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Sinusoidal Structure of the 1:1 Complex of Phenothiazine and 7,7,8,8-Tetracyanoquinodimethane, PTZ–TCNQ

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The X-ray diffraction patterns of the crystals of the 1:1 complex of phenothiazine (PTZ) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) show satellite reflexions, which can be explained on the basis of a sinusoidally modulated structure. The cell constants of the fundamental lattice are $a=7{\cdot}04$ (2), $b=25{\cdot}38$ (2), $c=10{\cdot}51$ (8) Å, $\beta=92{\cdot}1$ (7)° and the space group is $C2/c$. The fundamental structure was determined from three-dimensional X-ray data recorded on equi-inclination Weissenberg photographs and refined by the block-diagonal least-squares method ($R=0{\cdot}120$). PTZ and TCNQ are stacked alternately in infinite columns along the *a* axis. The sequence of columns along **b** is sinusoidally modulated. This was deduced from satellite reflexions. The components of the transverse sinusoidal modulation wave are 0·85 and 0·75 Å along the $-\mathbf{a}$ and **c** directions, respectively. The period is $(4{\cdot}35\pm0{\cdot}37)b$. The most plausible structure is constructed from the paired columns, which are held together by hydrogen bonds of the N–H···N type.

Introduction

Crystal structures of some charge-transfer complexes containing TCNQ molecules as acceptors have been determined (Hanson, 1965; Williams & Wallwork, 1968; Colton & Henn, 1970; Goldberg & Shmueli, 1973). Most of the complexes have mixed stacking columns of alternating donor and acceptor (TCNQ) molecules. Crystals of carbazole–TCNQ are particularly interesting because they have domain structures consisting of mixed-stacks of TCNQ and carbazole (Kobayashi, 1973*a*). Another modified columnar structure will be reported in this paper. Crystals of the 1:1 complex of TCNQ and phenothiazine (PTZ) were subjected to X-ray crystal analysis in order to elucidate the sinusoidal structure of this complex.

Experimental

The complex of PTZ–TCNQ crystallizes in the form of needles elongated along the *a* axis. As reported briefly (Kobayashi & Saito, 1971), the crystal data of the fundamental structure are: $(C_{12}H_9NS)(C_{12}H_4N_4)$, F.W. 403·5; monoclinic, $a=7{\cdot}04$ (2), $b=25{\cdot}38$ (2), $c=10{\cdot}51$ (8) Å, $\beta=92{\cdot}1$ (7)°; space group, $C2/c$ or Cc from systematic absences; $U=1877{\cdot}7$ Å^3; $Z=4$, $D_x=1{\cdot}428$ g cm^{-3}.

Intensity data were recorded on equi-inclination Weissenberg photographs with Cu $K\alpha$ radiation. The multiple-film technique was employed. The relative intensities were estimated visually with a set of standard scales. The usual Lorentz–polarization and shape corrections were applied. No correction was made, however, for absorption in view of the small size of the crystal, which had a maximum dimension of about 0·25 mm. Some of the oscillation and Weissenberg photographs are shown in Fig. 1; satellite reflexions appear along the b^* axis. These diffraction patterns indicate that PTZ–TCNQ has a sinusoidally modulated lattice.

For the convenience of discussions, it may be worth while to quote the intensity formula of X-ray diffraction by the crystal with transverse phase modulation (Korekawa, 1964). Further details are shown in the Appendix. Consider the simple sinusoidal structure where the position of the *j*th atom of *n*th cell $[n=(n_1, n_2, n_3)]$ is given by†

$$\mathbf{r}_{nj}=n_1\mathbf{a}+n_2\mathbf{b}+n_3\mathbf{c}+\mathbf{d}_j+(p\mathbf{a}/a+q\mathbf{c}/c)\times\sin 2\pi\sigma n_2 \qquad (1)$$

where $\mathbf{d}_j$ is the positional vector of the *j*th atom in the fundamental lattice, *p* and *q* are components of the amplitude of the transverse modulation wave and b/σ is the period of modulation. The direction of propagation of the modulation wave is parallel to the *b* axis. Then the intensity formula can be written as:

$$\begin{aligned}I(\xi\eta\zeta)&=|F(\xi\eta\zeta)|^2\\&=N_1^2N_2^2N_3^2|F^0(\xi\eta\zeta)|^2\sum_n J_n^2[2\pi(p\xi/a+q\zeta/c)]\\&\quad\times\delta(\xi-h)\delta(\eta-k-n\sigma)\delta(\zeta-l)\\&=\begin{cases}N_1^2N_2^2N_3^2|F^0(hkl)|^2J_o^2[2\pi(ph/a+ql/c)]\ldots(hkl) & (2)\\ N_1^2N_2^2N_3^2|F^0(h,k\pm n\sigma,l)|^2J_n^2[2\pi(ph/a+ql/c)]\ldots(hk\pm n\sigma l) & (3)\end{cases}\end{aligned}$$

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† The phase factor of the wave is not important for the intensity formula in most cases (Korekawa, 1964).

where J_n is the nth order Bessel function and h, k and l are integers. The diffraction maxima corresponding to equations (2) and (3) represent main and satellite reflexions respectively. Schematic drawings of the sinusoidally modulated lattice and its diffraction patterns are shown in Fig. 2. Characteristic features of the oscillation and Weissenberg photographs (Fig. 1) are as follows:

(1) Satellite reflexions appear along the b^* axis at a constant interval.

(2) As shown in Fig. 1(*c*) and (*e*), almost all Bragg reflexions are accompanied by some satellite reflexions except the Bragg reflexions that lie on the b^* axis ($0k0$).

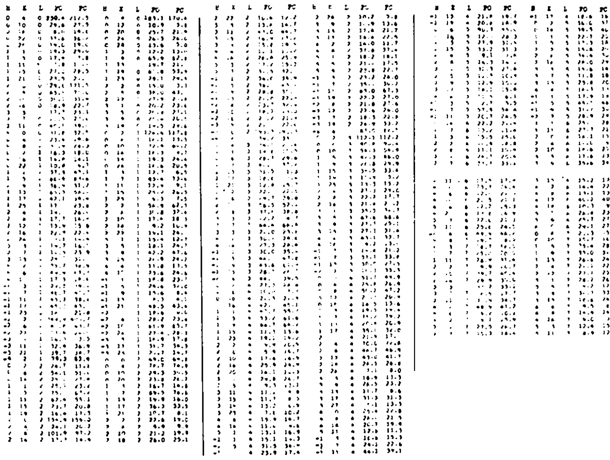
(3) The number of the observed satellites becomes larger with increase in Bragg indices h or l.

(4) Relative intensities of satellites increase as the intensity of the main reflexion decreases.

(5) In higher layer lines [Figs. 1(*d*) and (*f*)], the reflexions lying on the [$2k0$] (or [$0k2$]) axis have some satellites and those without satellites appear elsewhere in reciprocal space.

The above features of the diffraction patterns obtained agree excellently with the X-ray diffraction patterns by the model of the sinusoidal structure shown in Fig. 2.

Table 1. *Observed and calculated structure factors of the fundamental structure*



Determination of the fundamental structure

Considering the properties of Bessel functions [$\sum_{n=-\infty}^{\infty} J_n^2(x)=1$], the structure amplitudes of the fundamental structure are given by

$$|F(hkl)|^2 \doteqdot \sum_n |F(hk\pm n\sigma l)|^2 ,$$

where $F(hk\pm n\sigma l)$ is given in equations (2) and (3) (see also Appendix). $F(hkl)$ is approximately equal to $F^0(hkl)$ $\{=\sum_j f_j \exp[2\pi i(hx_j+ky_j+lz_j)]\}$. The intensity distribution of X-ray diffraction patterns of the fundamental structure of PTZ–TCNQ resembles that of *N*-methylphenothiazine–TCNQ (Kobayashi, 1973*b*). So the trial structure was easily deduced. The space group $C2/c$ was assumed and this seemed to be verified by the reasonable convergence of the structure at a

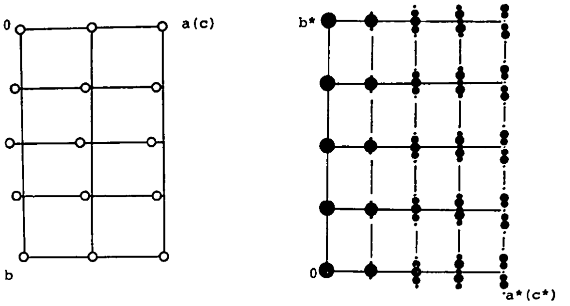


Fig. 2. Schematic drawing of a sinusoidally modulated lattice and its diffraction patterns.

