BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(4), 832—837 (1974)

The Crystal Structure of 2,4,6-Triphenylpyrylium-1,1,3,3-tetracyanopropenide, $[(C_{23}H_{17}O)^+ \cdot (C_7HN_4)^-]$[1]

Toshiaki TAMAMURA, Takashi YAMANE*[2], Noritake YASUOKA and Nobutami KASAI[3]

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565

**Institute for Protein Research, Osaka University, Yamadakami, Suita, Osaka 565*

(Received October 4, 1973)

The crystal structure of an organic charge transfer salt 2,4,6-triphenylpyrylium-1,1,3,3-tetracyanopropenide has been determined by means of X-ray diffraction. The crystals are monoclinic in the space group $P2_1/a$. The unit cell dimensions are: $a=13.024$, $b=21.357$, $c=8.324$ Å, $\beta=94.56°$. The cation and the anion are nearly planar and form an "ion-pair." The crystal is built up from infinite columns stacked by these ion-pairs along the c axis. Between two adjacent anions in the neighboring columns, a weak hydrogen bond (C–H···N 3.265 (5), H···N 2.185(4) Å) is present. The charge transfer interaction between the anion and the cation seems to have less influence on the crystal structure than the electrostatic force or the hydrogen bonding.

The charge transfer interaction has been observed spectroscopically in a number of ionic compounds composed of an electron-donating anion and an electron-accepting cation.[4] However, few systematic studies have been made on the physical properties and the crystal structure of these organic charge transfer salts. The effect of interionic charge transfer force on the crystal structure is almost unknown, because of the presence of the strong electrostatic force in addition to the charge transfer and van der Waals interaction between the anion and the cation.

In this paper we describe the crystal structure of an organic charge transfer salt 2,4,6-triphenylpyrylium (TPP)-1,1,3,3-tetracyanopropenide (TCP). A series of structural studies have been made on organic charge transfer salts,[5] as well as on the interionic charge transfer interaction in organic charge transfer salts consisting of a polycyanoacid anion and a heteroaromatic cation.[1,6] The charge transfer absorption of TPP-TCP is observed in non-polar solvents and also in solid state.[7] The study was also promoted by the interesting relationship between the crystal structure and the charge transfer dichroism.

Experimental

Crystal Data. $[(C_{23}H_{17}O)^+ \cdot (C_7NH_4)^-]$, F.W.=450.5, monoclinic, $a=13.024$, $b=21.357$, $c=8.324$ Å, $\beta=94.56°$, $Z=4$, $D_m=1.38\ \mathrm{g \cdot cm^{-3}}(CCl_4\text{–}C_6H_6)$, $D_x=1.32\ \mathrm{g \cdot cm^{-3}}$, space group; $P2_1/a$, absent spectra; $h0l$: $h \neq 2n$, $0k0$: $k \neq 2n$.

Dark red needles of TPP-TCP were recrystallized from a methanol solution.

Oscillation and Weissenberg photographs showed that the crystals belong to the monoclinic system, the space group being $P2_1/a$. Both the determination of cell constants and the collection of intensity data were carried out on a Rigaku four-cycle diffractometer.

The crystal used for the intensity measurement had the dimension 0.32×0.45×0.15 mm. The crystal was mounted on a goniometer-head along the c axis. Nickel-filtered Cu$K\alpha$ radiation was used. The ω-2θ scan technique was applied. The scan range, $\Delta(2\theta)$, of each reflection, was computed by the equation: $\Delta(2\theta)=(2.0°+0.3° \tan\theta_c)$. The starting angle of the scan is $(2\theta_c-1.0)°$, where θ_c is the calculated value of the Bragg angle for $\lambda(\mathrm{Cu}K\alpha_1)$ (=1.5405 Å), the scanning speed being 4° min^{-1}. The background was measured at both ends of each scan range. A total of 3394 independent reflections was obtained. No absorption correction was made ($\mu=8.2\ \mathrm{cm^{-1}}$ for Cu$K\alpha_1$).

