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The Crystal Structure of Quinolinium 2-Dicyanomethylene-1,1,3,3-tetracyanopropanediide, $[2(C_9NH_8)^+\cdot(C_{10}N_6)^{2-}]$

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$[2(C_9NH^8)^+\cdot(C_{10}N_6)^{2-}]$ crystallizes in the form of the space group of *Pbcn*, with four formula units in the unit cell, and the following unit-cell dimensions: $a=13.18$, $b=15.40$, and $c=11.56$ Å. The structure was determined by obtaining phases directly from the structure-factor magnitudes by means of the symbolic addition procedure. For 1580 non-zero reflections, the final R is 0.147. The crystal structure shows that the packing unit is an "ion-pair" consisting of one di-valent anion and two mono-valent cations. The anion is sandwiched by two cations with weak charge-transfer interaction between them; the closest atomic contact is 2.99 Å. These units stack infinitely, forming a column, along the a axis. Between these stacking columns, there exists a hydrogen bond (N–H···N, 2.84 Å) along the b axis. The $(C_{10}N_6)^{2-}$ anion has a C_2-2 symmetry; cyano-substituents are tilted out of the plane formed by four central carbon atoms, and the anion takes a propeller shape. The one arm is rotated 13° from the completely planar conformation, while the other two are rotated 24°. On the other hand, the $(C_9NH_8)^+$ cation seems not to be planar.

In the electronic spectra of some complexes, charge-transfer bands between organic cation and organic anion have been observed.[3] No studies have yet been reported, however, to explain the charge-transfer bands between organic cations and anions on the basis of the crystal structure.

The electronic spectra and the electrical and other physical properties of the salts of the 2-dicyanomethylene-1,1,3,3-tetracyanopropane anion and *N*-heteroaromatic cations have been studied by Sakanoue *et al.*[4] Among these substances is the quinolinium 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide. The absorption maximum of this salt at 410 nm has been assumed, on the basis of the behavior of this band in solutions, to be due to the charge-transfer interaction between the anion and the cation. This band is also observed in the solid absorption spectrum in 415 nm; the polarized absorption spectrum of single crystals was measured.[4] In order to establish the relationship between the orientation of the ions in the crystal and the polarization behavior of the band, a single-crystal structure analysis of the salts was undertaken by means of X-rays; the preliminary results have already been reported.[5] Interest in the structure of the anion in this crystal also prompted the present study in relation to the structure of the anion in the calcium salt.[6]

Experimental

Yellow crystals were obtained from a saturated aqueous solution by slow evaporation at room temperature. A small, regular-shaped crystal (about 0.20×0.22×0.24 mm) was selected.

Oscillation and Weissenberg X-ray photographs were taken, using nickel-filtered Cu$K\alpha$ radiation ($\lambda=1.5418$ Å), around the a and c axes. The unit-cell dimensions were determined from the Weissenberg photographs, on which powder diffraction patterns of tungsten ($a=3.16535$ Å) were superposed for calibration.

The crystals are orthorhombic, with the unit cell dimensions of $a=13.18$, $b=15.40$, and $c=11.56$ Å. The systematic absence of reflections, $0kl$ with $k\neq 2n$, $h0l$ with $l\neq 2n$, and $hk0$ with $h+k\neq 2n$, uniquely determined the space group to be *Pbcn*. The density, measured at 14°C by flotation in a benzene-carbon tetrachloride mixture, was 1.318 g·cm^{-3}, whereas the calculated value, assuming four formula units, $[2(C_9NH_8)^+\cdot(C_{10}N_6)^{2-}]$, per unit cell, was 1.314 g·cm^{-3}.

Using nickel-filtered Cu$K\alpha$ radiation, the intensity data were collected, by the multiple-film equi-inclination technique, for the layers from $0kl$ through $8kl$ and from $hk0$ through $hk8$.

The intensities were estimated visually, and were corrected for the Lorentz and polarization effects, but the absorption correction was ignored ($\mu=6.6$ cm^{-1} for Cu$K\alpha$). In all, 2003 independent (1580 non-zero) reflections were obtained.

Structure Determination

There were considerable difficulties in interpreting the sharpened and unsharpened Patterson maps computed from the three-dimensional data. The structure was established by obtaining phases directly from the structure-factor magnitudes by means of the symbolic addition procedure.[7]

The corrected intensity data were placed on an absolute scale, and both the structure-factor magnitude, $|F|$, and the normalized structure-factor magnitude, $|E|$, were computed (Table 1). Five reflections, with large $|E|$ magnitudes and also involving a large number of interactions in the $\sum_2$ relationship, were selected as a starting set. Positive signs were assigned to three linearly-independent reflections in order to specify the

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[3] M. Feldman and S. Winstein, *Tetrahedron Lett.*, **19**, 853 (1962); E. L. Golf and R. B. LaCount, *J. Amer. Chem. Soc.*, **85**, 1354 (1963).

[4] S. Sakanoue, T. Tamamura, S. Kusabayashi, H. Mikawa, N. Kasai, M. Kakudo, and H. Kuroda, This Bulletin, **42**, 2407 (1969).

[5] S. Sakanoue, N. Yasuoka, N. Kasai, M. Kakudo, S. Kusabayashi, and H. Mikawa, *ibid.*, **42**, 2408 (1969).

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TABLE 1. DISTRIBUTION OF NORMALIZED STRUCTURE FACTORS AND STATISTICAL AVERAGES

	Distribution of $\|E\|$		
	Theoretical (Centro-symmetric) (%)	Experimental (%)	Number of reflections
$\|E\|\geqq3.0$	0.3	0.35	7
$\|E\|\geqq2.0$	5.0	4.9	98
$\|E\|\geqq1.8$		7.9	160
$\|E\|\geqq1.6$		12.2	247
$\|E\|\geqq1.5$		14.3	289
$\|E\|\geqq1.0$	32.0	33.4	675
$<\|E\|>$	0.798	0.955	
$<\|E\|^2>$	1.000	0.709	
$<\|E\|^2-1>$	0.968	0.961	

TABLE 2. STARTING SET OF APPLICATION OF $\sum_2$ FORMULA

h	k	l	$\|E\|$	Phase
2	13	4	3.52	+
3	0	2	3.02	+
3	3	1	2.84	+
6	2	3	3.27	A
4	12	3	3.10	B

origin of the unit cell, and letter phases, A and B, were assigned to the remaining two reflections in order to facilitate the symbolic addition procedure (Table 2).