Table 2. *Atomic parameters of the fundamental structure*

Positional and thermal parameters of the non-hydrogen atoms, with their estimated standard deviations in parentheses. The B_{ij}'s are defined by $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2hlB_{13}+2klB_{23})]$.

	x ($\times 10^3$)	y ($\times 10^4$)	z ($\times 10^3$)	B_{11} ($\times 10^3$)	B_{22} ($\times 10^4$)	B_{33} ($\times 10^3$)	B_{12} ($\times 10^3$)	B_{13} ($\times 10^3$)	B_{23} ($\times 10^3$)
S	0	538 (3)	250	52 (5)	11 (1)	24 (2)	0	−22 (2)	0
N(1)	0	1736 (8)	250	24 (11)	14 (5)	8 (4)	0	13 (5)	0
C(1)	55 (4)	956 (9)	375 (2)	28 (10)	35 (6)	3 (3)	4 (2)	3 (4)	−1 (1)
C(2)	110 (4)	742 (9)	488 (2)	3 (7)	32 (6)	2 (3)	2 (2)	12 (4)	−1 (1)
C(3)	171 (4)	1014 (11)	588 (2)	16 (8)	50 (8)	4 (3)	0 (2)	10 (5)	−2 (1)
C(4)	135 (4)	1568 (12)	582 (2)	29 (10)	72 (10)	3 (3)	5 (2)	−6 (5)	0 (1)
C(5)	98 (5)	1801 (9)	468 (2)	84 (15)	22 (6)	13 (4)	−4 (2)	−15 (6)	3 (1)
C(6)	53 (3)	1527 (8)	365 (2)	21 (9)	20 (4)	7 (3)	−2 (2)	−2 (4)	−1 (1)
N(2)	664 (3)	428 (7)	624 (2)	54 (9)	15 (4)	27 (4)	−2 (2)	−16 (5)	−1 (1)
N(3)	655 (3)	2110 (7)	633 (2)	72 (10)	22 (4)	17 (3)	0 (2)	−17 (5)	0 (1)
C(7)	517 (4)	806 (7)	309 (2)	39 (9)	14 (4)	7 (4)	−2 (2)	−2 (6)	−1 (1)
C(8)	555 (4)	1299 (7)	377 (2)	12 (6)	17 (4)	3 (2)	2 (2)	1 (3)	1 (1)
C(9)	532 (2)	1786 (6)	308 (2)	4 (8)	10 (3)	13 (4)	0 (1)	−3 (4)	0 (1)
C(10)	605 (3)	1281 (6)	500 (2)	17 (7)	6 (3)	10 (3)	1 (1)	4 (4)	−1 (1)
C(11)	649 (3)	803 (9)	561 (2)	21 (9)	25 (5)	9 (4)	−1 (2)	14 (5)	0 (1)
C(12)	634 (4)	1754 (9)	574 (3)	56 (13)	23 (5)	19 (5)	−2 (2)	−22 (7)	0 (1)

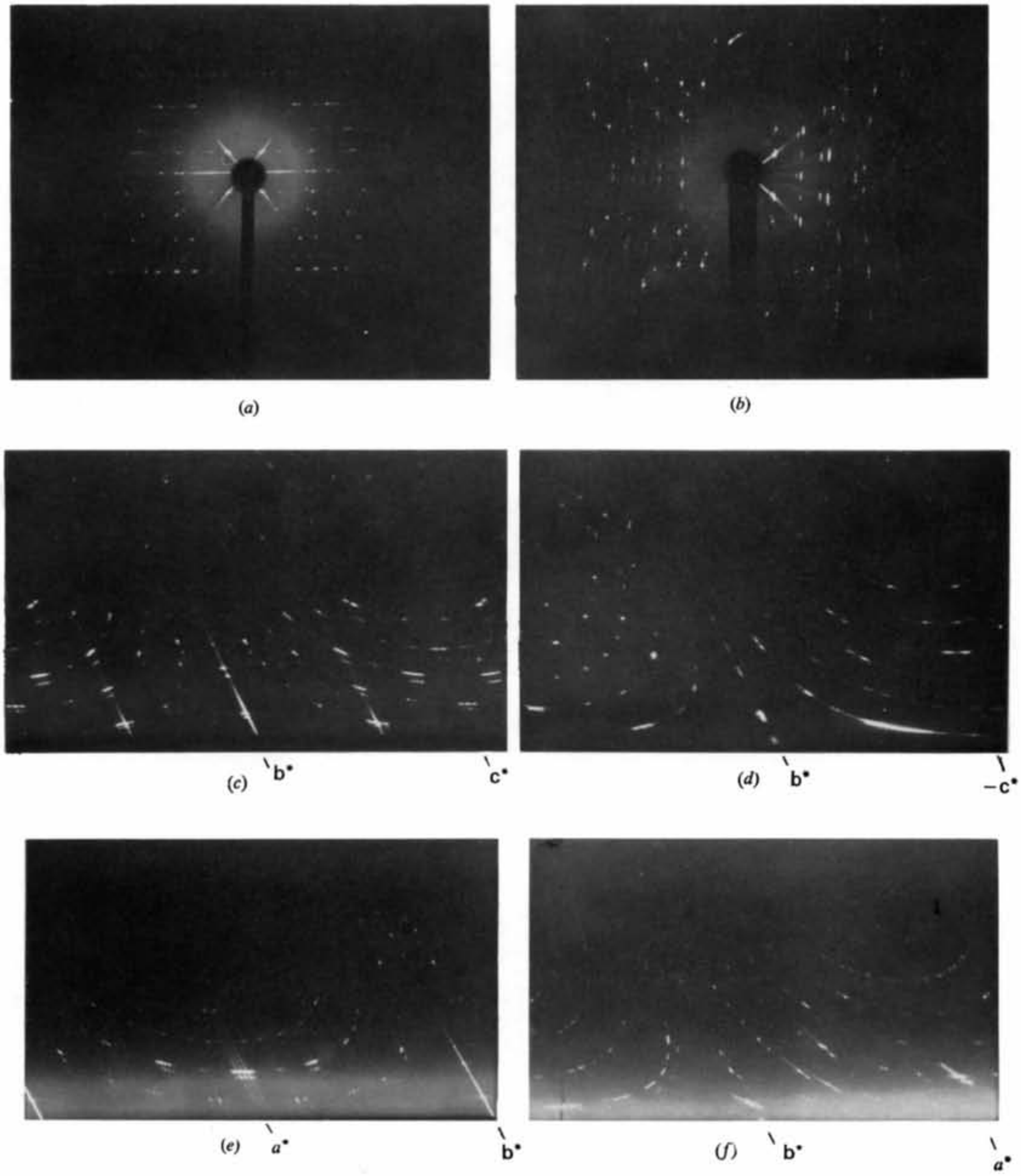


Fig. 1. Oscillation and Weissenberg photographs. (*a*) [100], (*b*) [010], (*c*) $(0\eta\zeta)$, (*d*) $(2\eta\zeta)$, (*e*) $(\xi\eta0)$, (*f*) $(\xi\eta2)$.

Table 2 (*cont.*)

Atomic parameters of the hydrogen atoms

	x ($\times 10^2$)	y ($\times 10^3$)	z ($\times 10^3$)	B (Å^2)
H(1)	0	212	250	4·0
H(2)	10	33	487	3·5
H(3)	10	217	467	5·0
H(4)	20	72	666	5·0
H(5)	15	180	660	5·0
H(6)	55	50	387	3·0
H(7)	55	210	367	3·0

later stage of the refinement. The atomic parameters were refined anisotropically. Isotropic thermal parameters were used for the hydrogen atoms, which were located from the difference Fourier syntheses and were included in the later calculations. The refinement was performed by the block-diagonal least-squares method. The R value converged at 0·120. The weight of the reflexion is 1·0 for all the observed reflexions. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Observed and calculated structure factors were compared in Table 1. The final atomic parameters are listed in Table 2.

