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The Crystal Structure of 1-Ethyl-2-methylquinolinium Iodide, $[(C_{12}H_{14}N)^+ \cdot I^-]$

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The crystal structure of an organic charge-transfer complex, 1-ethyl-2-methylquinolinium iodide, $[(C_{12}H_{14}N)^+ \cdot I^-]$, has been determined by means of three-dimensional X-ray data (Mo$K\alpha$). The crystals are monoclinic, space group $P2_1/c$, and have four formula units in a unit cell with the dimensions of $a=7.187\pm0.002$, $b=15.914\pm0.002$, $c=10.331\pm0.002$ Å, and $\beta=94.67\pm0.01°$. The structure is built up from an iodide anion and a planar 1-ethyl-2-methylquinolinium cation, which lie roughly on a plane. The cations are stacked approximately parallel to the a-plane, forming an endless column along the a axis; the interplanar spacings of these cations are alternately 3.4 and 3.6 Å. The iodide anions are located in the spaces between these columns and the ethyl groups of the cations. The closest distance between an iodide anion and the carbon atoms of a 1-ethyl-2-methylquinolinium ring is 3.93 Å.

The charge-transfer interaction of *N*-heteroaromatic iodide complexes in solution, in particular, the solvent effect and the effect of different cations on the transition energies, has been studied by Kosower[1] and by Mason.[2] The characteristic coloration of these complexes in the solid state seems to be due to the interaction between the *N*-heteroaromatic cation and the iodide anion.

It seemed that it would be interesting to obtain

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1) E. M. Kosower, *J. Amer. Chem. Soc.*, **80**, 3253, 3261, and 3267 (1958).

2) S. F. Mason, *J. Chem. Soc.*, **1960**, 2437.

information on the crystal structure by which to elucidate the charge-transfer interaction. A series of crystal structure analyses of several organic charge-transfer complexes has thus been carried out, and some preliminary results have already been reported.[3,4] This paper will deal with the crystal structure determination of 1-ethyl-2-methylquinolinium iodide, $[(C_{12}H_{14}N)^+ \cdot I^-]$.

Experimental

Yellowish-green crystals of 1-ethyl-2-methylquinolinium iodide, $[(C_{12}H_{14}N)^+ \cdot I^-]$, were supplied by Professor Hiroshi Mikawa of this university. A small, regular-shaped crystal was selected for investigation. Although the approximate cell dimensions had previously been determined by Neuhaus,[5] they were redetermined accurately on a Rigaku on-line controlled four-circle diffractometer with Mo$K\alpha_1$ radiation (λ=0.70926 Å).

The crystals obtained by the recrystallization from an ethanol solution are monoclinic with unit cell dimensions of $a=7.187\pm0.002$, $b=15.914\pm0.002$, $c=10.331\pm0.002$ Å, and $\beta=94.67°\pm0.01$. The density, 1.689 g·cm^{-3}, was determined at 14°C by flotation in a carbon tetrachloride-methyl iodide mixture, while the calculated value is 1.687 g·cm^{-3}, assuming four formula units per unit cell.

The space group, $P2_1/c$, was uniquely determined from the systematic absences of reflections ($h0l$ with $l\neq2n$, $0k0$ with $k\neq2n$).

The intensity data were collected at room temperature on the diffractometer by the ω-2θ scan technique:

Range of ω-scan$=1.0°+0.35\tan\theta_c$ and

Starting angle of the scan$=\theta_s-0.5°$,

where θ_c is the calculated value of the Bragg angle of the reflection to be measured. At the end of each scan the background scattering was measured for 10 sec by the stationary-crystal stationary-counter technique. The intensity was then corrected for the background scattering and for the Lorentz-polarization effects on an Aicom-C2 computer attached to the diffractometer. All the reflections within a range of $(\sin\theta)/\lambda=0.57$ were measured; in all, 1841 independent non-zero reflections were obtained.

Determination of the Structure

The position of the iodide anion was readily deduced from a three-dimensional Patterson map; the positions of the remaining atoms were found on successive three-dimensional electron density maps based on the phases determined by the iodide anion. The calculation of the structure factors with an isotropic temperature factor, B, of 3.0 Å^2 for all non-hydrogen atoms gave a discrepancy factor, $R=\sum||F_o|-|F_c||/\sum|F_o|$, of 0.25.