As a first step, the signs of 11 reflections out of 98, ($|E|\geqq2$), were determined by hand calculations. The determination was then carried out on a HITAC 5020E computer. After six cycles, the signs of 161 reflections were determined out of 247 reflections with $|E|\geqq1.6$ (Table 3). From the interaction list, the signs of the two letter phases were assigned as: $A=-$ and $B=+$. The E-map based on these signs permitted the approximate location of atoms, although a number of ghost peaks were present (Fig. 1). The signs of 21 reflections out of 161 were found to be falsely determined at the end of the structure determination.

Successive Fourier syntheses led to be identification of all the non-hydrogen atoms. At this stage, the calculation of structure factors with a single temperature factor, B, of 3.0 Å^2 for all the non-hydrogen atoms gave a discrepancy factor, R, of 0.34. The positional and thermal parameters of each atom were then refined by the block-diagonal least-squares procedure. In the refinement, the weight was taken as unity for all the reflections, and the hydrogen atoms were not included. Five cycles of refinement improved the R factor to 0.196. Anisotropic thermal parameters were introduced at this stage. After 3 cycles the R value converged to 0.147 for the observed non-zero reflections (the hydrogen atoms were not included in the refinement). The final atomic coordinates, along with their estimated standard deviations, are listed in Table 4. The thermal parameters are shown in Table 5, while the observed and calculated structure factors are given in Table 6. A composite drawing of the final electron density distributions viewed down along the

TABLE 3. PROCESS OF THE SYMBOLIC ADDITION PROCEDURE

Run number	Number of reflections	$\|E\|$	Number of phases determined
0			5 (starting set)
1	98	$\geqq2.0$	11 (hand calculation)
2	160	$\geqq1.8$	33 (cycle-1) 77 (cycle-2) 100 (cycle-3)
3	247	$\geqq1.6$	142 (cycle-1) 158 (cycle-2) 161 (cycle-3)

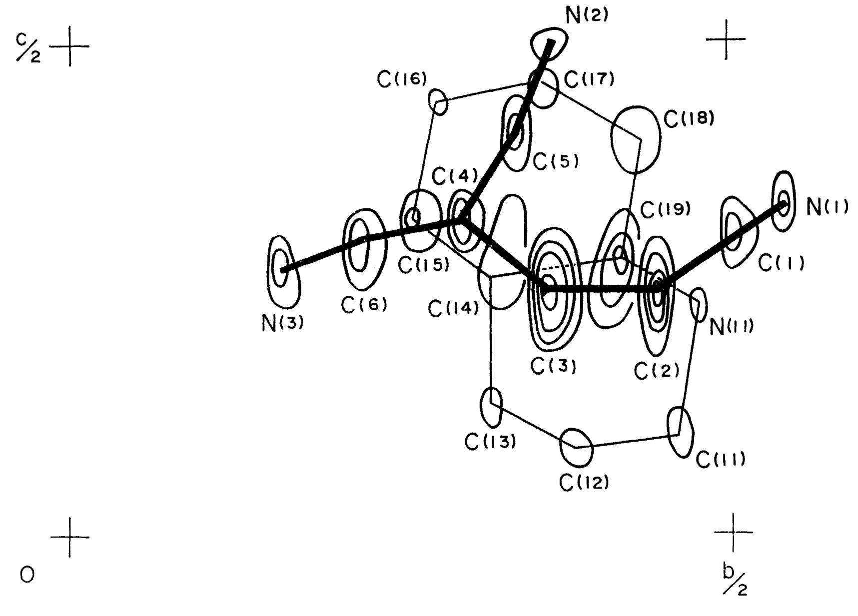

Fig. 1. The E-map computed by the use of 161 reflections (see text). Only the asymmetric unit is shown.

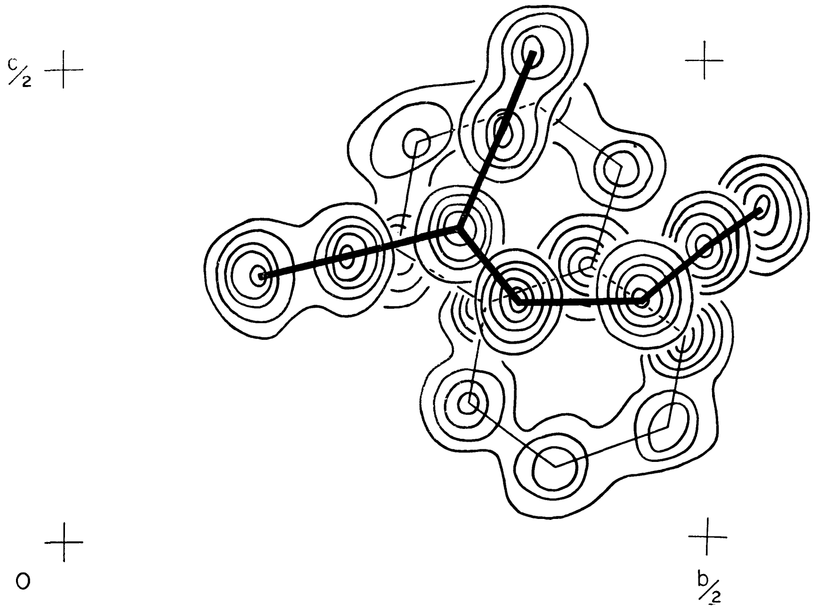

Fig. 2. The composite drawing of the final electron density viewed along the *a* axis. Contours at 1, 3, 5,…e.A^{-3}. Only the asymmetric unit is shown.