Description of the fundamental structure

The structure viewed along the a axis is shown in Fig. 3. PTZ and TCNQ are stacked alternately in infinite columns along the a axis. The intermolecular distance is 3·44 Å. The mode of overlapping is the ring-external bond type observed in other charge-transfer complexes containing TCNQ molecules and is shown in Fig. 4. It closely resembles the mode of overlapping found in *N*-methylphenothiazine-TCNQ (Kobayashi, 1973*b*). The short intermolecular contacts are listed in Table 3. TCNQ and PTZ are both planar and their molecular symmetries are C_2. The least-squares planes are

$$\text{PZT}: -0{\cdot}9640X+0{\cdot}0236Y+0{\cdot}2649Z+0{\cdot}8540=0{\cdot}0$$

$$\text{TCNQ}: -0{\cdot}9696X+0{\cdot}0160Y+0{\cdot}2444Z+4{\cdot}2018=0{\cdot}0\,,$$

where X, Y and Z are coordinates (in Å) referred to the crystal axes a, b and c^* respectively.

Table 3. *Interatomic distances for non-hydrogen atoms*

(i) $1+x,\ y,\ z$
(ii) $1-x,\ y,\ \frac{3}{2}-z$
(iii) $\frac{1}{2}-x,\ \frac{1}{2}-y,\ 1-z$
(iv) $1-x,\ -y,\ -z$

C(1)· · ·C(7)	3·37 (4) Å
C(3)· · ·C(10)	3·30 (3)
S· · · · · ·C(7)	3·73 (3)
C(11)· ·C(2^{i})	3·36 (4)
C(9) N(1^{i})	3·38 (2)
C(7)· · ·S^{i}	3·55 (3)
N(3)· · ·N(3^{ii})	3·35 (3)
N(3)· · ·N(1^{iii})	3·37 (3)
S· · · · · ·N(2^{iv})	3·63 (2)

The neutral molecules of PTZ (Bell, Blount, Briscoe & Freeman, 1968) and *N*-methylphenothiazine (Wakayama, 1971) are not planar but have a folded configuration, so the approximation used in the structure analysis is probably responsible for the planar structure of PTZ. Bond lengths and angles are shown in Fig. 5. The bonds of PTZ parallel to the twofold axis are normal but others are about 0·04 Å shorter than the usual values. A similar situation was found in the crystals of *N*-methylphenothiazine-TCNQ, where *N*-methylphenothiazine is planar owing to the disorder of the molecule. C-N(PTZ) is 1·36 Å and C-S is 1·73 Å. The values for a neutral PTZ are 1·41 and 1·77 Å, respectively (Bell, Blount, Briscoe & Freeman, 1968). The shortening of the bonds vertical to twofold axis is also observed in TCNQ. Nevertheless, the bond lengths seem to show a strong quinonoid character for TCNQ.

Determination of the parameters of the modulation wave

Equations (2) and (3) indicate that the main and satellite reflexions appear at intervals of σ along $\mathbf{b}^*$. The distances between these spots were measured on about 20 reflexions. The result gives σ of $0{\cdot}232 \pm 0{\cdot}020$. The period of the modulation wave, b/σ, is $109{\cdot}4 \pm 9{\cdot}4$ Å.

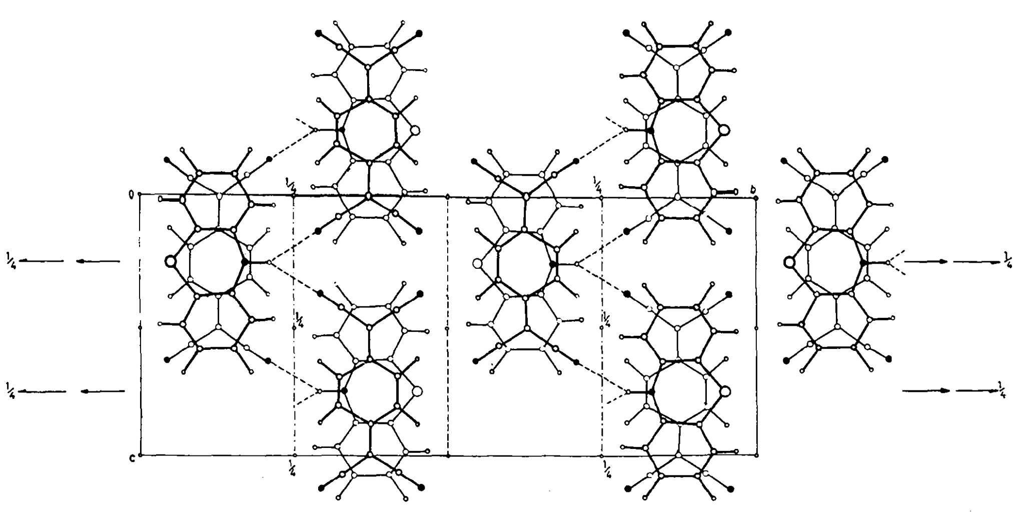


Fig. 3. The fundamental structure viewed along the a axis.

The amplitude of the transverse modulation wave was also determined from equations (2) and (3). Since $J_0(x)$ is zero when $x=2{\cdot}405$, the intensity of the main reflexion becomes zero when

$$2\pi(ph/a+ql/c)=2{\cdot}405\ , \tag{4}$$

where p and q are two independent components of amplitude of the transverse wave. $J_n(x)$ $(n=1,2,3,\ldots)$ is zero when $x=0{\cdot}0$. Then no satellite reflexion appears if

$$ph/a+ql/c=0{\cdot}0\ . \tag{5}$$

The components of the reciprocal vectors (ξa^*, ηb^*, ζc^*) which satisfy equations (4) or (5) are easily determined by looking for the positions where all satellites or main spots disappear on Weissenberg photographs. Then the following equations (4′) and (5′) hold.

$$2\pi(p\xi_i/a+q\zeta_i/c)=2{\cdot}405 \tag{4′}$$

$$p\xi_j/a+q\zeta_j/c=0{\cdot}0 \tag{5′}$$

These equations are easily solved using the observed values of $(\xi_i\eta_i\zeta_i)$. The mean values of p and q thus obtained are:

$$p=-0{\cdot}85\pm0{\cdot}10\ ,\quad q=0{\cdot}75\pm0{\cdot}10\ \text{Å}\ .$$

The amplitudes of the modulation wave are 0·85 and 0·75 Å in the $-\mathbf{a}$ and $\mathbf{c}$ directions respectively.

By inserting the observed values of p and q into equations (2) and (3), the relative intensities of the main and satellite reflexions were calculated. In the calculation the following equation is assumed:

$$\sum_k |F^0(hkl)|^2 \doteqdot \tfrac{1}{2}[\sum_k (|F^0(hk+n\sigma l)|^2 + |F^0(hk-n\sigma l)|^2)],\ (n=1,2,3,\ldots). \tag{6}$$

From equations (2), (3) and (6) and the properties of Bessel functions $[\sum_{n=-\infty}^{\infty} J_n^2(x)=1]$, we have

$$J_0^2[2\pi(ph/a+ql/c)] = \sum_k |F(hkl0)|^2/\sum_{n=-\infty}^{\infty}\sum_k |F(hkln)|^2 \tag{7}$$

$$J_n^2[2\pi(ph/a+ql/c)] = \sum_k [|F(hkln)|^2+|F(hkl-n)|^2]/2\sum_{n=+\infty}^{\infty}\sum_k |F(hkln)|^2 \tag{7′}$$

where $F(hkln)\equiv F(h,k+n\sigma,l)$. k runs through all the observed reflexions with the same indices of h and l. $\sum_{n=-\infty}^{\infty}|F(hkln)|^2$ stands for the sum of the intensities of the main reflexion and satellite reflexions associated with it. The satellites could be observed up to the 4th order ($|n|\le4$). In addition, the values of J_0^2 and J_n^2 were obtained from the tables of Bessel functions and compared with those calculated from observed intensities using equations (7) and (7′). The result is given in Fig. 6. The agreement is excellent.