The parameters of the I, N, and C atoms were then refined by the block-diagonal least-squares

Table 1. (a) The final atomic co-ordinates along with their estimated standard deviations within parentheses each multiplied by 10^2 (Å)

Atom	X	Y	Z
I	0.1650 (0.1)	0.1850 (0.1)	0.0238 (0.1)
N	0.7494 (1)	0.0861 (1)	0.3353 (1)
C (1)	0.6839 (2)	0.0609 (2)	0.0973 (2)
C (2)	0.7000 (1)	0.0363 (1)	0.2339 (2)
C (3)	0.6613 (2)	−0.0529 (2)	0.2635 (2)
C (4)	0.6808 (2)	−0.0827 (2)	0.3853 (2)
C (5)	0.7356 (1)	−0.0252 (2)	0.4909 (2)
C (6)	0.7644 (2)	−0.0601 (2)	0.6221 (2)
C (7)	0.8228 (2)	0.0009 (2)	0.7188 (2)
C (8)	0.8599 (2)	0.0793 (2)	0.6914 (2)
C (9)	0.8313 (2)	0.1168 (2)	0.5662 (2)
C (10)	0.7690 (1)	0.0582 (1)	0.4638 (1)
C (11)	0.7857 (2)	0.1785 (1)	0.3078 (2)
C (12)	0.6070 (2)	0.2284 (2)	0.3291 (2)

(b) The thermal parameters along with their estimated standard deviations each multiplied by 10^4

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I	192 (2)	34(0.4)	107 (1)	18 (2)	28 (3)	5 (1)
N	125(23)	32 (5)	109(15)	−14(19)	55(30)	−10(14)
C(1)	272(47)	64 (11)	88(10)	−57(36)	−49(47)	−14(22)
C(2)	126(29)	26 (6)	134(20)	4(22)	4(38)	−36(18)
C(3)	143(34)	67 (11)	168(27)	−6(32)	44(48)	−37(28)
C(4)	138(32)	25 (6)	187(26)	0(23)	80(46)	−10(20)
C(5)	80(28)	54 (9)	159(23)	30(25)	84(40)	− 9(24)
C(6)	156(37)	71 (11)	166(26)	68(33)	82(49)	50(28)
C(7)	134(34)	75 (12)	147(24)	42(33)	65(46)	42(27)
C(8)	184(40)	92 (14)	130(23)	142(39)	105(49)	27(29)
C(9)	130(31)	64 (10)	99(18)	−9(29)	8(38)	−18(22)
C(10)	80(24)	25 (6)	104(16)	0(19)	50(32)	3(15)
C(11)	222(38)	12 (5)	144(21)	−10(23)	−1(45)	7(17)
C(12)	200(41)	38 (8)	218(32)	2(57)	−21(57)	0(26)

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

3) S. Sakanoue, Y. Kai, N. Yasuoka, N. Kasai, M. Kakudo and H. Mikawa, *Chem. Commun.*, **1968**, 176.

4) S. Sakanoue, N. Yasuoka, N. Kasai, M. Kakudo, S. Kusabayashi and H. Mikawa, This Bulletin, **42**, 2408 (1969).

5) A. Neuhaus, *Z. Kristallogr.*, **104**, 403 (1942).