Table 4. The final atomic coordinates along with their estimated standard deviations within parentheses each multiplied by 10^4

Atom	*X*	*Y*	*Z*
N(1)	0.3600 (6)	0.5424 (4)	0.3445 (7)
N(2)	0.3516 (8)	0.3667 (5)	0.5104 (7)
N(3)	0.3741 (6)	0.1554 (4)	0.2773 (6)
C(1)	0.4223 (5)	0.4994 (4)	0.3032 (7)
C(2)	0.5	0.4494 (6)	0.25
C(3)	0.5	0.3571 (6)	0.25
C(4)	0.4324 (5)	0.3098 (4)	0.3241 (6)
C(5)	0.3879 (7)	0.3433 (5)	0.4267 (7)
C(6)	0.4015 (5)	0.2237 (5)	0.2963 (5)
N(11)	0.1772 (6)	0.4828 (6)	0.2130 (6)
C(11)	0.2265 (7)	0.4693 (6)	0.1145 (8)
C(12)	0.2454 (8)	0.3843 (7)	0.0754 (8)
C(13)	0.2133 (7)	0.3165 (5)	0.1409 (7)
C(14)	0.1607 (6)	0.3301 (4)	0.2461 (7)
C(15)	0.1252 (8)	0.2608 (6)	0.3184 (10)
C(16)	0.0776 (8)	0.2789 (8)	0.4201 (9)
C(17)	0.0606 (9)	0.3655 (8)	0.4569 (9)
C(18)	0.0920 (8)	0.4339 (7)	0.3878 (8)
C(19)	0.1430 (6)	0.4152 (5)	0.2824 (6)

Table 5. Thermal parameters along with their estimated standard deviations within parentheses each multiplied by 10^4

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	65(5)	21(3)	89(7)	23(6)	8(11)	3(7)
N(2)	125(8)	23(3)	60(6)	28(8)	95(13)	17(7)
N(3)	64(5)	20(3)	97(8)	−20(6)	25(11)	−10(7)
C(1)	46(5)	11(2)	45(6)	−7(6)	−7(9)	19(6)
C(2)	37(6)	7(3)	40(8)	0	5(12)	0
C(3)	33(6)	10(3)	28(7)	0	−1(11)	0
C(4)	42(4)	14(3)	24(5)	−3(6)	8(8)	7(6)
C(5)	72(6)	12(3)	57(7)	7(7)	11(12)	23(7)
C(6)	39(4)	18(3)	50(6)	−1(6)	4(9)	8(7)
N(11)	62(5)	16(3)	50(5)	−6(5)	−24(9)	14(6)
C(11)	64(7)	42(4)	51(7)	−18(9)	−27(12)	38(9)
C(12)	63(6)	52(5)	48(7)	5(10)	2(13)	1(10)
C(13)	64(6)	26(3)	49(7)	10(8)	−16(11)	−10(8)
C(14)	43(5)	16(3)	36(5)	−4(6)	7(9)	13(7)
C(15)	63(6)	25(4)	115(11)	−15(8)	32(14)	57(11)
C(16)	65(7)	73(7)	76(9)	−13(12)	14(14)	96(14)
C(17)	70(8)	83(7)	50(8)	28(13)	27(14)	48(13)
C(18)	71(7)	58(5)	39(7)	59(11)	2(12)	−24(10)
C(19)	41(5)	21(3)	33(6)	8(6)	−2(9)	−10(6)

The expression used is:

$$\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\}$$

a axis is shown in Fig. 2.

Calculations of the symbolic addition procedure were done with the SSGM program revised by one of the present authors (N.Y.). Almost all the calculations in this study were done on a HITAC 5020E computer at the University of Tokyo. The atomic scattering factors used in the calculations were taken from those given by Hanson and his co-workers.[8]

Description and Discussion of the Structure

Structure of the Anion and Cation. The skeleton of the ions, together with interatomic distances and angles, is illustrated in Fig. 3. The estimated standard deviations of the bond lengths and angles are about 0.015 Å and 1°, respectively.

The $(C_{10}N_6)^{2-}$ anion in this crystal has a C_2-2 symmetry instead of the C_3-3 (or approximately D_3-32) in hexahydrated calcium salt.[6] The four central carbon atoms are exactly coplanar (Table 7(a)). The three cyano-substituents, $-C(CN)_2$, are, however, tilted out of this plane; the anion takes a propeller shape. The one arm which lies on the 2-fold axis is rotated 13° from the completely planar conformation, while the

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8)* H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

