}-f_{C^-}|^2 \sum_{jj'}\langle(1-n_j)(1-n_{j'})\rangle \times \chi^C(j,j')e^{i\boldsymbol{k}\cdot(\boldsymbol{R}_j-\boldsymbol{R}_{j'})}, \quad (2)$$

where $\langle\ \rangle$ indicates the statistical average and $\chi^T(j,j')$ and $\chi^C(j,j')$ are correlation functions expressed as

$$\chi^T(j,j') = \langle(n_j-\langle n\rangle)(n_{j'}-\langle n\rangle)\rangle$$

and

$$\chi^C(j,j') = \langle(m_j-\langle m\rangle)(m_{j'}-\langle m\rangle)\rangle \quad (3)$$

The intensity formula is composed of the following terms:

$$I = I_B + I_D^1 + I_D^2$$

where

$$I_B = |\sum_j(\langle n\rangle f_T + (1-\langle n\rangle)\langle m\rangle f_{C^+} + (1-\langle n\rangle)(1-\langle m\rangle)f_{C^-})e^{i\boldsymbol{k}\cdot\boldsymbol{R}_j}|^2$$

$$I_D^1 = |(f_T - \langle m\rangle f_{C^+} - (1-\langle m\rangle)f_{C^-}|^2 \sum_{jj'}\chi^T(j,j')e^{i\boldsymbol{k}\cdot(\boldsymbol{R}_j-\boldsymbol{R}_{j'})}$$

and

$$I_D^2 = |(f_{C^+}-f_{C^-})|^2 \sum_{jj'}\langle(1-n_j)(1-n_{j'})\rangle\chi^C(j,j')e^{i\boldsymbol{k}\cdot(\boldsymbol{R}_j-\boldsymbol{R}_{j'})} \quad (4)$$

(1) I_B can be interpreted as the intensity of X-ray diffraction by the crystal with average structure. When $\langle n\rangle=1/2$, $\langle m\rangle=1/2$ (TCNQ and carbazole occupy each lattice point with equal probability, the orientation of carbazole being disordered), I_B gives the intensities of sharp spots in the integral layer lines (group I in Table 2) and can be written as

$$I_B = |\sum_j(f_T + (f_{C^+}+f_{C^-})/2)/2 \times e^{i\boldsymbol{k}\cdot\boldsymbol{R}_j}|^2$$

This intensity equation is the same as that used for the analysis of average structure.

(2) The second term I_D^1 involves the correlation function of TCNQ. Here, we take the average structure (Fig. 4b) in which the following assumptions were made.

1) The molecular arrangement of TCNQ and carbazole is ordered in each a-c layer.

2) The adjacent layers have no correlation irrespective of the molecular arrangement in the first a-c layer. Every lattice point in the second layer is occupied by TCNQ and carbazole with equal probability.

The correlation function $\chi^T(j,j')$ has non-zero value $(\pm 1/4)$ when the positions of the two lattice points j and j' are in the same a-c layer, and zero when they are not:

$$\chi^T(j,j') = \begin{cases} 1/4 \cdots n_1 + n_3 = 2m, & n_2 = 0 \\ -1/4 \cdots n_1 + n_3 = 2m+1, & n_2 = 0 \\ 0 \cdots n_2 \neq 0 \end{cases}$$

This means that the molecular arrangements in the a-c layer is ordered and no correlation exists between different layers. The adjacent layers are related with each other by the translational vector $(\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c})/2$. Thus we have $\boldsymbol{R}_j-\boldsymbol{R}_{j'}=n_1\boldsymbol{a}+n_2\boldsymbol{b}'+n_3\boldsymbol{c}$, where $\boldsymbol{b}'=(\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c})/2$. Judging from the molecular arrangement in the body centered lattice of the average structure, this type of stacking disorder is very liekly to occur in this crystal. With the use of Eq. (4) and the above values of $\chi^T(j,j')$, I_D^1 is written as follows.

$$I_D^1(\xi\boldsymbol{a}^*, \eta\boldsymbol{b}^*, \zeta\boldsymbol{c}^*) = \begin{cases} N^2|f_T - (f_{C^+}+f_{C^-})/2|^2/4 \\ \quad \cdots \xi = n+1/2,\ \zeta = m+1/2 \\ 0 \quad \cdots \xi \neq n+1/2 \text{ or } \zeta \neq m+1/2 \end{cases} \quad (5)$$

where N is the number of lattice points in the layer.