Table 2. The observed and calculated structure factors

K FO FC	K FO FC	K FO FC	K FO FC	K FO FC	K FO FC	K FO FC	K FO FC
H,L= 0 0	15 17 8	3 132-126	8 44 -41	9 84 81	13 130-127	7 141-139	0 597-582	10 51 56
2 36 -21	16 20 10	4 19 4	9 126-123	10 32 -35	14 42 -33	8 74 -70	1 301-309	11 112-114
4 0 12	H,L= 0 6	5 92 96	10 105 94	11 7 -2	15 107 105	9 97 103	2 93 -75	12 53 -51
6 169 173	0 159 159	6 36 37	11 152 152	12 0 -4	16 30 28	10 8 16	3 247 232	13 109 99
8 415-411	1 176-176	7 25 -24	12 63 -64	13 38 -34	17 76 -68	11 40 -40	4 0 -3	14 0 7
10 140 134	2 129-133	8 0 -6	13 148-143	H,L= 1 9	H,L= 1 3	12 0 -3	5 114 126	15 22 -14
12 37 56	3 48 48	9 51 -46	14 86 77	1 21 -20	1 45 38	13 46 -48	6 76 -73	H,L= 2 6
14 142-136	4 19 -8	10 27 -24	15 0 1	2 28 -36	2 240-242	14 21 -33	7 264-267	0 198-194
16 113 116	5 68 69	11 71 74	16 22 19	3 90 85	3 15 22	15 76 66	8 220 212	1 50 -48
18 48 -41	6 99 96	H,L= 1 -8	17 52 45	4 96 97	4 314 303	H,L= 2 -5	9 154 154	2 154 157
H,L= 0 1	7 137-136	0 190 191	H,L= 1 -2	5 77 -83	5 19 11	1 102 95	10 64 -57	3 25 20
1 36 -42	8 107-113	1 0 1	0 335 365	6 32 -29	6 204-202	2 169-173	11 34 -42	4 11 17
2 121-103	9 90 96	2 88 -87	1 297-296	7 57 21	7 0 -4	3 43 -52	12 68 -21	5 26 28
3 389-454	10 59 63	3 38 -36	2 331-304	8 0 -3	8 51 -47	4 248 245	13 82 -72	6 136-137
4 103 95	11 45 -39	4 13 5	3 81 76	9 38 29	9 18 -24	5 82 80	14 53 61	7 24 -17
5 376 399	12 34 35	5 15 -11	4 13 -25	10 44 41	10 178 169	6 164-168	15 101 104	8 160 168
6 122-112	13 43 -41	6 92 94	5 112 95	11 45 -51	11 54 48	7 0 10	16 54 -56	9 20 24
7 45 -45	14 57 -50	7 21 23	6 172 161	H,L= 1 10	12 108-143	8 52 -54	17 50 -52	10 84 -81
8 20 -19	15 70 61	8 116-122	7 265-258	0 67 -75	13 28 15	9 27 -33	H,L= 2 1	11 0 8
9 141-144	H,L= 0 7	9 7 -3	8 242-228	1 45 -43	14 97 91	10 138 128	1 133-116	12 31 -30
10 22 31	1 39 36	10 52 54	9 162 160	2 48 49	15 20 14	11 40 45	2 265-260	13 0 -17
11 219 207	2 135-139	11 7 9	10 100 109	3 10 15	16 17 21	12 119-120	3 185 188	14 73 73
12 41 -32	3 108-111	12 20 15	11 38 -43	4 18 11	17 0 6	13 42 -37	4 278 262	H,L= 2 7
13 151-154	4 171 172	13 0 0	12 43 43	5 21 24	H,L= 1 4	14 66 66	5 201-202	1 39 -35
14 0 6	5 80 80	H,L= 1 -7	13 91-103	6 37 -41	0 39 32	15 0 1	6 123-116	2 27 30
15 31 22	6 99 -98	1 95 97	14 93 -94	7 46 -38	1 300-297	16 25 27	7 71 71	3 179 185
16 25 21	7 0 0	2 12 4	15 67 71	8 59 57	2 43 -45	H,L= 2 -4	8 21 -11	4 18 13
17 51 56	8 8 1	3 170-173	16 65 67	9 13 26	3 128 118	0 50 56	9 45 44	5 140-141
18 0 -16	9 35 -26	4 20 -13	17 56 -54	H,L= 1 11	4 60 -51	1 321-313	10 151 142	6 7 1
H,L= 0 2	10 95 100	5 148 151	H,L= 1 -1	1 36 -24	5 165 162	2 32 -22	11 99 -90	7 34 20
0 315 335	11 59 66	6 11 -2	1 27 -12	2 34 -25	6 33 -33	3 89 89	12 130-129	8 16 -20