The analysis of the sinusoidal structure

The fundamental structure is modulated by the transverse wave. Its period is b/σ. In order to analyse by use of the program of normal structure analysis, an approximate value of σ was introduced, which satisfies the following equation,

$$N/M=1/\sigma\ ,$$

where N and M are integers and have no common divisor. Then the period along the b axis is Nb, that is, the lattice constant b of the sinusoidal structure is N times of that of the fundamental structure. The value of $1/\sigma=\frac{13}{3}$ $(\sigma=0{\cdot}2308)$ is a good approximation to σ_{obs} $(=0{\cdot}232\pm0{\cdot}020)$. In this case, the lattice spacing is about 329·9 Å (13b). $1/\sigma=4$ $(\sigma=0{\cdot}250)$ is a relatively poor approximation which gives a shorter spacing of 101·5 Å (4b). Schematic pictures of these structures are

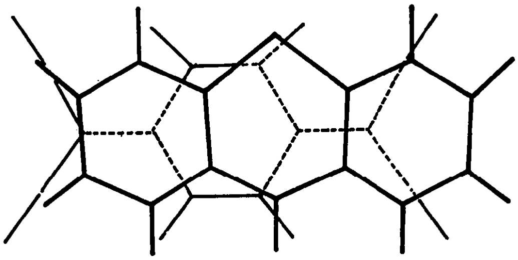


Fig. 4. Molecular overlap.

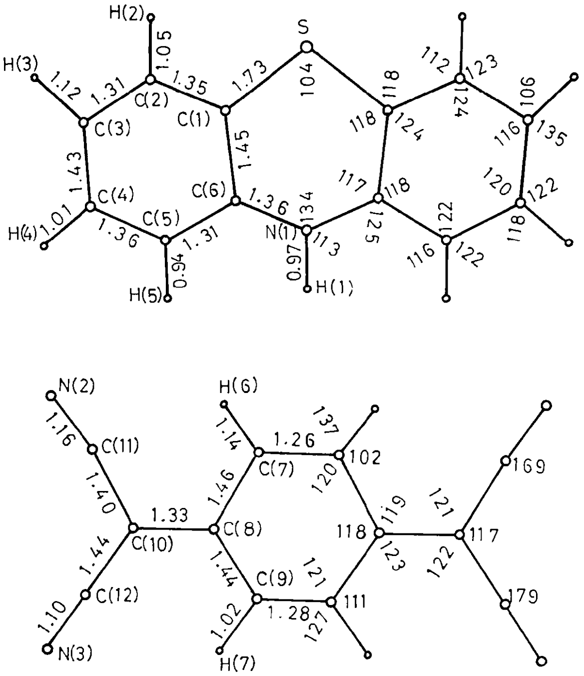


Fig. 5. Bond lengths (Å) and angles (°). Estimated standard deviations of bond lengths and angles are about 0·03 Å and 2·0°, respectively.

illustrated in Fig. 7. The space group the of the 'thirteenfold structure' (13*b*) is $P2_1/n$ and that of the 'fourfold structure' (4*b*) is $P2_1/c$.

Using these models, the observed and calculated structure factors were compared. The observed structures were obtained by visual estimation of the intensities of the individual main and satellite reflexions.

Owing to the limitation on the number of the observed reflexions, it is very difficult to make an analysis without any assumption, even if an approximate value of σ is used. The object of this section is mainly to obtain the simplest structural model which has the essential features of the true structure.

(i) *A model of the 'thirteenfold simple sinusoidal structure'*

The atomic positions are assumed to be

$$\mathbf{r}_j=\mathbf{d}_j+(-0{\cdot}85\mathbf{a}/a+0{\cdot}75\mathbf{c}/c)\sin 2\pi(0{\cdot}2308P)$$

where $\mathbf{d}_j\,[=(x_jy_jz_j)]$ is the positional vector of jth atom in the fundamental structure and P is the y coordinate of the centre of gravity of the column to which the jth atom belongs. The phase factor was neglected. Strictly speaking, the molecules related by the *n*-glide in the fundamental structure must be treated as crystallographically independent in the sinusoidal structure. But in this calculation these molecules were assumed to be related to each other by translational symmetry expressed by the transverse modulation wave. The number of independent atoms is 43 ($C_{12}H_9NS\,.\,C_{12}H_4N_4$) and the number of the symmetry operations is $13M$, where 13 is the number of translational symmetry and M is the number of independent symmetry operations of the space group $P2_1/n$. Comparison of the observed and calculated structure factors gave an R value of 0·195. The temperature factors used are the same as those of the fundamental structure.

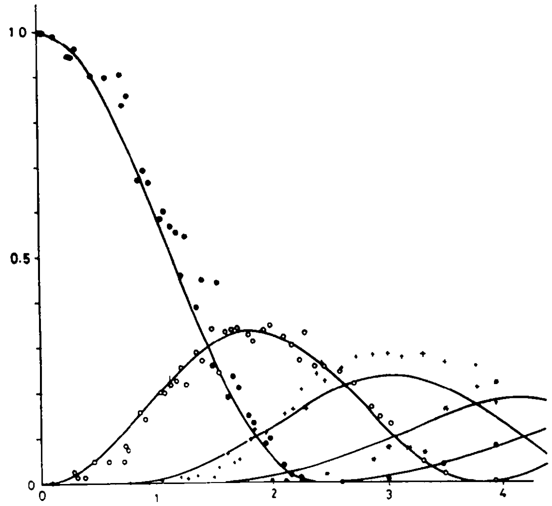


Fig. 6. Relative intensities of the main and satellite reflexions and comparisons with the values of the Bessel functions [see equations (7) and (7′)]. ●, main reflexions; ○, 1st satellites; +, 2nd satellites; *, 3rd satellites. Ordinate and abscissa represent relative intensities [or $J_n^2(x)$] and $2\pi(ph/a+ql/c)$ (or x), respectively.

(ii) *A model of the 'fourfold simple sinusoidal structure'*

The atomic position is given as,

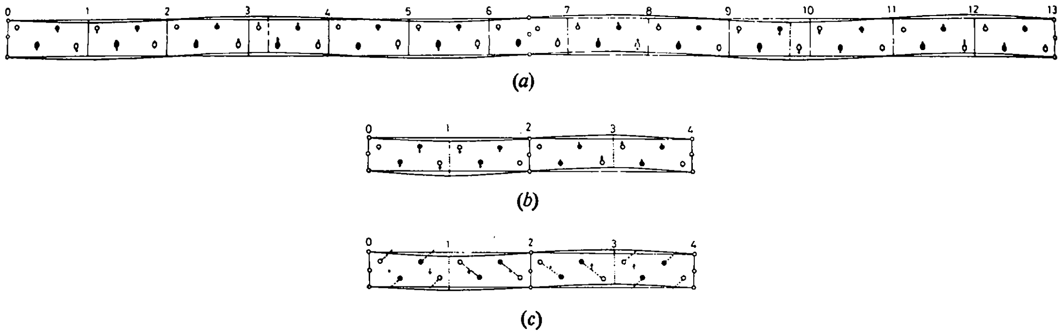
$$\mathbf{r}_j=\mathbf{d}_j+(-0{\cdot}85\mathbf{a}/a+0{\cdot}75\mathbf{c}/c)\sin 2\pi(0{\cdot}250P).$$

The 43 atoms are independent and the number of the symmetry operation is $4M$, where 4 is the number of the translational symmetry expressed by the transverse sinusoidal wave and M is the number of symmetry operations of space group $P2_1/c$. The comparison of the observed and calculated structure factors gave an R value of 0·20.

The thirteenfold structure is better than the fourfold structure but the difference is small. Therefore the fourfold structure is more suitable for the calculation and was refined by the block-diagonal least-squares method in order to examine the validity of this model. Assumed symmetry operations are listed in Table 4. The final R value was 0·178. The B_{33} of four atoms were negative, which is probably due to the fact that approximate symmetry operations were used for convenience in the calculation.

(iii) *A model of the 'paired column structure'*

Another model was also examined, which elucidates more clearly the origin of the sinusoidal modulation.



(*a*)

(*b*)

(*c*)

Fig. 7. Models of the sinusoidal structure. (*a*) The thirteenfold simple sinusoidal structure. (*b*) The fourfold simple sinusoidal structure. (*c*) The paired column structure.

Table 4. *The approximate symmetry operations assumed to simplify the calculations*

An atomic position is given as

$$x=R_1x_0+T_x\,,\quad y=R_2y_0+T_y\,,\quad z=R_3z_0+T_z$$

where (x_0,y_0,z_0) are the atomic coordinates of the fundamental structure [see equation (1) and Fig. 7].