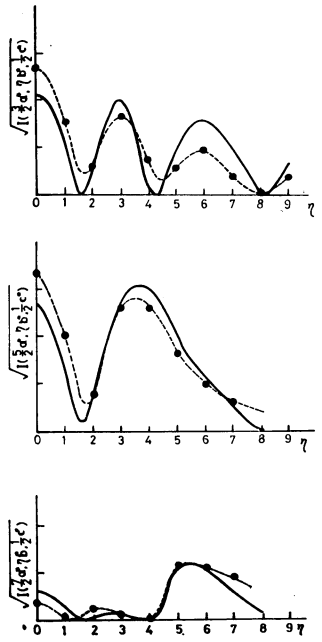


Fig. 5. The observed (solid lines) and calculated (broken lines) intensities of the streaks.

Equation (5) shows that the diffuse streaks appear in the diffraction patterns at the same positions as observed experimentally. The intensity along these streaks varies slowly according to the value of $|f^{T}-(f_{C^+}+f_{C^-})/2|^2$, some of which are shown in Fig. 5. The calculated value of $I_D{}^1$ agrees well with the visually estimated intensity of streaks.

(3) The third term $I_D{}^2$ depends on the correlation function involving the orientation of carbazole. The orientation of carbazole may be random in this disordered structure. Thus the correlation function $\chi^C(j,j')$ can be written as

$$\chi^C(j,j') = \delta_{jj'}/4 \qquad (6)$$

We obtain the equation for $I_D{}^2$ as follows:

$$I_D{}^2 = N|f_{C^+}-f_{C^-}|^2/8 \qquad (7)$$

From Eq. (7), we easily see that $I_D{}^2$ is not important because it indicates the faint scattering widely spread around the origin of the reciprocal lattice.

From the analysis of I_B, $I_D{}^1$, and $I_D{}^2$, we may say that the model of one-dimensionally disordered structure gives a fairly good explanation of the observed X-ray patterns.

Figures 2 and 4b show that the mixed stacks of carbazole and TCNQ exist along axis *c* like many other structures of CT complexes. The intermolecular distance between donor and acceptor molecules is 3.34 Å. The mode of overlapping can be considered to be the ring-external type observed in other CT complexes and radical salts of TCNQ.[1]

Interpretation of Sharp Reflections along the Streaks.
The diffuse streaks appear along the b^* direction, which indicate the stacking disorder along axis *b*.

1) H. Kobayashi, F. Marumo, and Y. Saito, *Acta Crystallogr.*, **B27**, 373 (1971); C. J. Fritchie, *ibid.*, **20**, 892 (1966); A. W. Hanson, *ibid.*, **19**, 610 (1965); R. M. Williams and S. C. Wallwork, *ibid.*, **B24**, 168 (1968).

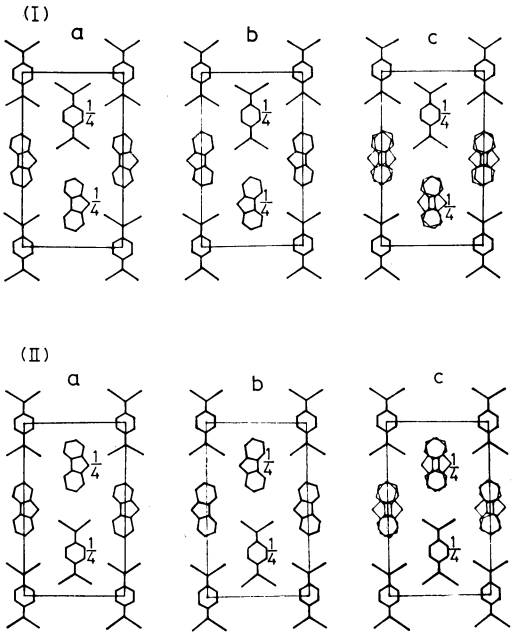


Fig. 6. The candidates of the ordered structures.