1 80 -83	12 80 -84	7 32 -38	2 295-313	3 54 52	7 241-243	4 18 -20	13 71 75	9 40 35
2 270-309	13 35 -36	8 16 13	3 238-241	4 25 32	8 21 14	5 177 175	14 66 59	10 21 -8
3 60 -36	14 30 33	9 64 -62	4 400 378	5 47 -47	9 173 171	6 64 -55	15 15 -10	11 99 -99
4 81 -71	H,L= 0 8	10 8 4	5 258 243	H,L= 2-11	10 23 9	7 212-206	16 0 13	12 0 0
5 71 56	0 52 53	11 103 103	6 131-143	1 28 23	11 53 -52	8 43 -46	17 30 -23	13 62 60
6 248 249	1 117-117	12 16 14	7 22 10	2 20 -25	12 22 28	9 200 202	H,L= 2 2	H,L= 2 8
7 65 -71	2 6 -15	13 76 -78	8 44 20	3 58 -58	13 87 -83	10 0 14	0 190-181	0 136-140
8 257-264	3 83 88	14 22 -5	9 48 -39	4 34 27	14 20 0	11 52 -49	1 260-256	1 0 0
9 73 63	4 24 16	H,L= 1 -6	10 153 139	5 53 53	15 99 107	12 31 31	2 181 184	2 66 71
10 127 125	5 87 94	0 266 267	11 134 134	H,L= 2-10	16 0 -5	13 109-109	3 30 38	3 45 -47
11 27 -25	6 43 45	1 12 -3	12 148-139	0 81 81	H,L= 1 5	14 0 17	4 13 7	4 15 -3
12 24 18	7 117-113	2 149-149	13 81 -76	1 54 -47	1 0 -14	15 88 87	5 101 100	5 13 -18
13 13 -19	8 50 -47	3 25 25	14 54 67	2 54 -55	2 255-253	16 0 8	6 187-181	6 96 -91
14 111-106	9 77 80	4 0 -9	15 25 27	3 14 13	3 103 97	H,L= 2 -3	7 223-219	7 10 9
15 31 31	10 0 6	5 26 19	16 29 35	4 0 -11	4 221 233	1 54 -46	8 202 196	8 95 95
16 109 111	11 0 -30	6 156 153	17 49 36	5 29 20	5 23 -28	2 238-232	9 174 182	9 8 -6
17 30 -26	12 21 2	7 52 -57	18 64 -59	6 39 41	6 168-175	3 14 1	10 75 -68	10 47 -49
H,L= 0 3	13 39 -44	8 224-226	H,L= 1 0	7 39 -41	7 15 5	4 317 319	11 0 6	11 0 14
1 213 217	H,L= 0 9	9 10 -24	0 228 225	8 61 -55	8 0 6	5 27 -26	12 0 3	12 0 -12
2 144-132	1 31 20	10 57 59	1 235-246	9 21 -25	9 26 29	6 211-212	13 67 -71	H,L= 2 9
3 373-387	2 95 -94	11 29 -24	2 155-150	10 184 179	H,L= 2 -9	7 21 24	14 70 71	1 39 -42
4 77 85	3 33 -35	12 10 18	3 167 192	11 75 -74	1 16 23	8 39 -27	15 84 86	2 2 19
5 249 254	4 104 102	13 15 -6	4 80 -64	12 101-107	2 53 -64	9 13 12	16 85 -83	3 93 96
6 135-142	5 24 8	14 82 -82	5 151 165	13 26 8	3 68 -75	10 153 148	17 56 -50	4 14 -25
7 122-132	6 68 -64	15 72 20	6 195 183	14 52 49	4 52 56	11 37 -39	H,L= 2 3	5 80 -81
8 0 -13	7 19 -14	H,L= 1 -5	7 33-285	15 0 -7	5 99 95	12 127-123	1 123-116	6 0 9
9 99-103	8 14 -6	1 79 83	8 145-138	16 30 23	6 54 -56	13 8 -2	2 119-118	7 28 23
10 100 102	9 29 -15	2 146-127	9 155 182	H,L= 1 6	7 0 -7	14 80 81	3 345 334	8 6 -4
11 210 219	10 63 59	3 320-313	10 102 92	0 84 -89	8 0 -7	15 10 0	4 249 249	9 46 44
12 36 -37	11 14 10	4 48 49	11 57 -53	1 197-194	9 38 -30	16 46 28	5 146-150	10 23 -7
13 85 -85	H,L= 0 10	5 202 202	12 23 28	2 77 81	10 35 41	17 17 2	6 72 -73	H,L= 2 10
14 49 53	0 0 12	6 41 -46	13 67 -78	3 59 58	11 37 51	H,L= 2 -2	7 98 93	0 81 -79
15 16 8	1 94 -90	7 57 -53	14 73 -70	4 0 -9	H,L= 2 -8	0 158-152	8 24 -24	1 27 31
16 0 8	2 8 -2	8 8 17	15 106 91	5 89 88	0 99 98	1 344-334	9 84 83	2 51 53