(i) Fourfold simple sinusoidal structure

	R_1	R_2	R_3	T_x	T_y	T_z
(1)	1	1	1	−0·02361	0·0	0·01389
(2)	1	1	1	0·39939	0·125	0·05920
(3)	−1	−1	−1	0·43278	0·125	0·03956
(4)	−1	−1	−1	0·88133	0·250	0·06983

(ii) Paired column structure

	R_1	R_2	R_3	T_x	T_y	T_z
(1)	1	1	1	−0·02361	0·0	0·01390
(2)	−1	−1	−1	0·43091	0·125	0·04054
(3)	1	1	1	0·41089	0·125	0·05245
(4)	−1	−1	−1	−0·13459	0·250	0·07909

In the fourfold structure, all the molecules move according to the coordinate of the mixed stacking column to which they belong, whereas in the 'paired column structure' two neighbouring columns (Fig. 7), which are interrelated by the *n*-glide in the fundamental structure, move in pairs; that is, the crystal is assumed to be constructed from the paired columns. The position of the centre of gravity of the pair moves sinusoidally. The structure was refined by the block-diagonal least-squares method with the starting parameters deduced from those of the fundamental structure. The approximate symmetry operations used are listed in Table 4. Some reflexions were not included in the calculation because a few higher-order satellite reflexions appeared in the middle of two neighbouring main reflexions and could not be indexed. After six cycles, the refinement converged with $R=0\cdot165$. The B_{33} of three atoms and B_{11} of one atom became negative. Thus the refinement is not complete. Nevertheless, considering the many assumptions made in this analysis, this result seems to be fairly satisfactory. The atomic coordinates obtained are essentially the same as those of the fundamental structure. Structure amplitudes of satellite reflexions are listed in Table 5 together with calculated structure amplitudes.

Discussion of the sinusoidal structure

The model of the 'paired column structure' seems to be a little better than the fourfold simple sinusoidal structure in view of the *R* value. Moreover, the paired column structure seems to indicate some clear physical implications on the origin of the sinusoidal structure. The paired column structure viewed along the *a* axis is shown in Fig. 8.

The interatomic distance between the nitrogen atoms of PTZ and TCNQ in neighbouring columns is 3·37 Å in the fundamental structure and the angle of N–H···N is about 140°. In the sinusoidal structure, the N···N distance is changed by the transverse modulation wave, which indicates that it can be reduced to about 3·24 Å. Considering that this contact

Table 5. *Calculated and observed structure amplitudes*

N indicates *n*th-order satellite.