Table 5. Reflections diffracted from the ordered structures

The Bragg indices refer to the unit cell listed in Table 1.

l	*k*	*h*	*h*
		I[a)]	II
0	2*n*	2*m*	2*m*
	2*n*+1	2*m*+1	2*m*+1
1/2	2*n*	2*m*+3/2	2*m*+1/2
	2*n*+1	2*m*+1/2	2*m*+3/2
1	2*n*	2*m*+1	2*m*+1
	2*n*+1	2*m*	2*m*
3/2	2*n*	2*m*+1/2	2*m*+3/2
	2*n*+1	2*m*+3/2	2*m*+1/2

a) Reflections correspond to those diffracted from structures Ia, Ib, and Ic.

Moreover, associated sharp spots do not lie exactly on the diffuse streaks but deviate slightly alternately from them. Thus the crystal seems to be not nuiform but composed of ordered and disordered domains.

Possible ordered structures are shown in Fig. 6. Six kinds of structures denoted by Ia, Ib, Ic, IIa, IIb, and IIc exist. The lattice spacings are twice those of average structure along directions *a* and *c*. Owing to the characteristic arrangement of molecules, additional and specific absence appears in X-ray diffraction patterns. They are summarized in Table 5 in terms of the basis vectors *a*, *b*, and *c* of average structure. The reflections from structure groups I and II correspond to those of groups IIIa and IIIb, respectively (Tables 2 and 5 and Fig. 1c). Specific features of these structures are as follows:

(1) Structures Ia and IIa are mirror images of each other, as likewise are Ib and IIb, and Ic and IIc.

(2) Ia, Ib, IIa, and IIb are polar due to the ordered orientation of carbazole molecules, while the lattices Ic and IIc are nonpolar due to disordered orientation.

(3) There are twofold axes along *b*. The lattices therefore might be monoclinic.

If the structures shown in Fig. 6 have rectangular unit cells, the sharp spots would be on the diffuse streaks. In order to explain the observed deviations, the structures should have monoclinic symmetry. It may be quite natural to assume that if the angles β of the unit cells of groups I and II (Fig. 6) are a little less or more than 90° the change in angles β of structures I and II would be equal in magnitude but opposite in sign, since the two structures are related to each other by the mirror planes perpendicular to axis *a*. If the structures of groups I and II are twinned submicroscopically by the mirror planes parallel to the *b*-*c* plane, the sharp spots may satisfy the specific extinction rules (Table 5), deviating alternately from the streaks.

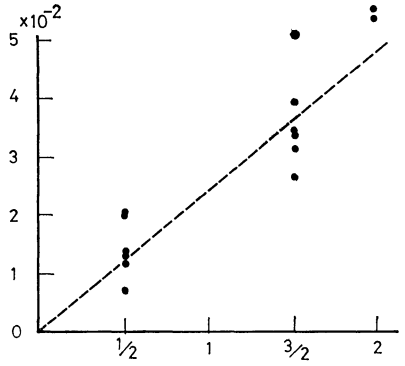


Fig. 7. The magnitude of the deviation of the spots from the streaks.
The numbers on the *abscissa* indicate the layer lines around axis *c* and those on the *ordinate* are $2|\Delta d|/d$, where *d* is the distance between two neighboring spots measured along axis a^*.