Structure Determination and Refinement

The phases of the reflections were determined by means of the symbolic addition procedure.[8] SIGMA program was used to compute the normalized structure factor magnitude $|E|$, and to list the $\sum_2$ relationships for each reflection. Three reflections, 0 3 2, 1 10 6, 11 5 5, were chosen in order to specify the origin, and two other reflections were assigned as phases A and B in order to facilitate the symbolic addition procedure (Table 1). The signs of 108 reflections out of 143 reflections ($|E| \geqq 2.0$) were determined by hand calculations. TANGENT FORMULA program was then used to calculate the phases of 628

TABLE 1(a). DISTRIBUTION OF NORMALIZED STRUCTURE FACTORS AND STATISTICAL AVERAGES

	Distribution of $\lvert E\rvert$	
	Experimental (%)	Theoretical (centrosymmetric) (%)
$\lvert E\rvert \geqq 3.0$	0.8	0.5
$\lvert E\rvert \geqq 2.0$	4.2	5.0
$\lvert E\rvert \geqq 1.8$	29.0	32.0
$\langle \lvert E\rvert \rangle$	0.752	0.798
$\langle \lvert E\rvert^2 \rangle$	0.996	1.000
$\langle \lvert E\rvert^2-1 \rangle$	1.027	0.968

TABLE 1(b). STARTING SET OF APPLICATION OF $\sum_2$ FORMULA

h	k	l	$\lvert E\rvert$	Phase
0	3	2	4.44	+
1	10	6	4.91	+
11	5	5	3.59	+
0	4	2	5.55	A
9	13	$\bar{2}$	4.83	B

TABLE 1(c). PROCESS OF THE SYMBOLIC ADDITION PROCEDURE

Run number	Number of reflections	$\lvert E\rvert$	Number of phases determined
0	5		Starting set
1	143	$\geqq 2.0$	108 (hand calculations)
2	628	$\geqq 1.3$	579

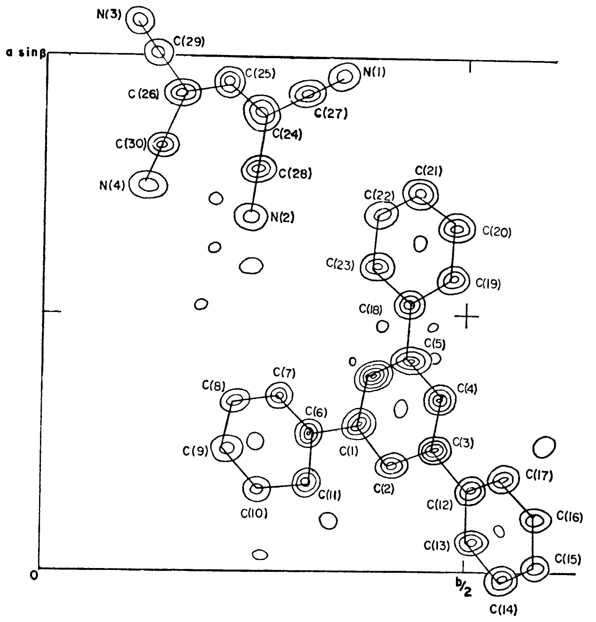

Fig. 1. E map viewed along the c axis.

reflections with $|E|\geq 1.3$. From the interaction list the signs of phases A and B were both assigned to be negative.

The positions of all non-hydrogen atoms were found from E map (Fig. 1). The oxygen atom in the pyrylium ring was identified by the Fourier synthesis based on these atomic coordinates assuming that all the atoms in the ring are carbon ($B=3.5$ Å^2). This was confirmed by the block-diagonal least-squares refinement using the FBLS program. Four cycles of isotropic refinement reduced the R value to 0.150. Three cycles of anisotropic refinement using 2867 reflections ($\sin\theta/\lambda\leq 0.53$) reduced the R value to 0.084. The positions of hydrogen atoms were found from the difference Fourier synthesis computed at this stage. Further refinement including hydrogen atoms gave the final R value as 0.053 for non-zero reflections (0.058 for all reflections). In the refinement the function minimized was $\sum w(F_o-k|F_c|)^2$, where $w=1.00$ for all reflections. The atomic scattering factors were taken from the values determined by Hanson and his co-workers.[9]

The final positional and anisotropic thermal parameters of non-hydrogen atoms are listed in Tables 2 and 3, respectively, the coordinates and isotropic temperature factors of hydrogen atoms in Table 4, and the observed and calculated structure factors in Table 5.[10]

Table 2. Positional parameters of non-hydrogen atoms and their estimated standard deviations (in parentheses)