TABLE 6. THE OBSERVED AND CALCULATED STRUCTURE FACTORS

K	FO	FC
H,L=	0	0
2	33	-22
4	27	-11
6	206	273
8	71	51
10	111	-109
12	41	38
14	13	18
16	8	-10
18	14	9
H,L=	1	0
1	56	-14
3	147	152
5	39	21
7	175	155
9	80	-64
11	11	7
13	83	-82
15	73	77
17	0	3
19	91	36
H,L=	2	0
0	74	-42
2	170	-147
4	19	23
6	72	-61
8	0	-8
10	21	-26
12	0	-4
14	83	84
16	23	20
18	24	19
H,L=	3	0
1	238	242
3	36	-41
5	197	177
7	48	-29
9	35	-22
11	105	100
13	64	60
15	39	-36
17	10	15
19	19	-15
H,L=	4	0
0	403	-473
2	138	119
4	49	-39
6	11	-6
8	10	-20
10	89	90
12	90	-88
14	47	-44
16	41	47
18	25	-22
H,L=	5	0
1	83	-76
3	113	-106
5	165	-141
7	159	-147
9	42	25
11	137	-144
13	69	65
15	10	-12
17	0	-12
H,L=	6	0
0	137	-110
2	118	107
4	83	-61
6	56	48
8	36	-22
10	79	-80
12	0	11
14	37	-31
16	22	-27
18	38	-31
H,L=	7	0
1	100	91
3	7	-4
5	37	-33
7	23	-17
9	21	-21
11	138	-149
13	67	-67
15	0	-1
17	19	-17
H,L=	8	0
0	121	86
2	7	-3
4	104	-90
6	88	-75
8	0	8
10	127	-136
12	13	-16
14	8	-8
16	49	-52
H,L=	9	0
1	21	9
3	8	-1
5	60	-49
7	56	58
9	44	-39
11	35	6
13	14	23
H,L=	10	0
0	27	-20
2	30	-25
4	63	64
6	9	-2
8	0	-2
10	24	-21
12	0	-7
14	42	40
H,L=	11	0
1	26	25
3	32	-32
5	26	-22
7	44	43
9	23	-22
11	21	25
13	17	18
H,L=	12	0
0	60	54
2	32	31
4	20	16
6	0	12
8	8	12
10	27	28
H,L=	13	0
1	13	11
3	24	20
5	26	29
7	24	23
9	12	15
H,L=	14	0
0	62	57
2	0	10
4	11	-2
6	10	9
8	20	-25
H,L=	15	0
1	39	35
3	0	8
5	34	34
H,L=	16	0
0	13	13
2	0	0
4	10	-13
H,L=	0	1
2	347	432
4	23	-14
6	119	114
8	29	28
10	74	-61
12	100	99
14	31	28
16	27	28
18	70	66
H,L=	1	1
2	44	-47
3	101	-100
4	102	99
5	193	-202
6	113	112
7	53	44
8	41	34
9	13	0
10	25	18
11	19	-10
12	77	84
13	65	-63
14	0	-4
15	12	14
16	26	-27
17	16	-21
H,L=	2	1
1	45	-53
2	17	-15
3	10	5
4	9	3
5	251	250
6	26	-24
7	60	-50
8	9	-10
9	60	-40
10	28	-21
11	0	-5
12	66	-67
13	15	-6
14	56	-55
15	24	-24
16	16	3
17	14	-13
18	29	-30
H,L=	3	1
1	192	216
2	337	-367
3	144	152
4	76	64
5	178	173
6	30	11
7	136	129
8	13	-15
9	31	32
10	26	-24
11	29	26
12	0	-5
13	60	57
14	0	3
15	22	-23
16	0	-4
17	33	33
H,L=	4	1
1	151	144
2	117	107
3	71	67
4	16	-12
5	5	-15
6	41	29
7	17	-12
8	118	110
9	47	42
10	85	76
11	20	16
12	36	-35
13	0	-15
14	47	-49
15	10	6
16	19	-16
17	8	20
18	38	-41
H,L=	5	1
1	108	-97
2	56	51
3	96	78
4	16	11
5	118	106
6	106	-88
7	112	-107
8	0	3
9	7	2
10	26	24
11	49	-47
12	0	-4
13	65	-61
14	0	3
15	42	-42
16	9	0
H,L=	6	1
1	31	19
2	23	18
3	18	5
4	6	-4
5	136	-134
6	12	-4
7	61	-56
8	24	17
9	40	31
10	8	11
11	26	-27
12	31	-26
13	27	-27
14	50	56
15	29	36
16	6	9
H,L=	7	1
1	25	-16
2	27	-26
3	41	25
4	12	-5
5	75	-71
6	39	35
7	24	21
8	0	11
9	53	46
10	24	-29
11	33	-14
12	23	-13
13	19	-36
14	19	23
15	8	12
H,L=	8	1
1	21	14
2	35	-31
3	0	0
4	75	67
5	0	-2
6	58	-53
7	50	47
8	52	-45
9	0	4
10	0	2
11	8	7
12	44	-42
13	24	26
14	0	-3
15	0	-2
H,L=	9	1
1	55	49
2	39	38
3	37	33
4	27	24
5	52	-39
6	26	23
7	22	17
8	12	-2
9	51	47
10	0	1
11	29	-32
12	0	1
13	0	-5
14	9	-14
15	47	51
H,L=	10	1
1	40	-37
2	14	-12
3	16	-17
4	39	35
5	25	23
6	17	13
7	0	-1
8	64	62
9	0	-8
10	0	8
11	0	1
12	0	-12
13	0	1
14	27	-31
H,L=	11	1
1	54	47
2	17	14
3	15	13
4	26	-26
5	45	39
6	0	12
7	0	-14
8	0	-14
9	0	7
10	0	-3
11	0	-5
12	0	6
13	17	-20
H,L=	12	1
1	0	-5
2	52	51
3	0	2
4	0	4
5	0	3
6	0	-1
7	0	10
8	43	47
9	0	-9
H,L=	13	1
1	0	-14
2	0	11
3	0	-14
4	0	-10
5	0	9
6	0	-20
7	0	-2
8	16	-16
9	0	5
10	16	17
H,L=	14	1
1	0	-4
2	27	31
3	0	-2
4	0	-18
5	0	0
6	0	11
7	0	5
8	22	-25
9	13	-15
10	11	-13
H,L=	15	1
1	0	6
2	0	-2
3	0	17
4	0	-9
5	26	-27
6	0	7
7	37	40
H,L=	0	2
0	392	-474
2	79	-64
4	323	-314
6	148	-114
8	118	83
10	26	-16
12	122	-125
14	9	8
16	16	13
18	12	-22
H,L=	1	2
0	103	116
1	24	-17
2	103	-95
3	161	-152
4	66	54
5	40	-27
6	99	-93
7	40	26
8	37	-24
9	19	-10
10	77	-77
11	17	-5
12	37	29
13	75	70
14	51	45
15	70	-67
16	15	-21
17	20	-20
18	24	20
H,L=	2	2
0	50	-49
1	112	109
2	39	-17
3	116	114
4	44	26
5	167	152
6	31	23
7	146	131
8	40	-24
9	95	-77
10	22	15
11	70	65
12	46	45
13	80	-73
14	36	-24
15	0	6
16	26	-26
17	7	-5
18	6	-5
H,L=	3	2
0	606	738
1	307	-366
2	40	-34
3	227	233
4	115	79
5	66	-55
6	60	51
7	145	-128
8	26	-21
9	44	32
10	8	-9
11	15	7
12	13	9
13	73	-73
14	0	-5
15	16	4
16	10	5
17	15	7
18	7	11
H,L=	4	2
0	245	203
1	151	-132
2	43	-27
3	11	-7
4	96	83
5	42	-28
6	34	-23
7	55	46
8	7	0
9	0	1
10	40	31
11	67	61
12	81	78
13	0	10
14	21	-24
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TABLE 6 (continued)