As shown in Fig. 7, the spots deviate more largely from the streaks in higher layer lines. Some elongated spots in the Weissenberg film of the upper layer around axis *c* split into two spots. A similar situation was observed for axis *a*. The magnitude of the change of β is about 0.2°. The crystal symmetry is reduced from Immm to C2 (or C2/m). The relationship between these cells is shown in Fig. 8. The lattice constants of

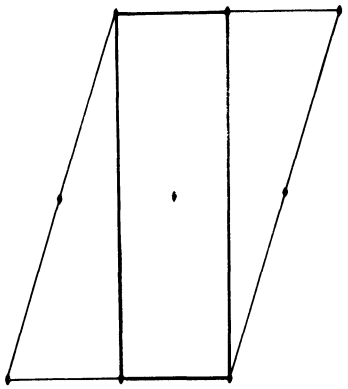


Fig. 8. The relationship between the cells of Immm and C2. The small change of β is neglected in this figure.

monoclinic cell are: $a=11.27$, $b=12.94$, $c=6.78$ Å, $\beta=107.4°$ and $Z=2$.

Using atomic parameters of the average structure and the models of ordered structures shown in Fig. 5, a comparison of the calculated and observed structure factors was made only for strong reflections ($h/2$, k, $1/2$) (Table 2) owing to difficulty in the visual estimation of the intensity of the spots in the streaks. *R*-value is about 0.19 (Table 6). The difference between models (Ia and IIc) is comparatively small. Thus no refinement was performed.

Description of the Domain Structure. The crystal of carbazole–TCNQ is hardly soluble in acetone, acetonitrile or tetrahydrofuran. The black needles precipitate when the acetone solutions of the components are mixed. From the fact that most non-ionic CT complexes of TCNQ are very soluble and the CT spectrum appears in the visible region, precipitation of black crystals seems to indicate that carbazole–TCNQ is a complex of ionic type, where the CT interaction between donor and acceptor is very strong. However, this is not cosistent with the fact that the CT interaction is very weak, since the visible spectrum of the acetone solution of carbazole–TCNQ closely resembles that of TCNQ (only one strong absorption maximum appears at 4000 Å) with no CT absorption. This fact indicates that the crystal structure of carbazole–TCNQ has somewhat unusual features.

The ordered domain composed of structures Ia, IIa,

TABLE 6. COMPARISON OF THE OBSERVED AND CALCULATED STRUCTURE FACTORS
Reflections belong to groups IIIa and IIIb (Table 2).

h ×2	k	l ×2	F_o	F_c	h ×2	k	l ×2	F_o	F_c	h ×2	k	l ×2	F_o	F_c
1	10	1	5.76	3.49	1	11	1	5.46	4.69	1	12	1	5.62	3.94
3	0	1	17.58	27.33	3	1	1	9.59	15.46	3	2	1	7.06	6.82
3	3	1	14.34	16.36	3	5	1	8.01	5.53	3	6	1	11.29	9.63
3	7	1	6.63	4.31	5	0	1	29.33	34.84	5	1	1	15.31	20.84
5	2	1	11.29	7.76	5	3	1	25.87	26.96	5	4	1	31.17	26.75
5	5	1	16.06	16.76	5	6	1	10.62	8.74	5	7	1	6.95	5.98
5	8	1	5.71	4.90	7	0	1	8.90	3.29	7	5	1	12.22	11.86
7	6	1	10.11	11.41	7	7	1	7.70	5.98	9	0	1	8.10	9.53
9	3	1	6.78	5.50	9	4	1	10.11	8.48	9	5	1	7.06	8.04
13	0	1	7.33	7.07	13	3	1	5.78	5.52	15	4	1	7.77	9.47
15	5	1	12.57	11.59	15	6	1	9.11	9.93	15	7	1	6.38	5.66
17	4	1	5.18	6.05										