Atom	x	y	z
O	0.3831(2)	0.3841(1)	0.9618(3)
C(1)	0.2826(3)	0.3723(2)	0.9807(4)
C(2)	0.2089(3)	0.4100(2)	0.9053(4)
C(3)	0.2366(3)	0.4616(2)	0.8153(4)
C(4)	0.3418(2)	0.4718(2)	0.8022(4)
C(5)	0.4139(3)	0.4325(2)	0.8728(4)
C(6)	0.2671(3)	0.3181(2)	1.0825(4)
C(7)	0.3486(3)	0.2785(2)	1.1292(4)
C(8)	0.3331(3)	0.2272(2)	1.2262(5)
C(9)	0.2375(3)	0.2152(2)	1.2788(5)
C(10)	0.1554(3)	0.2548(2)	1.2328(5)
C(11)	0.1694(3)	0.3062(2)	1.1351(5)
C(12)	0.1590(3)	0.5041(2)	0.7371(4)
C(13)	0.0582(3)	0.5052(2)	0.7858(5)
C(14)	−0.0143(3)	0.5453(2)	0.7115(5)
C(15)	0.0105(3)	0.5838(2)	0.5881(5)
C(16)	0.1091(3)	0.5828(2)	0.5387(5)
C(17)	0.1833(3)	0.5437(2)	0.6125(5)
C(18)	0.5257(2)	0.4360(2)	0.8651(4)
C(19)	0.5689(3)	0.4831(2)	0.7782(5)
C(20)	0.6755(3)	0.4859(2)	0.7703(5)
C(21)	0.7376(3)	0.4415(2)	0.8477(5)
C(22)	0.6959(3)	0.3953(2)	0.9359(5)
C(23)	0.5904(3)	0.3921(2)	0.9462(5)
C(24)	0.3866(3)	0.2438(2)	0.7116(4)
C(25)	0.4501(3)	0.2833(2)	0.6323(4)
C(26)	0.4260(3)	0.3355(2)	0.5401(4)
C(27)	0.4289(3)	0.1928(2)	0.8027(5)
C(28)	0.2785(3)	0.2507(2)	0.7078(5)
C(29)	0.5052(3)	0.3679(2)	0.4661(5)
C(30)	0.3261(3)	0.3616(2)	0.5066(5)
N(1)	0.4621(3)	0.1507(2)	0.8756(5)
N(2)	0.1913(3)	0.2563(2)	0.7064(5)
N(3)	0.5670(3)	0.3947(2)	0.4040(5)
N(4)	0.2487(3)	0.3855(2)	0.4769(5)

Results and Discussion

Structure of TPP Cation. The bond lengths and bond angles in the TPP cation are given in Fig. 2(a). The dimensions of the pyrylium ring, which contains 6π electrons as well as benzene and pyridinium rings, have so far not been reported. The pyrylium ring is almost planar with a maximum deviation of 0.015 Å from the best plane (Table 6). The bond angle of oxygen is 122.5(3)° and the two C–O bond lengths are both 1.355(4)Å, which are slightly shorter than that for conjugated *O*-heterocyclic, furan (1.371(5) Å).[11] The bond lengths of C(1)–C(2) and C(4)–C(5) are significantly shorter, however, those of C(2)–C(3) and C(3)–C(4) are slightly longer than the value accepted for the benzene ring (1.397 Å).[12]

The three C–C bond lengths connecting the benzene rings with the pyrylium ring (1.456(5), 1.471(5) and 1.461(5)Å) gave value for a single bond between two sp^2 hybridized carbon atoms. The considerably small angles of O–C(1)–C(6) and O–C(5)–C(18), 113.6(3) and 113.3(3)° might be due to the absence of a hydrogen atom bonded with the oxygen atom. The three benzene rings are planar within experimental error, but tilt from the plane of the pyrylium ring at angles of 10.4, 18.0 and 2.3° for A, B and C rings, respectively. No unusual bond lengths and bond angles were found.

Structure of TCP Anion. The bond lengths and bond angles in the anion are given in Fig. 2(b). The

TABLE 3. ANISOTROPIC THERMAL PARAMETERS OF NON-HYDROGEN ATOMS ($\times 10^5$) EXPRESSED IN THE FORM: $\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\}$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O	476	202	1655	12	77	60
C(1)	471	210	1409	−76	160	−179
C(2)	443	200	1461	−20	11	−45
C(3)	472	196	1321	−16	33	−197
C(4)	425	186	1346	29	−18	−76
C(5)	515	182	1308	—63	137	−43
C(6)	510	196	1342	−64	6	−86
C(7)	647	234	1639	14	35	150
C(8)	755	269	2094	28	−51	133
C(9)	866	252	1863	−136	−106	167
C(10)	693	286	2084	−232	139	58
C(11)	564	247	1839	−64	35	129
C(12)	441	189	1477	−1	−70	−170
C(13)	492	260	2118	44	222	22
C(14)	485	275	2689	77	143	−57
C(15)	584	230	2458	80	−363	−133
C(16)	726	265	2058	67	−225	211
C(17)	547	234	1752	2	51	97
C(18)	431	185	1354	5	141	−54
C(19)	555	249	1717	30	219	180
C(20)	585	282	1903	−91	472	100
C(21)	540	287	2080	88	235	161
C(22)	584	274	2403	194	72	162
C(23)	501	242	2076	89	107	183
C(24)	428	213	1610	−1	−9	−147
C(25)	406	221	1573	15	−22	−202
C(26)	394	231	1683	34	122	−117
C(27)	461	239	1796	−69	75	−76
C(28)	397	292	1844	−88	52	−75
C(29)	541	244	2052	104	249	83
C(30)	515	231	1562	16	−37	−89
N(1)	649	283	2548	−30	68	230
N(2)	505	471	2924	−112	120	75
N(3)	723	341	3265	93	837	626
N(4)	602	342	2498	223	−219	−73