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9	24	24
10	25	-18
11	32	31
H,L=	12	6
0	44	-47
1	38	41
2	10	8
3	0	12
4	0	0
5	21	-19
6	13	13
7	5	11
8	8	7
9	23	-21
H,L=	13	6
0	33	-39
1	18	23
2	18	-19
3	20	-19
4	32	11
5	8	27
H,L=	14	6
0	13	14
1	15	12
2	13	1
3	7	-5
4	10	-1
5	6	-8
6	16	20
H,L=	0	7
2	107	-83
4	100	-101
6	44	-51
8	50	-58
10	10	-7
12	50	38
14	13	-15
16	30	25
H,L=	1	7
1	7	5
2	8	-17
3	54	-51
4	7	6
5	39	34
6	70	62
7	30	29
8	9	-9
9	92	-91
10	74	-77
11	0	4
12	14	11
13	30	28
H,L=	2	7
1	0	11
2	35	35
3	0	-3
4	38	-39
5	21	15
6	0	11
7	89	90
8	25	21
9	78	69
10	10	-5
11	14	-9
12	50	54
13	14	11
14	0	-4
15	24	31
16	0	-4
17	38	-30
H,L=	3	7
1	22	-19
2	39	32
3	47	-41
4	49	49
5	34	27
6	46	-34
7	35	-36
8	0	0
9	0	-1
10	10	10
11	20	24
12	10	3
13	10	5
14	10	8
H,L=	4	7
1	38	30
2	7	6
3	0	8
4	0	2
5	28	-29
6	0	-2
7	25	-21
8	17	-15
9	23	-22
10	27	-24
11	34	-29
12	11	4
13	11	-14
14	10	2
H,L=	5	7
1	11	-16
2	0	0
3	0	-11
4	87	-60
5	45	-32
6	9	4
7	10	-6
8	60	48
9	29	25
10	33	33
11	10	10
12	0	-1
13	30	36
14	13	9
H,L=	6	7
1	69	-69
2	56	-54
3	26	29
4	58	60
5	34	36
6	20	17
7	76	-77
8	49	-41
9	25	-14
10	25	25
11	9	21
12	31	-11
13	0	8
14	14	26
H,L=	7	7
1	71	-64
2	13	10
3	9	-6
4	0	-9
5	52	-48
6	17	-12
7	25	-26
8	49	-47
9	25	-19
10	0	9
11	0	0
12	15	-21
13	0	19
14	15	-15
H,L=	8	7
1	32	-23
2	69	-64
3	35	-22
4	0	-3
5	0	13
6	10	-8
7	49	54
8	32	-33
9	0	-3
10	0	-10
11	31	25
12	0	-10
13	27	28
H,L=	9	7
1	45	-38
2	0	-11
3	10	20
4	48	50
5	31	27
6	36	33
7	20	-16
8	9	-7
9	9	16
10	0	-7
11	24	22
H,L=	10	7
1	10	16
2	0	-18
3	0	-7
4	14	-2
5	26	-27
6	19	-7
7	0	-3
8	0	5
9	0	8
10	0	-5
11	17	-23
12	24	21
H,L=	11	7
1	0	17
2	0	17
3	0	-13
4	0	-9
5	0	1
6	0	-18
7	0	-20
8	20	21
H,L=	12	7
1	38	36
2	27	-27
H,L=	13	7
1	16	21
2	24	-28
H,L=	0	8
0	21	-17
2	69	64
4	79	-70
6	10	17
8	79	-68
10	82	-75
12	16	-16
14	19	-23
H,L=	1	8
0	16	-13
1	24	-21
2	79	80
3	32	-19
4	53	51
5	57	-45
6	10	24
7	10	-15
8	28	22
9	47	37
10	0	0
11	91	-95
12	51	-48
13	0	-1
14	44	-37
H,L=	2	8
0	72	-64
1	31	23
2	47	44
3	32	-31
4	40	-38
5	0	-12
6	80	-76
7	105	-109
8	23	18
9	31	-39
10	31	-33
11	0	-5
12	25	-22
H,L=	3	8
0	102	-92
1	47	37
2	22	-20
3	37	-36
4	0	-9
5	17	24
6	21	27
7	19	16
8	52	-42
9	82	-76
10	16	12
11	0	8
12	15	-24
13	0	6
14	37	-37
15	0	-20
16	27	31
H,L=	4	8
0	64	54
1	13	7
2	27	-19
3	9	16
4	76	74
5	47	44
6	15	11
7	23	-25
8	0	6
9	20	18
10	23	-17
11	0	-11
12	0	8
H,L=	5	8
0	45	42
1	55	55
2	36	-25
3	21	20
4	101	-105
5	19	-22
6	28	-16
7	52	45
8	0	0
9	31	-32
10	0	-4
11	0	1
12	0	3
13	16	13
14	0	3
15	37	40
H,L=	6	8
0	133	135
1	61	-55
2	49	-54
3	51	-45
4	45	-35
5	26	25
6	68	64
7	0	1
8	29	23
9	0	3
10	0	2
11	18	17
12	0	0
13	0	-16
14	24	26
H,L=	7	8
0	64	64
1	59	63
2	0	-3
3	30	23
4	23	13
5	23	20
6	35	32
7	0	8
8	16	11
9	0	2
10	0	-5
11	0	7
12	20	18
H,L=	8	8
0	51	39
1	11	9
2	31	28
3	26	29
4	16	18
5	39	-31
6	40	42
7	0	7
8	0	-15
9	15	-12
10	0	11
11	0	5
12	26	-23
H,L=	9	8
0	0	9
1	0	-3
2	0	-2
3	48	-15
4	0	40
5	11	13
6	22	-9
7	0	-20
8	0	-2
9	0	4
10	0	-5
11	0	6
12	22	-20
H,L=	10	8
0	11	7
1	30	27
2	23	20
3	22	20
4	0	-14
5	0	5
6	0	-15
7	17	26
8	0	-14
9	0	-3
10	0	-1
11	20	18
H,L=	11	8
0	42	-39
1	0	7
2	0	13
3	0	-5
4	20	18
5	24	19
6	30	-31
7	12	-6
H,L=	12	8
0	0	6
1	0	-9
2	0	-5
3	0	-4
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H,L=	13	8