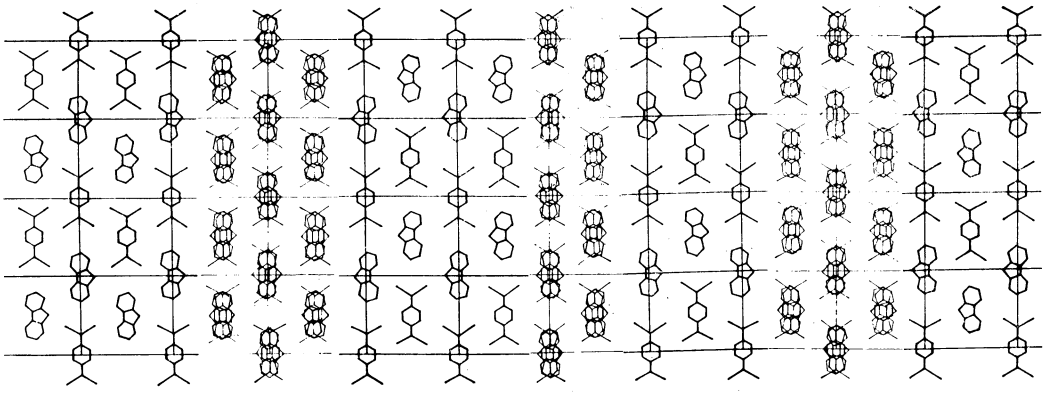


Fig. 9. Schematic drawing of the domain structure.

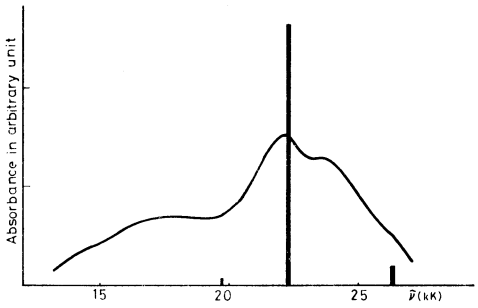
Ib and IIb has dipole moment along the $\boldsymbol{b}$ and $-\boldsymbol{b}$ directions, respectively. On the other hand, the one-dimensionally disordered structure is non-polar. Thus, an adequate combination of these structures might interpret the appearance of the domain structure. Such a model seems to be stable because it resembles the well-known domain structures of ferromagnetic or ferroelectric substances. The most plausible structure may be that shown in Fig. 9. This structure indicates the strong interaction between domains with positive polarity and those with negative polarity, the domains with opposite polarities tending to gather together.

The crystal should contain an equal amount of positive and negative domains. However, it is difficult to estimate the ratios Ia/Ib and IIa/IIb. The thickness of random domain seems to be larger than that found in ferroelectrics or ferromagnetics, the intensity of the streaks being fairly strong. The space group of the ordered domain is C2.

The domain structure consisting of non-polar structures Ic and IIc can also explain the features of X-ray diffraction patterns. In this case, the ordered domain closely resembles the crystal structure of *N*-methylphenothiazine–TCNQ.[2] The orientation of an *N*-methylphenothiazine molecule is disordered like the carbazole molecule. Both structures contain mixed stacking columns of donors and acceptors. In spite of the assumed similarity of molecular arrangements, the properties of both complexes differ, *viz.*, *N*-methylphenothiazine–TCNQ is very soluble and the solution is strongly colored. This indicates that the non-polar domain dose not seem to be possible. The structure of polar domain structure seems to be confirmed by the appearance of various types of domain structures.

Absorption Spectra of the Crystal of Carbazole–TCNQ. The visible absorption spectrum of the solution of carbazole–TCNQ is similar to that of TCNQ. It is of interest that the CT band appears in the spectrum of a powdered sample (Fig. 10). The SCF-MO's of carbazole–TCNQ complex was calculated by assuming a complex as a single π-conjugated system using the semiempirical parameters.

The two center resonance integral is estimated by using the equation



Assignment		Character of transitions				
	$\bar{\nu}$(kK)	$(DD)_m$	$(AA)_m$	$(DA)_m$	$(AD)_m$	f
(1)	19.70 CT(D→A)	0.026	0.016	0.950	0.000	0.005
(2)	22.55 LE(A^*)	0.014	0.905	0.051	0.030	1.985
(3)	26.05 CT(D→A)	0.024	0.066	0.906	0.002	0.136
(4)	29.60 CT(D→A)+LE(A^*)	0.018	0.293	0.674	0.007	0.070
(5)	31.95 LE(A^*)	0.013	0.877	0.073	0.023	0.018