TABLE 4. ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS FOR HYDROGEN ATOMS

Each hydrogen atom bears the same number as that of the carbon atom to which it is attached.

Atom	x	y	z	B (Å^2)
H(3)	0.130	0.400	0.913	1.8
H(5)	0.366	0.510	0.735	1.6
H(7)	0.424	0.287	1.089	1.9
H(8)	0.396	0.196	1.260	2.2
H(9)	0.226	0.176	1.353	1.9
H(10)	0.081	0.145	1.275	2.2
H(13)	0.038	0.475	0.883	1.9
H(14)	−0.090	0.546	0.750	2.0
H(15)	−0.047	0.614	0.531	2.3
H(16)	0.129	0.613	0.440	2.3
H(17)	0.259	0.543	0.573	2.1
H(19)	0.520	0.517	0.715	2.3
H(20)	0.708	0.523	0.703	2.3
H(21)	0.819	0.443	0.840	2.1
H(22)	0.745	0.361	0.997	2.3
H(23)	0.558	0.355	1.016	2.1
H(25)	0.529	0.272	0.644	1.6

The average estimated standard deviations are $\sigma(x)=0.002$, $\sigma(y)=0.001$, and $\sigma(z)=0.003$ and $\sigma(B)=0.6$Å^2.

TABLE 6. LEAST-SQUARES PLANES AND DEVIATIONS OF THE ATOMS

Equation of the plane: $AX+BY+CZ=D$, where $X=ax+cz\cdot\cos\beta$, $Y=by$, $Z=cz\cdot\cos\beta$.

(I) Best plane through the TPP cation					
$0.0168X+0.5961Y+0.8027Z=4.7142$					
O	−0.005 Å	C(8)	0.245 Å	C(16)	0.338 Å
C(1)	0.041	C(9)	0.069	C(17)	0.329
C(2)	0.078	C(10)	−0.112	C(18)	−0.060
C(3)	0.013	C(11)	−0.119	C(19)	−0.086
C(4)	−0.052	C(12)	0.010	C(20)	−0.092
C(5)	−0.037	C(13)	−0.306	C(21)	−0.055
C(6)	0.058	C(14)	−0.306	C(22)	−0.040
C(7)	0.234	C(15)	0.018	C(23)	−0.049
(II) Best plane through the pyrylium ring					
$-0.0205X+0.5773Y+0.8163Z=4.3721$					
O	−0.002 Å	C(2)	0.015 Å	C(4)	−0.011 Å
C(1)	−0.012	C(3)	−0.003	C(5)	0.014
(III) Best plane through benzene ring-A					
$0.1608X+0.5625Y+0.8110Z=4.9282$					
C(6)	0.001 Å	C(8)	0.003 Å	C(10)	−0.001 Å
C(7)	−0.003	C(9)	−0.001	C(11)	0.001
(IV) Best plane through benzene ring-B					
$0.2160X+0.7150Y+0.6649Z=6.7314$					
C(12)	−0.000 Å	C(14)	−0.004 Å	C(16)	0.004 Å
C(13)	0.005	C(15)	−0.000	C(17)	−0.004
(V) Best plane through benzene ring-C					
$0.0196X+0.5815Y+0.8138Z=4.6481$					
C(18)	0.006 Å	C(20)	−0.008 Å	C(22)	0.001 Å
C(19)	0.001	C(21)	0.007	C(23)	−0.007
(VI) Best plane through the TCP anion					
$0.0680X+0.5773Y+0.8138Z=8.1201$					
C(24)	−0.001 Å	C(28)	0.036 Å	N(2)	0.053 Å
C(25)	−0.012	C(29)	0.012	N(3)	0.042
C(26)	−0.015	C(30)	−0.024	N(4)	−0.051
C(27)	−0.020	N(1)	−0.020		