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1	0	-10
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3	20	-12
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H,L=	0	9
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4	37	-38
6	28	14
8	20	21
10	33	-32
H,L=	1	9
1	43	-40
2	0	-9
3	18	0
4	61	-60
5	42	50
6	37	44
7	32	-29
8	42	45
9	13	12
10	18	25
11	0	-5
12	0	16
13	0	-6
14	31	31
H,L=	2	9
1	28	-28
2	24	26
3	24	20
4	75	63
5	24	17
6	43	-40
7	29	-24
8	14	6
9	93	-92
10	43	49
11	29	-34
12	32	-30
13	10	7
14	9	-12
H,L=	3	9
1	65	60
2	31	31
3	28	15
4	111	-121
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6	28	-26
7	57	54
8	0	-12
9	14	10
10	0	2
11	12	-26
12	11	-10
13	10	-17
H,L=	4	9
1	14	23
2	35	39
3	0	19
4	14	3
5	14	16
6	0	9
7	46	49
8	46	41
9	20	14
10	13	-4
11	0	10
12	0	-15
13	10	16
H,L=	5	9
1	29	25
2	62	47
3	46	37
4	25	14
5	14	-5
6	0	14
7	0	7
8	0	-1
9	45	39
10	0	-4
11	0	0
12	0	7
13	35	-36
14	27	-34
H,L=	6	9
1	13	22
2	50	42
3	40	-43
4	23	-30
5	0	-14
6	0	-7
7	0	4
H,L=	7	9
1	28	24
2	0	-1
3	0	1
4	34	37
5	0	3
6	0	6
7	0	7
8	0	1
9	12	-10
10	11	-11
11	10	2
12	25	30
H,L=	0	10
0	39	31
2	42	42
4	77	78
6	65	-52
8	67	66
10	29	40
12	22	22
14	30	35
H,L=	1	10
0	41	-42
1	0	-17
2	0	11
3	31	-24
4	65	-62
5	27	21
6	73	-69
7	59	59
8	0	0
9	0	13
10	0	0
11	49	51
H,L=	2	10
0	21	-16
1	67	-60
2	39	-35
3	67	58
4	42	29
5	47	41
6	0	1
7	20	-6
8	24	-19
9	33	39
10	32	40
11	0	-5
12	39	38
H,L=	3	10
0	39	-29
1	15	7
2	55	57
3	80	75
4	0	9
5	14	-2
6	20	-16
7	14	-21
8	0	-12
9	30	34
10	17	-15
11	0	0
12	14	10
13	8	0
H,L=	4	10
0	57	-61
1	40	-48
2	15	16
3	0	6
4	0	4
5	45	-46
6	14	18
7	0	-19
8	14	-22
9	0	12
H,L=	5	10
0	0	-3
1	0	-18
2	21	17
3	47	-50
4	15	-20
5	0	-7
6	14	-3
7	49	-47
8	45	54
9	12	-9
10	26	-22
11	0	-2
12	12	-14
13	6	7
H,L=	6	10
0	62	-63
1	48	50
2	0	-5
3	0	-7
4	33	-36
5	13	-2
6	13	-7
7	0	21
8	0	17
9	22	-21
H,L=	0	11
2	71	-59
4	123	130
6	45	37
8	20	5
10	12	2
12	37	45
H,L=	1	11
1	0	-13
2	0	-24
3	62	-63
4	58	54
5	0	8
6	28	-26
7	13	0
8	34	-30
H,L=	2	11
1	0	-11
2	15	-7
3	49	-36
4	0	-7
5	21	21
6	30	-43
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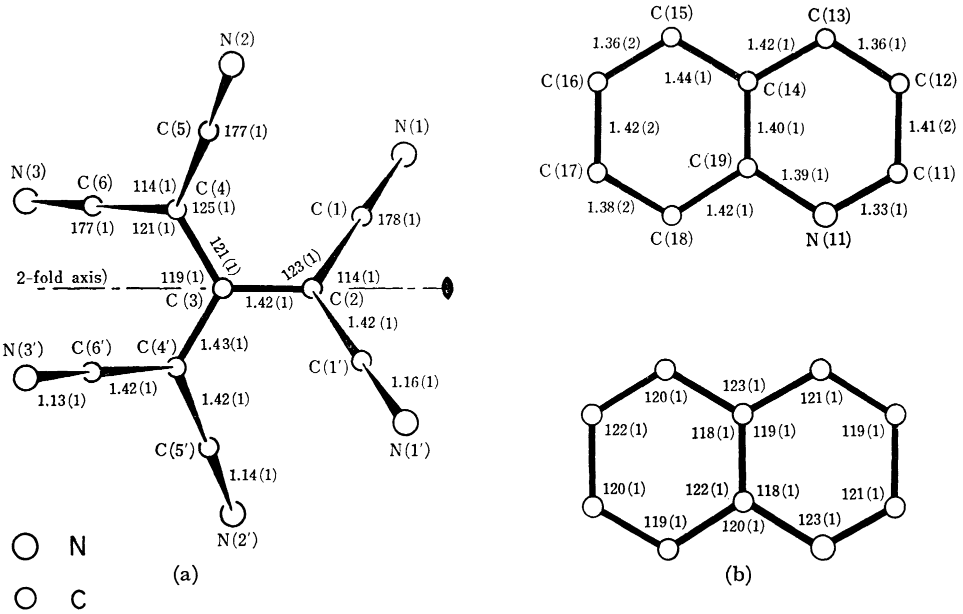
8	31	-29
9	26	22
10	27	-26
11	10	-3
H,L=	3	11
1	15	-22
2	0	-10
3	15	16
4	21	20
5	15	16
6	14	-17
7	0	-24
8	13	9
9	12	8
10	11	1
H,L=	5	11
1	15	-2
2	0	19
3	0	17
4	0	1
5	32	-39
6	37	-34
7	13	-8
8	33	40
9	32	-31
10	31	33
11	25	-31
H,L=	6	11
1	0	-7
2	0	-8
3	0	11
4	0	-16
5	0	11
6	0	9
7	0	5
8	15	-37
9	0	-15
10	20	28
H,L=	7	11
1	0	-14
2	0	-3
3	0	1
4	0	-6
5	0	10
6	0	-3
7	27	29
H,L=	0	12
0	0	5
2	64	-62
4	58	-49
6	27	20
8	13	-29
10	33	-36
H,L=	1	12
0	0	12
1	60	58
2	0	-20
3	31	-32
4	26	19
5	0	-9
6	0	8
7	0	-1
8	0	0
H,L=	2	12
0	17	14
1	0	-10
2	0	6
3	16	8
4	36	32
5	16	12
6	0	13
7	14	-4
8	23	-23
9	0	9
10	0	-2
11	18	30
H,L=	3	12
0	23	8
1	16	-24
2	0	20
3	23	-36
4	66	51
5	15	0
6	14	-14
7	0	-1
8	0	0
9	11	-26
10	13	11
H,L=	4	12
0	16	21
1	0	12
2	16	19
3	16	-16
4	15	-8
5	51	51
6	48	-36
7	13	17
H,L=	5	12
0	39	44
1	0	15
2	0	2
3	26	38
4	0	-26
5	0	11
6	0	-4
7	22	26
H,L=	6	12
0	42	33
H,L=	0	13
2	26	7
4	29	-38
6	29	26
H,L=	2	13
1	15	-17
2	15	28
3	0	-18
4	20	-6
5	36	40
H,L=	3	13
1	20	30
2	14	1
3	0	-4
4	30	30
5	22	-32
6	16	10
7	10	12
8	9	25
H,L=	4	13
1	0	12
2	0	13
3	27	-36
4	37	38
5	12	-11
H,L=	5	13
1	27	26
2	29	27
3	12	8
4	0	2
5	41	9