Fig. 10. Absorption spectra of the powdered samples of carbazole–TCNQ and calculated results of SCF-MO-CI.

$$\beta_{\mu\nu} = -\kappa S_{\mu\nu}(I_\mu + I_\nu)/2$$

where $S_{\mu\nu}$ is overlap integral calculated by use of the Slater atomic orbitals, I_μ (I_ν) is ionization potential of the μ-th (ν-th) atom and κ is assumed to be 0.85 when μ and ν belong to the same molecule and 2.0 when they belong to different molecules. The two-center repulsion integral $\gamma_{\mu\nu}$ is evaluated according to the Nishimoto-Mataga method. Semiempirical constants I_μ and $\gamma_{\mu\nu}$ are the same as those given in Ref. 3 ($I_p(C^+)=11.16$, $I_p(N^+)=14.12$, $I_p(N^{++})=26.70$, $\gamma_{C^+C^+}=11.13$, $\gamma_{N^+N^+}=12.34$, $\gamma_{N^{++}N^{++}}=17.44$ eV). The relative arrangement of the constituent molecules is taken as shown in Fig. 2. After five cycles of SCF-MO calculation, the CI calculation was carried out with the lowest 25 singly-excited configulations. Characterization of transition was made according to the method described in Ref. 3.

The results are summarized in Fig. 10. Agreement between the calculated transitions and observed spectra is not satisfactory. The broad peak at about 18 kK, which cannot be observed in the spectra of component molecules, may be regarded as the CT absorption.

2) H. Kobayashi, This Bulletin, to be published.

3) T. Ohta, H. Kuroda, and T. L. Kunii, *Theor. Chim. Acta*, **19**, 167 (1970).

The strong peak at 22.5 kK can be assigned to the local excitation of TCNQ. The amount of charge transferred from carbazole to TCNQ is calculated to be 0.05 e. The small value seems to correspond to the weak interaction.

Various Types of Domain Structure. Since the crystal is made up from a combination of ordered

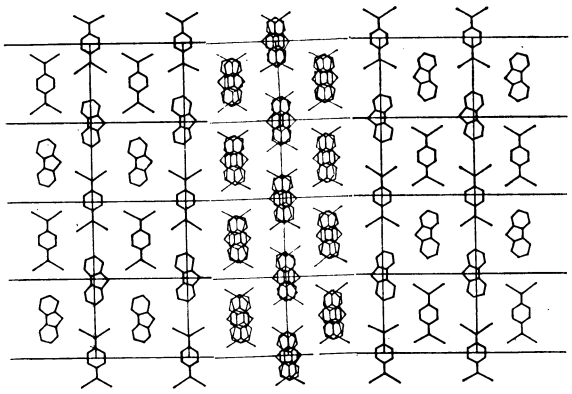


Fig. 11 (a)

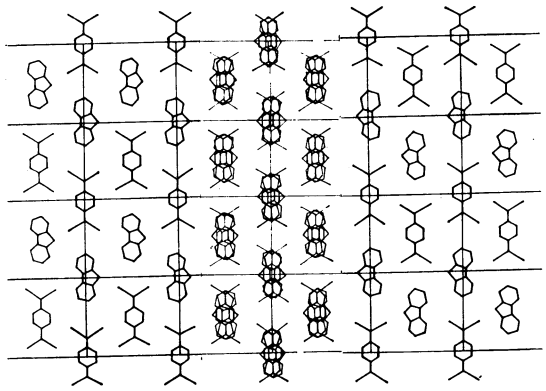


Fig. 11 (b)