TCP anion is also approximately planar, the maximum deviations from the least-squares plane being 0.053 Å (above) for N(2) and −0.051 Å (below) for N(4). However, two C–C(CN)$_2$ groups are planar within 0.0017 Å, and both tilt at an angle of 1.3° from the best plane of the anion. The large bond angle of C(24)–C(25)–C(26), 129.6°, presumably indicates a steric repulsion between the C(CN)$_2$ groups. The conjugated C–C bonds between two sp^2 carbon atoms, C(24)–C(25) = 1.388(5) and C(25)–C(26) = 1.379(5)Å, are significantly shorter than the C–C bond associated with the CN group, the average value being 1.41 Å. Molecular orbital calculation shows that the bond order is 0.61 for the former and 0.49 for the latter. The result is consistent with the observed bond lengths. The average C≡N bond length, 1.145 Å, is in agreement with that observed in other polycyanoacid anions.[5c,13)]

Crystal Structure. The packings of cations and anions in the unit cell viewed along the c and a axes are respectively shown in Figs. 3 and 4. Interionic atomic contacts less than 3.6 Å are given in Table 7.

The crystal structure consists of parallel columns

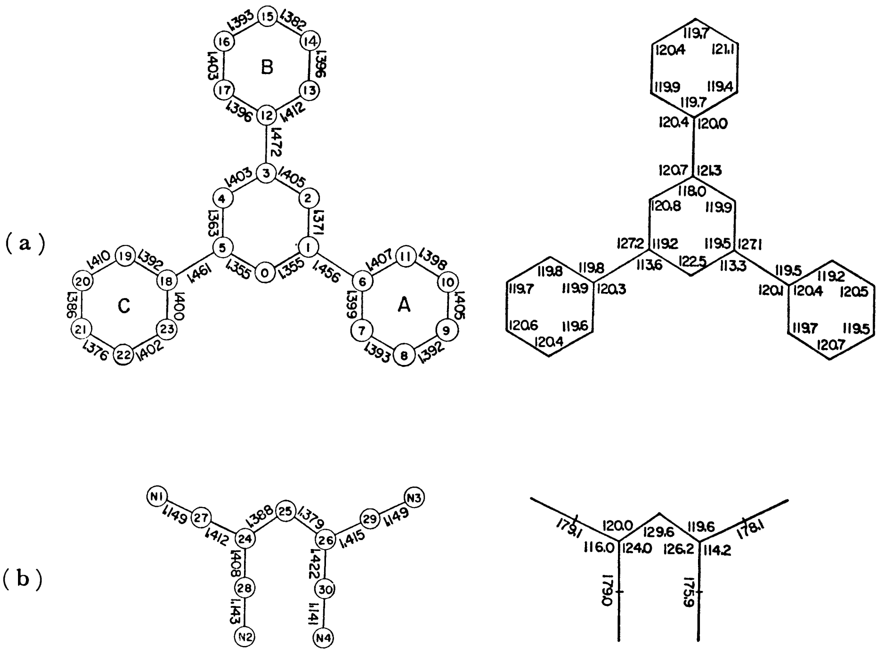

Fig. 2. Bond lengths (Å) and bond angles (°).
The estimated standard deviations are in 0.004—0.006Å for bond lengths and in 0.3—0.4° for bond angles.
(a) TPP cation, (b) TCP anion.

Table 7. Interionic atomic contacts (less than 3.6 Å)

Within an ion-pair.			
C(26)···C(5)	3.472(5) Å	N(2)···C(1)	3.512(5) Å
C(27)···C(7)	3.504(5)	N(2)···C(6)	3.468(5)
C(28)···C(1)	3.449(5)	N(4)···C(3)	3.267(5)
C(28)···C(6)	3.450(5)	N)4)···C(4)	3.417(5)
C(30)···C(4)	3.400(5)	N(4)···C(12)	3.588(5)
C(30)···C(5)	3.511(5)		
Between ion-pairs.			
N(4)$^{\mathrm{i}}$···C(11)$^{\mathrm{ii}}$	3.401(5) Å		
Between anions.			
C(25)$^{\mathrm{i}}$···N(2)$^{\mathrm{iv}}$	3.265(5) Å		
Between cations.			
C(5)$^{\mathrm{i}}$···C(19)$^{\mathrm{iii}}$	3.411(5) Å	O$^{\mathrm{i}}$···(19)$^{\mathrm{iii}}$	3.480(5) Å
C(3)$^{\mathrm{i}}$···C(21)$^{\mathrm{iii}}$	3.480(5)		
Between nonoverlapping anion and cation.			
N(3)$^{\mathrm{i}}$···C(4)$^{\mathrm{iii}}$	3.579(5) Å	N(1)···C(11)$^{\mathrm{iv}}$	3.446(5) Å
N(3)$^{\mathrm{i}}$···C(17)$^{\mathrm{iii}}$	3.520(6)	N(1)···C(21)$^{\mathrm{vi}}$	3.517(6)
N(3)$^{\mathrm{i}}$···C(19)$^{\mathrm{iii}}$	3.438(6)	N(3)···C(9)$^{\mathrm{v}}$	3.446(6)
N(1)$^{\mathrm{i}}$···C(2)$^{\mathrm{iv}}$	3.457(5)	N(4)···C(15)$^{\mathrm{vii}}$	3.439(6)