(c) Non-bonded distances in the anion (Å)

N(1)-N(1')	4.29(2)	C(1)-C(1')	2.39(2)
N(1)-N(2)	3.32(1)	C(1)-C(5)	2.83(1)
N(2)-N(3)	4.24(1)	C(5)-C(6)	2.39(1)
N(3)-N(3')	3.38(2)	C(6)-C(6')	2.81(2)
		C(2)-C(4)	2.48(1)
		C(4)-C(4')	2.47(2)

Fig. 3. Interatomic distances and angles in the anion and the cation, together with the e.s.d.'s in parentheses.

TABLE 7.

(a) Equations of the least-squares planes through atoms in the ion pair

Least-squares plane[a]	Atom	Deviation (Å)	Least-squares plane[a]	Atom	Deviation (Å)
$(C_{10}N_6)^{2-}$ ion:				C(6)	−0.008
1) $-0.6934X-0.0000Y-0.7205Z$	C(2)	0.000		N(3)	0.008
$+6.6499=0$	C(3)	−0.000		C(3)	0.007
	C(4)	0.000	$(C_9NH_8)^+$ ion:		
	C(4')	0.000	4) $-0.8794X-0.0007Y-0.4762Z$	N(11)	−0.016
2) $-0.5109X-0.0000Y-0.8596Z$	N(1)	0.003	$+3.2136=0$	C(11)	−0.045
$+5.4854=0$	C(1)	−0.006		C(12)	−0.048
	C(2)	0.000		C(13)	−0.036
	C(3)	0.000		C(14)	−0.006
	C(1')	0.006		C(15)	0.008
	N(1')	−0.004		C(16)	−0.001
3) $-0.7732X+0.3597Y-0.5224Z$	N(2)	0.001		C(17)	−0.001
$+4.6323=0$	C(5)	0.006		C(18)	0.009
	C(4)	−0.014		C(19)	−0.002

(b) Dihedral angles

between the planes 1) and 2):	13.2°	between the planes 1) and 3):	24.2°

a) *X*, *Y*, and *Z* are the coordinates corresponding to the crystal axes *a*, *b*, and *c*, respectively.

rest are 24° (Table 7(b)). In the calcium salt[6] all the tilt angles are reported to be 24°. Each bond distance and bond angle show an accordance, within the limits of error, with the corresponding distance of the same anion in the calcium salt,[6] except for the C(2)–C(1)–N bond angle, where the difference slightly exceeds three times the estimated standard deviation. The non-bonded N···N distances show a shortening due to the above-mentioned tilt of the cyano-substituents: the N(1)···N(2) distance is 3.32(2), and the N(3)···N(3') distance, 3.38(2) Å, while 3.48 and 3.48 Å are the corresponding distances in the calcium salt.

TABLE 8. INTERATOMIC DISTANCES WITHIN THE ION-PAIR (LESS THAN 3.8 Å), ALONG WITH THEIR E.S.D.'S IN PARENTHESES

N(1)-N(11)	2.99(1) Å
C(6)-C(13)	3.38(1)
N(1)-C(11)	3.38(1)
C(1)-N(11)	3.40(1)
C(1)-C(11)	3.41(1)
N(1)-C(19)	3.54(1)
C(4)-C(13)	3.58(1)
C(6)-C(14)	3.62(1)
N(3)-C(13)	3.62(1)
C(5)-C(14)	3.66(1)
N(3)-C(15)	3.69(1)
C(6)-C(15)	3.69(1)
C(4)-C(14)	3.71(1)
C(5)-C(19)	3.80(1)

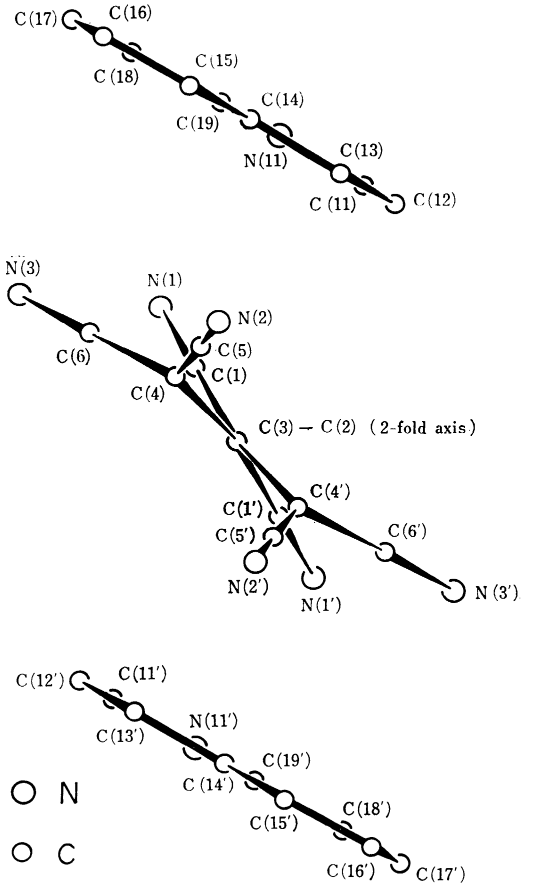


TABLE 9. INTERATOMIC DISTANCES BETWEEN THE ION-PAIRS (LESS THAN 3.8 Å) ALONG WITH THEIR E.S.D.'S IN PARENTHESES

$C(19)-C(18)^{i}$	3.68(1) Å
$C(14)-C(17)^{i}$	3.78(2)
$C(15)-C(15)^{i}$	3.66(2)
$C(14)-C(16)^{i}$	3.76(2)
$N(1)-N(3)^{ii}$	3.63(1)
$N(1)-C(15)^{ii}$	3.38(1)
$C(19)-N(3)^{ii}$	3.71(1)
$N(11)-N(3)^{ii}$	2.84(1) (hydrogen bond)
$C(11)-N(3)^{ii}$	3.68(1)
$N(1)-C(11)^{iii}$	3.59(1)
$N(1)-C(12)^{iii}$	3.27(1)
$N(2)-C(11)^{iii}$	3.25(1)
$C(18)-C(11)^{iii}$	3.50(2)
$C(16)-C(4)^{iv}$	3.78(1)
$C(16)-C(5)^{iv}$	3.59(2)
$C(17)-C(6)^{iv}$	3.80(2)
$C(13)-C(5)^{v}$	3.74(1)