K	N	FO	FC
H,L= 0 0			
4	0	180	171
8	0	156	147
10	0	28	27
12	0	9	16
18	0	8	9
20	0	22	22
22	0	33	30
24	0	22	22
26	0	16	15
H,L= 1 0			
1	0	15	17
1	-1	[illegible]	5
1	1	6	[illegible]
3	0	9	15
3	-1	4	9
3	1	4	6
5	0	14	12
5	1	4	6
9	0	50	42
9	-1	13	16
9	1	16	[illegible]
11	0	6	6
13	0	16	18
15	0	20	22
15	1	9	10
19	0	46	41
19	-1	16	15
19	1	15	16
21	0	19	14
23	0	22	23
25	-1	9	12
H,L= 2 0			
0	0	60	60
0	-2	24	32
0	-1	59	68
4	0	30	27
4	-2	4	6
4	-1	20	25
4	1	36	35
4	2	17	20
8	0	16	15
8	-2	8	14
8	-1	19	21
8	1	17	14
8	2	5	7
10	0	16	14
10	-1	15	16
10	1	12	17
16	0	8	8
16	-1	12	12
16	1	6	8
H,L= 3 0			
1	0	3	1
1	-1	6	10
1	1	11	12
1	2	8	14
3	-2	8	15
3	-1	11	11
3	1	5	9
5	-2	[illegible]	10
5	-1	11	8
5	1	7	10
5	2	6	5
7	-1	8	13
7	1	[illegible]	[illegible]
7	2	10	8
9	-1	7	10
9	1	13	10
9	2	8	13
11	-2	17	17
11	-1	22	16
11	1	16	16
11	2	9	14
19	-2	10	12
19	-1	10	14
19	1	8	12
H,L= 4 0			
0	1	8	5
0	2	14	9
0	3	8	8
2	-1	19	21
2	0	91	87
2	1	12	19
4	-1	2	2
4	0	17	17
4	1	6	6
6	-1	5	2
6	0	11	12
8	-1	7	4
8	0	22	22
8	1	7	5
10	-1	19	20
10	0	56	50
12	0	12	14
12	1	7	4
14	-1	4	4
14	0	4	3
14	1	3	4
16	0	11	11
18	0	15	18
22	0	9	7
24	0	12	16
H,L= 1 1			
1	0	27	30
1	1	5	6
3	-1	2	1
3	0	6	8
3	1	5	5
5	-1	11	14
5	0	62	64
5	1	6	9
7	-1	4	7
7	0	62	64
7	1	8	13
9	-1	6	8
9	0	26	23
11	-1	7	4
11	0	4	[illegible]
11	1	[illegible]	5
13	-1	5	16
13	0	47	46
15	0	[illegible]	19
17	-1	7	7
17	0	36	31
23	0	7	8
25	0	17	19
H,L= 2 1			
2	-1	18	22
2	0	32	34
2	1	19	22
4	-1	7	9
4	0	10	14
4	1	7	9
6	-1	6	9
6	0	17	17
6	1	13	13
8	-1	7	5
8	0	9	10
8	1	5	9
10	-1	4	5
10	0	9	9
10	1	8	5
12	0	8	8
12	1	6	8
14	0	7	8
16	-1	10	9
16	0	14	16
22	-1	7	12
22	0	10	14
22	1	6	7
24	0	7	8
H,L= 3 1			
3	-2	[illegible]	7
3	-1	9	9
3	0	4	5
3	1	5	8
3	2	4	3
5	-2	6	8
5	-1	11	12
5	0	5	6
5	1	5	10
7	1	6	8
7	2	5	6
9	-2	8	9
9	-1	17	18
9	0	11	10
9	1	12	18
9	2	10	9
13	-2	[illegible]	8
13	0	9	8
13	1	15	12
13	2	6	8
15	-2	6	9
15	-1	13	12
15	0	7	6
15	1	10	11
15	2	6	6
H,L= 4 1			
2	-2	9	9
2	-1	11	13
2	1	14	12
2	2	16	17
4	-1	5	4
4	1	5	3
6	-2	22	22
6	-1	18	17
6	1	17	16
6	2	14	14
10	-2	8	5
10	-1	8	9
10	1	9	7
10	2	10	7
14	-2	7	6
14	-1	6	6
14	1	6	7
14	2	5	9
H,L= 0 1			
4	0	17	17
4	1	6	6
6	1	8	4
6	0	13	12
8	-1	8	4
8	0	25	22
8	1	9	5
10	-1	22	20
10	0	51	50
12	0	13	14
12	1	6	4
14	-1	4	4
14	0	5	3
14	1	3	4
16	0	14	11
18	0	17	18
22	0	9	7
24	0	15	16
H,L=-1 1			
1	-1	6	9
1	0	11	12
1	1	7	10
3	-1	12	13
3	0	17	16
3	1	10	13
5	-1	11	16
5	0	17	18
5	1	11	13
7	-2	8	10
7	-1	22	22
7	0	26	25
7	1	12	14
9	0	10	7
9	1	7	6
11	-2	8	7
11	-1	20	17
11	0	20	21
11	1	19	17
11	2	6	7
17	-2	8	9
17	-1	22	21
17	0	23	24
17	1	13	15
21	-1	16	19
21	0	28	26
21	1	20	21
23	-1	8	7
23	1	12	11
H,L=-2 1			
2	-4	8	5
2	-3	27	40
2	-2	86	97
2	-1	156	161
2	0	76	67
2	1	160	161
2	2	100	110
2	3	36	39
2	4	11	9
6	-2	20	25
6	-1	26	23
6	0	[illegible]	8
6	1	14	19
10	-2	17	16
10	-1	26	29
10	0	14	12
10	1	30	28
10	2	18	20
22	-1	9	9
22	1	10	12
24	-2	9	9
24	-1	14	15
24	0	7	6
24	1	12	13
H,L=-3 1			
1	-2	8	7
1	-1	7	6
3	1	7	7
3	2	11	12
10	-2	10	13
10	-1	11	11
10	1	13	13
10	2	17	17
17	-2	14	15
17	-1	13	11
17	1	10	10
17	2	12	10
21	-2	18	16
21	-1	15	13
21	1	14	12
21	2	14	14
H,L=-4 1			
2	0	12	18
2	1	13	6
2	2	36	25
2	3	32	29
2	4	7	8
2	-3	18	20
2	-2	29	18
2	-1	9	5
H,L= 0 2			
2	0	16	8
2	-1	9	5
2	1	2	4
4	-2	6	8
4	-1	27	27
4	0	48	45
4	1	18	19
8	-2	4	8
8	-1	21	22
8	0	35	32
8	1	10	12
10	-1	9	11
10	0	19	19
10	1	8	8
18	-1	6	12
18	0	17	20
18	1	9	9
20	-2	6	8
20	0	16	18
20	1	8	11
H,L= 1 2			
1	0	20	19
3	-1	4	4
3	0	9	11
3	1	5	2
5	0	57	52
7	0	68	64
11	0	47	47
13	0	15	15
15	0	18	18
17	0	28	27
19	0	12	16
21	0	8	9
H,L= 2 2			
0	0	113	113
0	1	32	38
2	-1	3	2
2	0	17	13
4	-1	12	12
4	0	13	12
4	1	5	4
6	0	4	5
8	-1	24	27
8	0	72	71
8	1	16	20
10	-1	6	0
10	0	15	14
14	0	13	10
18	-1	7	4
18	0	17	18
18	1	7	8
22	0	8	9
24	0	8	3
H,L= 3 2			
3	0	10	8
9	-1	6	5
9	0	3	5
9	1	4	5
11	-1	18	18
11	0	21	19
11	1	18	19
13	-1	8	7
13	0	8	8
13	1	7	9
15	-1	8	8
15	0	8	8
15	1	6	6
17	0	11	10
17	1	9	9
19	-1	8	8
19	0	9	9
H,L= 4 2			
2	-2	6	6
2	-1	8	6
2	1	7	4
4	-2	6	5
4	-1	6	4
8	-2	15	14
8	-1	19	15
8	0	5	3
8	1	11	11
8	2	7	6
16	-2	13	11
16	-1	14	12
16	1	7	9
H,L= 5 2			
1	-2	7	9
1	-1	6	5
1	1	7	6
1	2	8	10
3	-2	11	7
3	-1	7	2
7	-2	14	12
7	-1	9	9
7	1	9	7
7	2	15	11
9	-2	6	6
9	-1	7	4
9	1	8	5
9	2	12	9
H,L=-1 2			
1	-2	5	12
1	-1	14	19
1	0	14	14
1	1	15	19
1	2	6	11
3	-1	8	11
3	0	9	9
3	1	12	13
3	2	4	8
5	-2	5	9
5	-1	16	16
5	0	13	13
5	1	18	19
5	2	8	9
7	-2	5	7
7	-1	15	16
7	0	14	11
7	1	16	14
7	2	5	10
9	-2	6	12
9	-1	15	18
9	0	10	10
9	1	11	10
11	-2	11	14
11	-1	27	28
11	0	21	21
11	1	29	29
11	2	12	15
13	-1	8	8
13	0	10	8
13	1	10	13
19	-1	8	12
19	0	8	10
19	1	12	14
H,L=-2 2			
4	-2	8	12
4	-1	8	14
4	1	10	12
4	2	10	20
8	-2	11	11
8	-1	10	12
8	1	7	11
10	-2	6	1
10	-1	5	4
10	1	6	9
10	2	[illegible]	9
12	-2	12	12
12	-1	9	13
12	1	6	10
12	2	6	6
14	-1	7	7
16	1	10	7
16	2	10	8
H,L=-3 2			
7	-2	10	9
7	1	5	3
7	2	8	11
9	-3	6	12
9	-2	12	11
9	2	8	7
19	-3	8	13
19	-2	14	14
19	2	10	11
H,L=-4 2			
8	-3	16	15
8	-2	9	8
8	0	6	8
8	2	8	6
8	3	12	10
H,L= 0 3			
2	-1	44	44
2	0	47	47
2	1	41	39
2	2	12	15
4	-1	7	12
4	0	15	13
4	1	9	11
6	-2	9	11
6	-1	30	31
6	0	43	39
6	1	41	39
6	2	13	17
8	-1	6	4
8	0	12	8
8	1	10	11
10	-2	6	7
10	-1	23	23
10	0	26	27
10	1	26	25
10	2	10	11
16	-1	15	12
16	0	[illegible]	14
16	1	11	13
H,L= 1 3			
5	-1	[illegible]	7
5	0	30	31
5	1	9	12
7	0	30	29
9	0	20	21
13	-1	11	13
13	0	36	37
13	1	11	10
15	0	26	28
17	-1	11	10
17	0	9	13
19	0	6	6
21	0	10	12
25	0	10	12
H,L= 2 3			
2	-1	2	1
2	0	16	16
2	1	2	1
4	0	21	22
6	-1	8	8
6	0	21	22
8	0	17	16
10	-1	10	8
10	0	42	40
14	[illegible]	16	16
18	-1	6	4
18	0	27	32
H,L= 3 3			
1	-1	7	8
1	0	21	19
1	1	14	12
3	-1	4	5
3	0	5	7
3	1	6	5
5	-1	22	26
5	0	43	42
5	1	17	20
7	-1	21	19
7	0	39	36
7	1	20	21
9	-1	6	8
9	0	16	17
9	1	12	9
13	-1	6	10
13	0	13	14
13	1	6	5
15	-1	13	14
15	0	19	20
15	1	7	12
H,L= 4 3			
2	-1	13	12
2	0	13	8
2	1	14	11
4	-1	15	18
4	0	13	12
4	1	22	18
4	2	13	11
H,L=-1 3			
1	-2	12	11
1	-1	14	16
1	0	5	4
1	1	11	12
1	2	6	6
3	-2	4	7
3	-1	5	10
3	1	9	11
3	2	9	6
5	-3	5	7
5	-2	16	16
5	-1	21	22
5	0	8	6
5	1	17	17
5	2	11	10
7	-2	8	6
7	-1	13	12
7	0	6	5
7	1	18	19
7	2	14	13
9	-2	22	21
9	-1	31	29
9	0	9	8
9	1	24	24
9	2	14	13
13	-2	8	9
13	-1	14	13
13	0	6	4
13	1	13	12
13	2	7	9
15	-2	9	10
15	-1	12	12
15	1	13	13
15	2	8	9
H,L=-2 3			
2	-2	5	9
2	-1	5	5
2	1	4	4
4	-3	9	10
4	-2	20	16
4	-1	14	11
4	0	4	7
4	1	12	15
4	2	15	13
4	3	5	9
H,L= 0 4			
2	-2	9	8
2	-1	13	14
2	0	7	8
2	1	7	11
4	-2	9	8
4	-1	14	11
4	0	7	8
4	1	4	13
8	-1	13	17
8	0	15	12
8	1	27	23
8	2	16	17
10	-2	4	8
10	-1	11	9
10	0	9	6
10	1	11	12
10	2	4	8
12	-1	6	9
12	0	5	7
12	1	13	11
12	2	9	8
16	-2	6	10
16	-1	16	18
16	0	12	11
16	1	21	20
16	2	13	13
18	-1	7	5
18	0	6	3
18	1	6	7
H,L= 1 4			
1	-1	15	17
1	0	[illegible]	30
1	1	17	18
3	-1	4	3
3	0	13	12
3	1	7	11
5	-1	16	18
5	0	29	33
5	1	21	23
5	2	8	7
7	-2	7	6
7	-1	27	27
7	0	42	44
7	1	26	26
7	2	5	8
9	-1	22	23
9	0	39	38
9	1	20	23
13	-1	7	7
13	0	11	12
13	1	9	9
15	-1	6	4
15	0	6	10
17	-1	11	14
17	0	21	22
17	1	11	13
23	-1	7	6
23	0	11	12
23	1	6	8
H,L= 2 4			
0	0	17	13
2	-1	3	3
2	0	8	16
2	1	4	2
4	-1	12	10
4	0	52	52
6	0	6	16
8	-1	10	10
8	0	34	31
10	0	13	12
12	-1	8	7
12	0	32	33
16	-1	7	6
16	0	18	20
18	0	20	21
20	0	11	8
26	0	5	10
H,L= 3 4			
1	-1	7	8
1	0	21	21
3	-1	4	4
3	0	14	10
5	0	7	11
9	0	20	17
11	0	8	3
13	0	9	7
15	0	7	6
15	1	6	2
17	0	24	24
19	0	8	7
19	1	4	3
23	0	9	10
27	0	9	11
H,L= 4 4			
0	0	12	12
0	1	11	9
4	-1	6	7
4	0	9	6
4	1	5	3
8	-2	6	4
8	-1	12	9
8	0	13	11
8	1	6	9
18	-1	7	6
18	0	12	8
18	1	8	7
H,L= 5 4			
1	-1	7	7
1	1	7	8
11	-1	7	5
11	1	6	6
H,L=-1 4			
1	-2	6	14
1	-1	6	8
1	1	6	7
1	2	5	6
3	-2	7	7
3	-1	8	4
3	1	6	4
3	2	4	4
5	-3	5	7
5	-2	13	14
5	-1	12	11
5	1	11	13
5	2	11	9
5	3	4	6
7	-3	4	7
7	-2	10	9
7	-1	9	10
7	1	10	7
7	2	12	11
7	3	5	7
9	-2	7	11
9	-1	10	8
9	1	11	5
9	2	[illegible]	[illegible]
11	-3	7	10
11	-2	18	16
11	-1	15	12
11	1	13	12
11	2	11	12
13	-2	11	9
13	-1	10	6
13	1	6	8
13	2	5	6
17	-1	7	7
17	1	10	7
17	2	8	11
19	-2	13	11
19	-1	9	6
H,L=-2 4			
8	-3	11	13
8	-2	17	14
8	-1	7	8
8	0	7	12
8	1	9	7
8	2	22	18
8	3	15	17
H,L= 0 5			
2	-2	13	12
2	-1	15	15
2	1	10	13
2	2	7	7
6	-3	16	17
6	-2	34	33
6	-1	36	35
6	0	9	5
6	1	26	27
6	2	18	18
14	-2	17	17
14	-1	18	19
14	1	13	14
14	2	7	10
H,L= 1 5			
1	-1	8	9
1	0	8	10
1	1	9	12
1	2	4	8
3	-1	5	12
3	0	10	11
3	1	14	13
3	2	6	7
5	-1	15	14
5	0	5	7
5	1	8	7
5	2	6	3
15	-1	15	14
15	0	11	12
15	1	13	12
H,L= 2 5			
2	0	11	13
4	0	6	8
6	-1	7	9
6	0	21	17
6	1	6	4
8	0	9	9
16	-1	8	7
16	0	17	17
H,L= 3 5			
1	0	21	21
3	0	11	10
5	0	8	6
7	0	12	14
9	0	9	8
13	0	16	16
17	0	12	11
H,L= 4 5			
4	0	11	8
H,L=-1 5			
1	-3	5	3
1	-2	6	2
1	2	7	5
1	3	4	4
3	-1	4	3
3	1	5	1
3	2	5	1
5	-3	9	15
5	-2	17	18
5	-1	13	11
5	1	12	10
5	2	15	16
7	-3	11	12
7	-2	20	16
7	-1	13	8
7	0	5	8
7	1	12	13
7	2	22	27
7	3	13	14
9	-3	7	9
9	-2	13	10
9	-1	6	8
9	1	6	4
9	2	12	8
9	3	7	6
11	-2	5	9
11	-1	7	5
11	1	7	4
11	2	8	7
H,L=-2 5			
2	-3	13	11
2	-2	11	8
2	0	5	8
2	2	6	8
2	3	6	12
H,L= [illegible] 6			
14	1	10	8
H,L= 1 6			
1	-2	5	[illegible]
1	-1	10	11
1	0	5	5
1	1	9	10
1	2	5	4
7	-1	6	5
7	1	6	4
11	-2	6	5
11	-1	[illegible]	8
11	0	6	8
11	1	10	8
11	2	7	6
13	-2	6	5
13	-1	8	6
H,L= 2 5			
0	0	6	7
0	1	6	4
2	-1	7	9
2	0	7	9
4	-1	5	1
4	0	7	1
8	0	7	3
8	1	7	11
10	0	7	14
10	1	6	9
H,L= 3 6			
1	0	16	12
3	0	11	11
7	0	21	23
9	0	23	26
11	0	11	14
15	0	10	8
H,L= 4 6			
0	0	15	16
2	0	9	14
6	0	8	14
12	0	26	27
8	0	8	7
14	0	8	10
18	0	7	7
20	0	9	11
H,L= 5 6			
1	-1	8	6
1	0	13	10
1	1	8	8
7	-1	7	7
7	0	11	9
7	1	7	5
9	-1	11	10
9	0	12	15
11	-1	8	7
11	0	13	10
11	1	7	7
H,L=-2 6			
4	-4	14	15
4	-3	19	17
4	-2	11	7
4	0	5	8
4	2	8	4
4	3	13	9
4	4	8	4
H,L= 0 7			
6	-2	8	4
6	-1	7	2
6	1	7	3
6	2	8	5
8	-2	7	4
8	-1	7	2
8	1	7	1
8	2	8	3
10	1	8	4
10	2	10	7
H,L= 1 7			
3	-2	6	7
3	-1	8	9
3	1	8	7
3	2	6	6
5	-2	8	8
5	-1	10	10
5	1	11	12
5	2	9	11
7	-2	7	3
7	-1	9	3
7	1	10	8
7	2	11	8
9	-2	12	10
9	-1	13	13
9	1	13	10
9	2	12	9
11	-2	10	11
11	-1	13	13
11	1	18	15
11	2	14	12
13	-2	16	10
13	-1	12	11
H,L= 2 7			
2	-1	11	13
2	0	12	10
2	1	14	13
4	-1	9	7
4	0	9	5
4	1	9	6
10	-2	9	7
10	-1	18	14
10	0	12	12
10	1	18	16
10	2	9	6
12	-2	8	6
12	-1	15	11
12	0	9	7
12	1	8	8
14	-2	9	8
14	-1	17	13
14	0	8	9
14	1	9	9
H,L= 3 7			
1	-1	8	8
1	0	18	16
1	1	9	8
3	-1	7	11
3	0	22	20
3	1	10	8
5	0	7	8
7	0	9	9
7	1	8	7
9	-1	9	8
9	0	20	19
9	1	12	10
11	0	18	20
11	1	15	9
13	-1	8	6
13	0	11	13
H,L= 4 7			
2	0	37	31
4	0	7	8
6	0	7	7
8	0	11	9
12	0	7	11
H,L= 5 7			
1	0	21	13
7	0	12	11