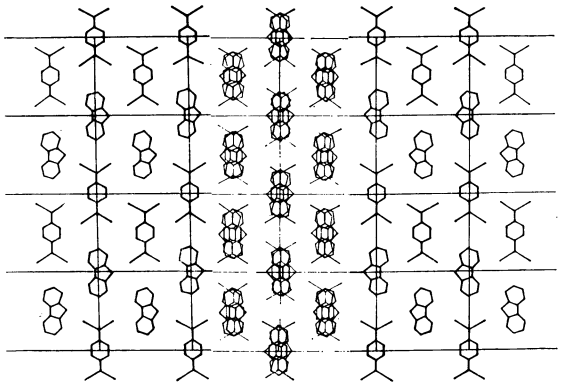


Fig. 11 (c)

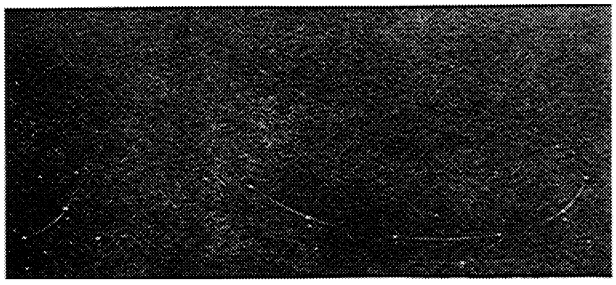


Fig. 11 (c')

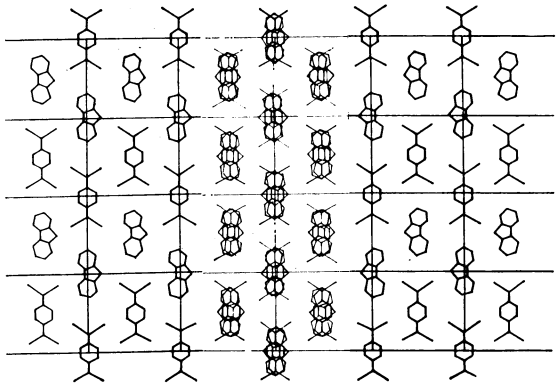


Fig. 11 (d)

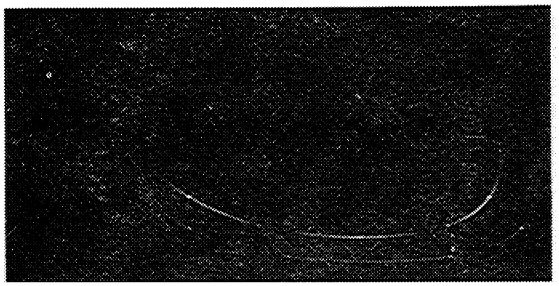


Fig. 11 (d')

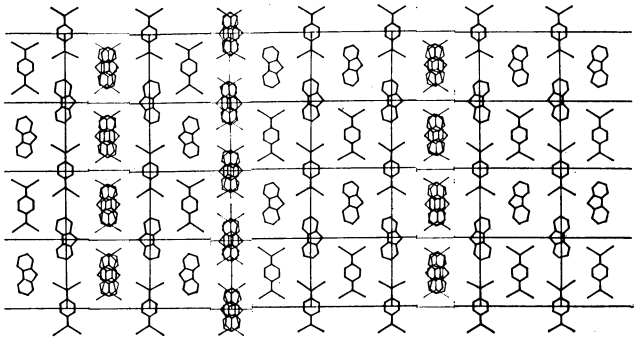


Fig. 11 (e)

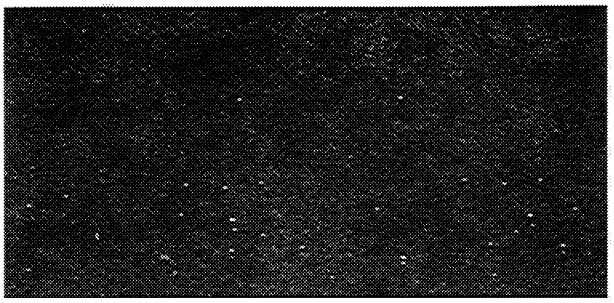


Fig. 11 (e')