Codes for superscripts

i	x,	y,	z,	v	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$-1+z$,
ii	x,	y,	$-1+z$,	vi	$-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	z,
iii	$1-x$,	$\frac{1}{2}-y$,	$1-z$,	vii	$-x$,	$1-y$,	$1-z$,
iv	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	z,				

of infinite length along the c axis in which the cations and anions stack alternately (Fig. 4). The least-squares planes of the cation and the anion are almost parallel to the a axis, the former inclining to the c axis at 53.0° and the latter at 53.7°, and the dihedral angle between them being 3.2°. In the column, although the TCP anion is sandwiched by TPP cations and *vice versa*, the TCP anion has a larger overlap and closer contact with one of the cations than the other. Thus, the TCP anion and TPP cation can be considered to form an "ion-pair" in the crystal as a stacking unit.

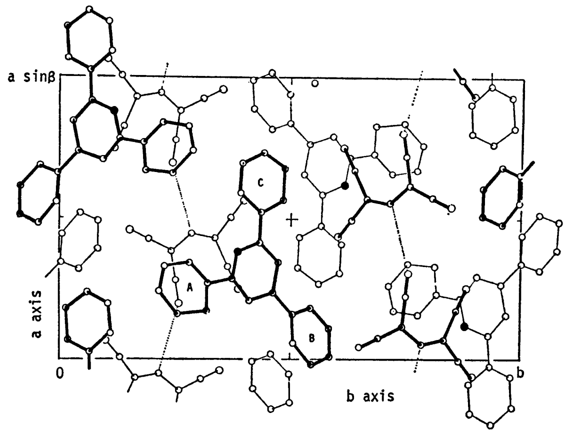

Fig. 3. The crystal structure viewed along the c axis. The dotted lines show the presence of the hydrogen bonding.

The relative arrangement between the cation and the anion in the column is shown in Fig. 5. In the ion-pair the anion overlaps mainly with the pyrylium ring of the cation. The average interplanar spacing between the best planes of the anion and the pyrylium ring is 3.31 Å, and the closest atomic contact is N(4)–C(3), 3.267(5)Å. They are slightly shorter than the corresponding van der Waals distances. In addition to the alternate arrangement and close contact of the

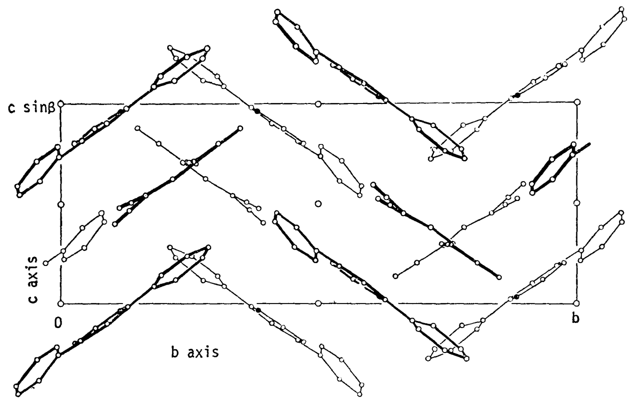

Fig. 4. The crystal structure viewed along the a axis. The benzene ring-B in each TPP cation (shown in Fig. 3) is omitted.

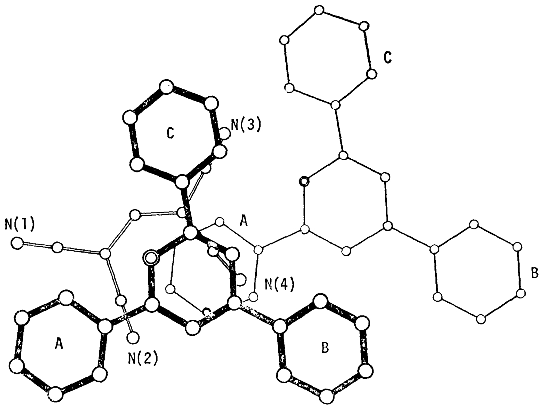

Fig. 5. The relative arrangement of the cation and the anion in the column projected on the best plane of the anion.