(3·37 Å) is the shortest between these two adjacent columns in the fundamental structure, the decrease in the distance of N···N seems to increase the atomic repulsion. Therefore it may be reasonable to conclude that the two atoms are linked by hydrogen bonds of the N–H···N type. The N···N distance in hydrogen bonds of the N–H···N type ranges from 2·8 to 3·4 Å (Pimentel & McClellan, 1960). The distance of 3·37 Å (fundamental structure) indicates that the hydrogen bond is very weak even if it exists, whereas the value of 3·24 Å (sinusoidal structure), calculated from the amplitude of the modulation wave, indicates weak hydrogen bonds in the sinusoidal structure.

Considering the existence of the charge-transfer interaction within a column and the hydrogen bonds formed between adjacent columns, a stable conformation of paired columns may be constructed (Fig. 9). As can be easily seen from the fundamental structure, hydrogen bonds can be formed between two equivalent pairs. Fig. 10 illustrates the two types of hydrogen bonds, which may distort to some extent the crystal lattice according to the strength of the hydrogen bond. Many types of modulated structures will appear by various combinations of these two structures. If two types of the hydrogen bonds are repeated alternately at every four cells, an approximately sinusoidal structure may result. There must be some origin for the force that prevents the infinite sequence of one type of hydrogen bond or the random sequence of two types of hydrogen bonds in order to explain the appearance of the sinusoidal structure. It may be a long-range force. Considering the polar structure of PTZ, it seems to be dipole–dipole interaction, which probably gives the largest stabilization energy in the regular arrangement of molecules and may act as a restoring force against the lattice distortion produced by the formation of hydrogen bonds. Thus the appearance of the sinusoidal structure may be due to the delicate balance of the short-range forces (hydrogen bonding, charge-transfer interaction, van der Waals force,...) and the long-range forces (dipole–dipole interaction between PTZ molecules,...). The interatomic distances for N···N obtained by the refinement of the simple sinusoidal structure and the paired column structure are 3·27 and 3·30 Å (with e.s.d.'s of about 0·05 Å), respectively. The value estimated using the parameters of the modulation wave is 3·24 Å as described previously. All these values indicate weak hydrogen bonding and may support the above picture of the origin of the sinusoidal structure.