Key for superscripts:

i	$-x$,	y,	$1/2-z$
ii	$1/2-x$,	$1/2+y$,	z
iii	x,	$1-y$,	$1/2+z$
iv	$-1/2+x$,	$1/2-y$,	$1-z$
v	$1/2-x$,	$1/2-y$,	$-1/2+z$

From these facts, it may be concluded that the steric repulsions between cyano-groups in adjacent arms are considerably increased by the reduction of the tilt angle of the arm which lies on the 2-fold axis from 24° to 13°, while the π-overlap is increased a little, and that these effects may be due to weak interaction between the anion and the cation.

The quinolinium cation, $(C_9NH_8)^+$, was expected to be planar, but an intersting tendency is observed for the C(11), C(12), and C(13) atoms to deviate slightly toward the anion from the least-squares plane (Table 7(a)). Of these deviated atoms, C(11) makes close contact with N(1) and C(1), which belong to the arm of the anion having the smallest tilt angle. C(13) is also located close to C(6), C(4), and N(3) of a different arm of the anion (Table 8).

Crystal Structure. The crystal structure viewed down the *a* and *b* axes is shown in Fig. 4. The packing unit of the crystal is an ion pair consisting of one divalent anion and two mono-valent cations, and the anion lies on a crystallographic 2-fold axis between two cations forming a sandwich structure. The tilt angle of the plane of the cation to the *a* axis is about 60°. The N(1)-N(11) distance is 2.99(1) Å (Fig. 5), which is the closest atomic contact between ions in this unit. These sandwiched units stack infinitely, forming a column, along the *a* axis (Fig. 4(b)). The polarized absorption spectra of a single crystal of this

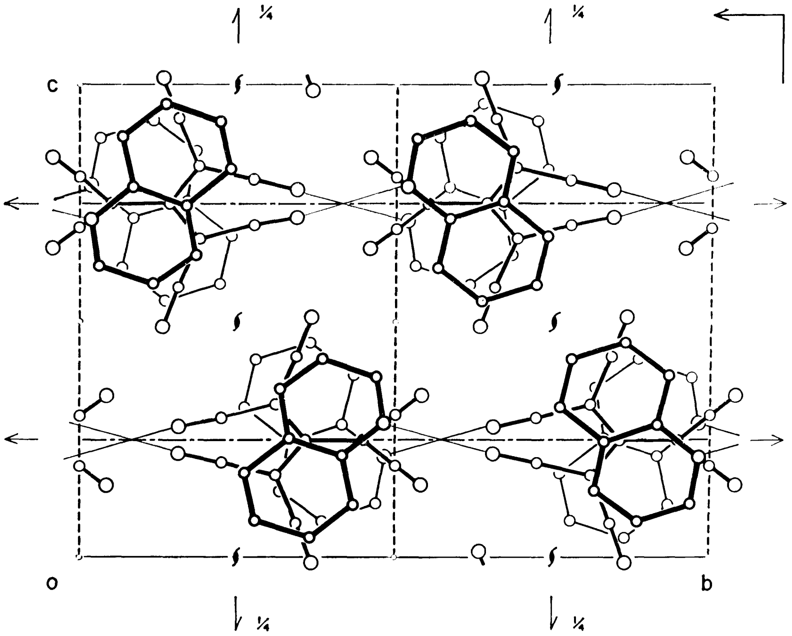


Fig. 4(a). Crystal stustructure viewed down along the *a* axis. Hydrogen bondings are shown by thin solid lines.

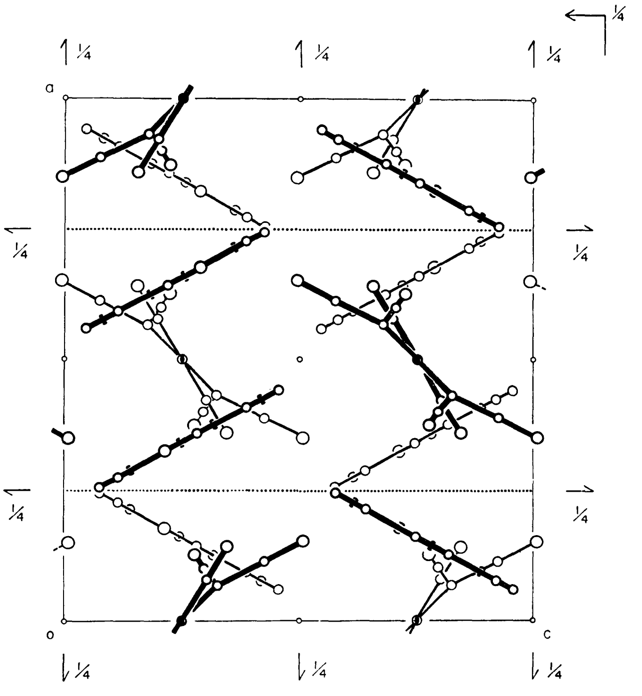


Fig. 4(b). Crystal structure viewed down along the *b* axis.

complex was measured.[4] The optical density of the charge-transfer band at 415 nm is much higher in the *a*-polarization spectrum than in the *c*-polarization spectrum. This result can be explained well in terms of the crystal structure (see Fig. 4(b)) as being due to the charge-transfer phenomenon between ions within the ion pair.

In the contacts between these stacks, the hydrogen bond exists along the *b* axis between the N(3) atom of one unit and the N(11) of the other unit, and the distance is 2.84(1) Å. Some close inter-ionic atomic contacts, including the hydrogen bond, are shown in Table 9.

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