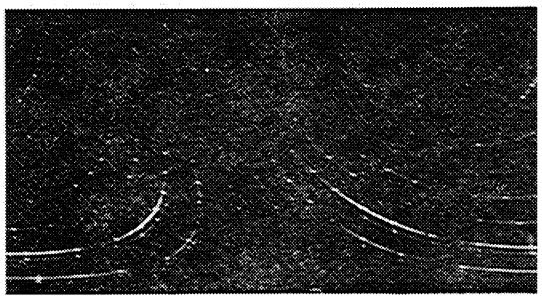


Fig. 11 (f)

(g)

Fig. 11. Various types of diffraction patterns and the corresponding domain structures.

and disordered structures, various types of crystals may appear according to the mode of combination. We examined the X-ray diffraction patterns of crystals grown from solvents such as acetone, acetonitrile and tetrahydrofuran, and found many types of patterns, but no solvent effect.

As judged from the X-ray diffraction patterns, the domain structure seems to be formed according to the following conditions:

From the necessity to cancel the polarity of the crystal, there should be equal amounts of positive and negative structures. The thickness of the domain wall will differ to some extent with the sample, since the non-polar structure seems to be less important in view of the stability of the crystalline state.

Type I: The structure composed of Ia, Ib, IIa, IIb and random structure (Fig. 9) gives the X-ray diffraction patterns shown in Fig. 1. The same patterns can also be observed from structures Ia, IIb and random structure (Fig. 11a) or of Ib, IIa and random structure (Fig. 11b). Thus we can not decide from the diffraction patterns which structure is realized in the crystal. All of the three structures might coexist.

Type II: The structure composed of Ia, Ib and random structure (Fig. 11c) gives the X-ray pattern shown in Fig. 11c′, that consisting of IIa, IIb and random structure (Fig. 11d) gives the X-ray pattern shown in Fig. 11d′. The order component of both structures bear twin relationship with each other and patterns are closely related. It may be interesting that the synthesis of Figs. 11c′ and 11d′ gives the same pattern as that of Fig. 1a. Concerning the ordered domain, both structures are made up of the half components of the structure shown in Fig. 9. This is the reason why the number of spots in Figs. 11c′ and 11d′ is a half of those in Fig. 1a.

Type III: Some crystals give diffraction patterns with very faint streaks as shown in Fig. 11e′. The corresponding crystal will be constructed from the regions of Ia and Ib, small amount of IIa and IIb and a very little of random domain (Fig. 11e).

Type IV: There seems to be a domain wall of one-dimensionally disordered structure, in which some inter-layer correlation exists, since in some films the apparent diffuse maxima are observed between sharp spots as shown in Fig. 11f. This type of diffuse maxima has been extensively discussed.[4]

Type V: It may be easily recognized that the sharp spots appear at the positions of the diffuse maxima described in type IV, if the inter-layer correlation becomes complete. Figure 11g shows that the above situation is realized in some crystals. In this case there exist some domain walls whose lattice constant b is twice as large as that of the average structure.

Similar types of X-ray diffraction patterns were reported for the crystals of *o*-chlorobenzamide.[5]

An attempt was made to prepare crystals with a completely polarized structure, which might have similar physical properties to the so-called electret. Silver-paste was coated on both sides of the wall of a 10 mm diam. glass tube, a voltage of 500 V being applied between them. Crystals were prepared by the diffusion method in this tube, but the experiment was not successful, the crystals precipitated appearing to be similar to those obtained before. The results seems to indicate that the stability due to interaction between the polar domains overcomes the stability due to the effect of an external electric field.

The author would like to express his sincere thanks to Prof. Yoshihiko Saito for his keen interest and encouragement. He is also grateful to Prof. Takaaki Danno for his encouragement and to Dr. Ichimin Shirotani for the experiment of visible absorption spectra.

4) A. J. C. Willson, *Acta Crystallogr.*, **2**, 245 (1949); H. Jagodginski, *ibid.*, **2**, 201 (1949); *ibid.*, **2**, 208 (1949).

5) K. Sakurai, Y. Takaki, and Y. Kato, 9th International Congress of Crystallography, Kyoto (1972), Collected Abstracts, p. 211.