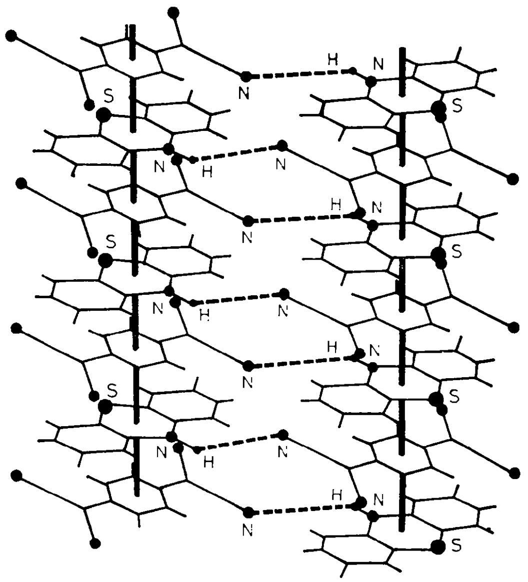


Fig. 9. The paired column of PTZ and TCNQ.

Recently, Bhat & Kinoshita (private communication) have examined infrared spectra of PTZ–TCNQ and found a small band shift of ν_{N-H}. The frequency ν_{N-H} of PTZ in the complex and of the neutral PTZ are 3362 and 3440 cm^{-1}, respectively. They have concluded that the small shift of 78 cm^{-1} indicates the existence of a weak hydrogen bond with an N···N distance of about 3·30 Å, which was calculated from the empirical formula of $\Delta\nu_{N-H}=1{\cdot}05\times10^3\ (3{\cdot}38'-R)$. Their conclusion is in fairly good agreement with the result of the present X-ray analysis.

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APPENDIX

Consider a modulated lattice in which an atomic position of the nth cell $[n=(n_1,n_2,n_3)]$ is displaced from its original position through a distance $(p\mathbf{a}/a+q\mathbf{c}/c)$ sin $2\pi\sigma n_2$. The structure amplitude of the crystal is given by

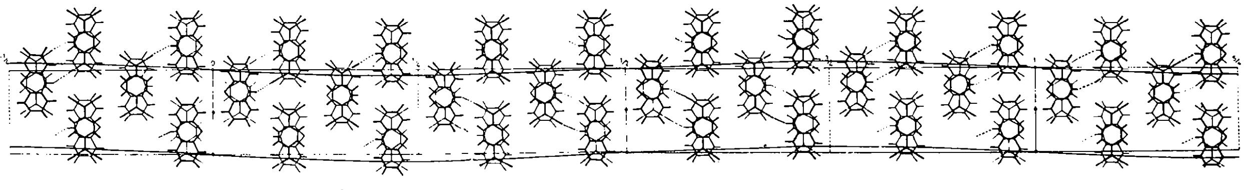

Fig. 8. The paired column structure viewed along the a axis.

$$F(\xi\eta\zeta)=\sum_{n_1=1}^{N_1}\sum_{n_2=1}^{N_2}\sum_{n_3=1}^{N_3}\{\sum_j f_j$$
$$\times\exp[2\pi i(\xi x_j+\eta y_j+\zeta z_j)]$$
$$\times\exp\{2\pi i[\eta_1\xi+n_2\eta+n_3\zeta+(p\xi/a+q\zeta/c)$$
$$\times\sin 2\pi\sigma n_2]\}$$

where the scattering vector **s** is represented by

$$\mathbf{s}=\xi\mathbf{a}^*+\eta\mathbf{b}^*+\zeta\mathbf{c}^*$$

and

$$\mathbf{d}_j=x_j\mathbf{a}+y_j\mathbf{b}+z_j\mathbf{c}\,.$$

The first term in the triple summation, $\sum_j f_j \exp[2\pi i(\xi x_j+\eta y_j+\zeta y_j)]$ is the structure factor of the crystal without modulation. The intensity formula of the X-ray diffraction is given as follows:

$$I(\xi\eta\zeta)=|F(\xi\eta\zeta)|^2$$
$$=|F^0(\xi\eta\zeta)|^2|G(\xi)|^2|G(\zeta)|^2\sum_m\sum_n G^*(\eta+\sigma m)$$
$$\times G(\eta+\sigma n)J_m[2\pi(p\xi/a+q\zeta/c)]J_n[2\pi(p\xi/a+q\zeta/c)]$$

where

$$F^0(\xi\eta\zeta)=\sum_j f_j \exp[2\pi i(\xi x_j+\eta y_i+\zeta z_j)]\,,$$
$$G(\xi)=\exp[\pi i(N_1-1)\xi]\sin N_1\pi\xi/\sin\pi\xi\,,$$
$$G(\eta+\sigma m)=\exp[\pi i(N_2-1)\eta]\sin N_2\pi(\eta+\sigma m)$$
$$/\sin\pi(\eta+\sigma m)$$

and J_n is an *n*th order Bessel function. From the well-known properties of the Laue function $G(x)$, maxima occur at

$$\eta+\sigma m=k'$$
$$\eta+\sigma n=k''$$

where k' and k'' are integers. Higher-order Bessel functions are very small for the values of p, q and σ used in this paper. Therefore, $\sum_m\sum_n G^*(\eta+\sigma m)G(\eta+\sigma n)$ is approximately equal to $\sum_n |G|(\eta+\sigma n)|^2$. Then the intensity formula becomes

$$I(\xi\eta\zeta)=|F(\xi\eta\zeta)|^2$$
$$=N_1^2N_2^2N_3^2|F^0(\xi\eta\zeta)|^2\sum_n J_n^2[2\pi(p\xi/a+q\zeta/c)]$$
$$\times\delta(\xi-h)\delta(\eta-k-n\sigma)\delta(\zeta-l)$$
$$=\begin{cases}N_1^2N_2^2N_3^2|F^0(hkl)|^2J_o^2[2\pi(ph/a+ql/c)]\ \ldots\\ (hkl)\\ N_1^2N_2^2N_3^2|F^0(hk\pm n\sigma l)|^2J_n^2[2\pi(ph/a\\ +ql/c)]\ \ldots\ (hk\pm n\sigma l)\end{cases}$$

where h, k and l are integers and $n=1,2,3,\ldots.$

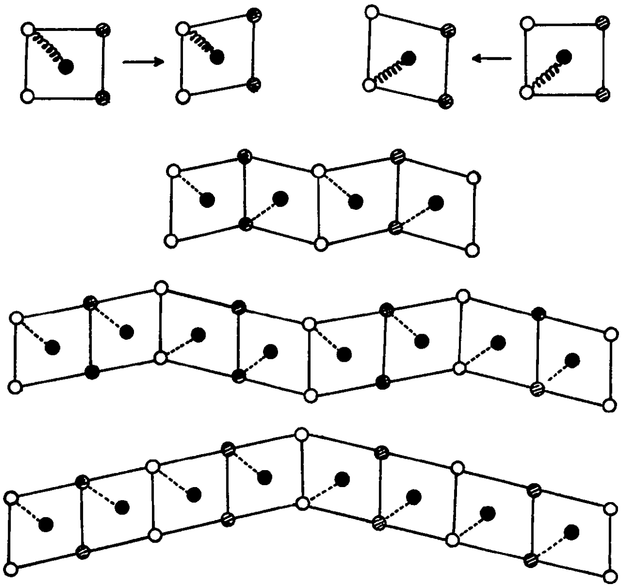

Fig. 10. Two models of the cells distorted by formation of hydrogen bonds and some possible superlattice structures constructed of these two cells.

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