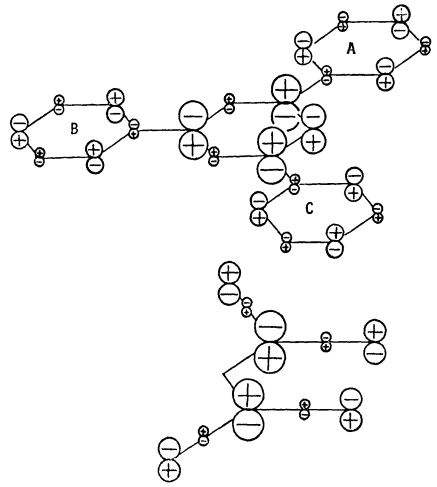

Fig. 6(a). The shapes of the lowest vacant molecular orbital of the cation and the highest occupied molecular orbital of the anion calculated by Hückel MO method using ω-technique.

The parameters were assumed as follows; the resonance integrals are $1.0\beta_0$ for all C-C bonds, $0.9\beta_0$ for two C-O bonds, and $1.2\beta_0$ for C-N bonds, and the Coulombic integrals are α_0 for all C atoms, $\alpha_0+2.5\beta_0$ for O atom, and $\alpha_0+1.0\beta_0$ for four N atoms, and the parameters $\omega=1.4$.

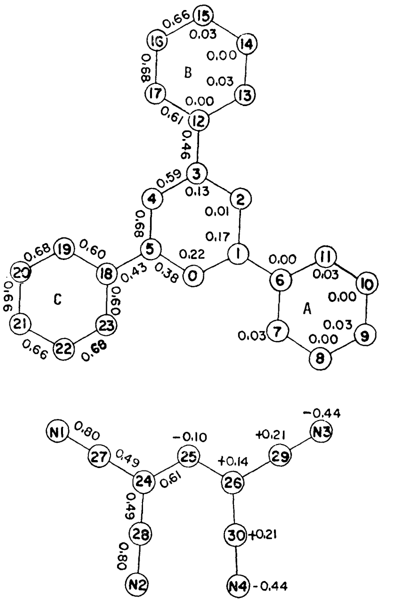

Fig. 6(b). The charge distributions (shown in the right half of the molecule) and the bond orders (shown in the left half of the molecule) calculated by Hückel MO method using ω-technique. The negative values of the charge density indicate the excess of negative charge.

two components characteristic of organic charge transfer complexes, the overlap between the highest occupied molecular orbital of the anion and the lowest vacant molecular orbital of the cation can be considered as a measure of the charge transfer interaction. The shapes of these orbitals, charge distributions and bond orders, shown in Figs. 6(a) and 6(b), were calculated by the Hückel MO method using the ω-technique.[14] However, they cannot explain the observed overlapping between the cation and the anion in terms of the interionic charge transfer interaction. Only slight coincident overlaps between the atoms are observed in Fig. 5. This does not indicate an appreciable contribution of charge transfer force on the relative arrangement of the cation and the anion.

Figure 6(b) shows that the negative charge in the anion is significantly distributed on four nitrogen atoms, whereas the positive charge in the cation is localized at the oxygen and neighboring carbon atoms in the pyrylium ring. The observed overlap of the cation with the anion in which the oxygen atom of the cation is located approximately above the center of the anion, can thus be explained mainly by the electrostatic interaction.

A short atomic contact between the C(25) atom of the TCP anion and the N(2) atom of the adjacent TCP anion along the a axis (dotted line in Fig. 3) indicates the existence of a strong interaction like hydrogen bond between anions in the neighboring columns. The C(25)···N(2)$^{\mathrm{iv}}$ and H(25)···N(2)$^{\mathrm{iv}}$ distances are 3.265(5) and 2.185(5) Å, respectively, and the C(25)–H(25)···N(2)$^{\mathrm{iv}}$ angle is 170°. Although the C–H···N hydrogen bond was scarcely observed, in the present case this type of hydrogen bond is present, which is probably caused by the activation of H(25) atom by four electron-withdrawing cyano groups. The relative

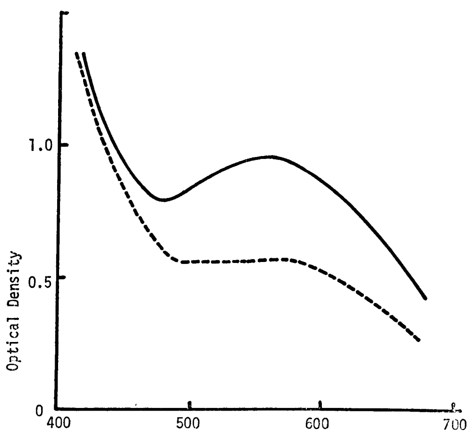

Fig. 7. Polarized absorption spectrum of TPP-TCP single crystal.
—— // c axis, ---- ⊥ c axis.

arrangement of the anion also seems to be affected by this interaction.

The tilt angles of the three benzene rings from the pyrylium ring may be affected by the degree of the overlap with the TCP anion. The C-ring, with the least tilt angle, overlaps the anion in the ion-pair where the interplanar spacing is fairly short. However, the contact between the A-ring and the anion is in the van der Waals distance, which may slightly restrict free rotation of the benzene ring (Fig. 5). On the other hand, the slight overlap observed between the B-ring and the anion allows rotation of the B-ring.

The polarized absorption spectrum of a single crystal of this salt is given in Fig. 7. The optical density of the absorption band at 535 nm, usually assigned to interionic charge transfer band, is about 1.65 times higher in the c-polarization spectrum than the other. Assuming that the direction of the transition moment is perpendicular to the planes of the anion and the cation, which is inclined to the c axis by *ca.* 37°, the ratio of two components of the dipole moment parallel and perpendicular to the c axis is given by $\cos 37°/\cos 53°$ $(=1.32)$. The dichroism ratio, therefore, is $(\cos 37°/\cos 53°)^2$, 1.74. This agrees approximately with the observed dichroism ratio. Thus the polarized absorption spectrum can be explained in terms of the crystal structure.

All the programs used for the structure analysis were written by Professor T. Ashida. The program of ω-technique used for the molecular orbital calculations was written by one of us (T. T.). Most of the calculations were carried out at Kyoto university on a FACOM 230-60 computer.

The authors wish to express their deep thanks to Prof. Masao Kakudo, and Prof. Tamaichi Ashida for their valuable suggestions and encouragement in the X-ray structure analysis, and also to Prof. Hiroshi Mikawa and Prof. Shigekazu Kusabayashi for their helpful discussions.

References

1) Organic Charge Transfer Salts. IV. Part II of this series; T. Tamamura, M. Yokoyama, S. Kusabayashi and H. Mikawa, This Bulletin, **47**, 442 (1974).

2) Present address; Welding Research Institute, Osaka University, Suita, Osaka 565.

3) To whom any correspondence should be addressed.

4) *a*) E. M. Kosower and P. A. Klinedinst, Jr., *J. Amer. Chem. Soc.*, **78**, 3493 (1956). *b*) S. F. Mason, *J. Chem. Soc.*, **1960**, 2437. *c*) E. L. Goff and R. B. LaCount, *J. Amer. Chem. Soc.*, **85**, 1354 (1963). *d*) G. Briegleb, W. Jung, und W. Herr, *Z. Phys. Chem.* (Frankfurt), **38**, 253 (1963). *e*) A. T. Balaban, M. Mocanu, and Z. Simon, *Tetrahedron*, **20**, 119 (1964).

5) *a*) S. Sakanoue, Y. Kai, N. Yasuoka, N. Kasai, and M. Kakudo, This Bulletin, **43**, 1306 (1970). *b*) K. Nakamura, N. Yasuoka, N. Kasai, H. Mikawa, and M. Kakudo, *Chem. Commun.*, **1970**, 1135. *c*) S. Sakanoue, N. Yasuoka, N. Kasai, and M. Kakudo, This Bulletin, **44**, 1 (1971).

6) T. Tamamura, H. Yasuba, K. Okamoto, T. Imai, S. Kusabayashi, and H. Mikawa, This Bulletin, **47**, 448 (1974).

7) H. Yasuba, T. Imai, K. Okamoto, S. Kusabayashi, and H. Mikawa, *ibid.*, **43**, 3101 (1970).

8) J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).

9) H. F. Hanson, F. Hermann, J. D. Lea, and S. Skillman, *ibid.*, **17**, 1040 (1964).

10) Table 5 is filed at the Chemical Society of Japan, (Document No. 7407), 1–5, Kanda-Surugadai, Chiyoda-ku, Tokyo.

11) A. Almennings, O. Bastiansen, and L. Hansen, *Acta Chem. Scand.*, **9**, 1306 (1955).

12) L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca N. Y. (1960).

13) *a*) R. Desiderato and R. L. Sass, *Acta Crystallogr.*, **18**, 1 (1965). *b*) J. Konnert and D. Britton, *Inorg. Chem.*, **6**, 1193 (1967). *c*) P. Andersen, B. Klewe, and E. Thom, *Acta Chem. Scand.*, **21**, 1530 (1967). *d*) D. A. Beoke, P. K. Gantzel, and K. N. Trueblood, *Acta Crystallogr.*, **22**, 657 (1967).

14) A Streitwieser, Jr., *J. Amer. Chem. Soc.*, **82**, 4123 (1960).