17 59 51	3 37 35	9 47 -48	16 65 65	6 45 -53	1 101-104	2 56 42	10 46 49	3 7 -17
H,L= 0 4	4 0 0	10 90 88	17 76 -74	7 170-171	2 77 -76	3 113 117	11 185-188	4 14 6
0 306 313	5 40 36	11 170 165	18 22 -15	8 75 75	3 54 58	4 0 9	12 111-107	5 2 -13
1 266-255	6 3 8	12 39 -35	H,L= 1 1	9 98 95	4 25 -23	5 162 150	13 80 80	6 41 -50
2 142-146	7 79 -78	13 86 -84	1 133 135	10 19 -20	5 71 76	6 22 16	14 6 16	7 36 26
3 64 76	8 0 -10	14 11 11	2 295-321	11 41 -44	6 67 66	7 276-273	15 22 -19	H,L= 2 11
4 28 47	9 56 58	15 21 12	3 184-186	12 0 3	7 89 -86	8 36 23	16 32 24	1 17 -23
5 106 103	H,L= 0 11	16 0 4	4 451 441	13 56 -53	8 76 -68	9 219 205	H,L= 2 4	2 26 23
6 267 257	1 18 2	H,L= 1 -4	5 149 142	14 10 25	9 56 61	10 34 -33	0 312-314	3 41 40
7 115-118	2 55 -55	0 291 296	6 174-164	15 73 73	10 53 50	11 30 -35	1 76 -80	H,L= 3-11
8 181-180	3 26 9	1 154-150	7 110-109	H,L= 1 7	11 27 -25	12 0 2	2 142 144	1 15 3
9 117 122	4 71 68	2 163-162	8 13 -20	1 24 -20	12 0 19	13 82 -79	3 67 63	2 56 -52
10 82 80	5 0 -7	3 62 65	9 97 -90	2 113-107	H,L= 2 -7	14 0 0	4 76 -68	3 13 -9
11 41 -36	6 43 -40	4 16 29	10 218 208	3 69 72	1 40 36	15 114 111	5 60 56	4 55 56
12 27 1	H,L= 1-11	5 30 35	11 74 82	4 150 148	2 109-110	16 21 -19	6 192-186	H,L= 3-10
13 65 -67	1 12 22	6 208 202	12 189-178	5 72 -71	3 91 -86	17 66 -70	7 105 -98	0 0 1
14 109-106	2 40 30	7 87 -89	13 42 -46	6 93 -97	4 169 161	H,L= 2 -1	8 177 178	1 71 -68
15 50 56	3 44 -50	8 211-208	14 95 91	7 32 22	5 69 70	1 295 263	9 60 56	2 0 5
16 77 75	4 34 -37	9 84 79	15 0 -21	8 26 -24	6 80 -82	2 471-440	10 83 -79	3 55 53
17 37 -41	5 48 51	10 92 99	16 37 34	9 30 31	7 31 -30	3 246 229	11 0 -7	4 12 -8
H,L= 0 5	6 35 23	11 26 -16	17 0 18	10 91 90	8 9 -4	4 255 252	12 23 -7	5 57 52
1 27 18	H,L= 1-10	12 36 -25	H,L= 1 2	11 44 -39	9 33 -25	5 169-148	13 20 -25	6 4 -10
2 108-109	0 86 89	13 47 -35	0 106 108	12 78 -76	10 102 102	6 228-230	14 78 77	7 66 -67
3 219-218	1 36 34	14 70 -76	1 430-454	13 47 42	11 48 47	7 36 -39	15 31 40	8 0 0
4 184 184	2 54 -58	15 17 34	2 10 -15	14 26 35	12 86 -81	8 49 -44	16 69 -71	H,L= 3 -9
5 145 137	3 12 -26	16 88 82	3 205 184	H,L= 1 8	13 35 -32	9 22 32	H,L= 2 5	1 0 -5
6 121-121	4 6 -9	17 30 -26	4 13 9	0 157-156	14 22 29	10 214 213	1 89 -87	2 107-108
7 34 -32	5 29 -24	H,L= 1 -3	5 159 156	1 143-142	H,L= 2 -6	11 84 -72	2 73 -77	3 37 37
8 20 -36	6 57 54	1 144 147	6 60 67	2 21 25	0 56 62	12 186-181	3 219 216	4 69 64
9 70 -64	7 43 38	2 152-146	7 287-291	3 19 9	1 206-200	13 57 64	4 70 71	5 3 -3
10 104 100	8 67 -66	3 320-316	8 54 -47	4 5 2	2 64 -74	14 70 72	5 181-169	6 69 -69
11 96 103	9 31 -30	4 164 157	9 209 203	5 39 36	3 77 76	15 3 -11	6 28 -28	7 0 8
12 86 -89	H,L= 1 -9	5 273 260	10 7 -12	6 44 -41	4 0 -1	16 26 31	7 39 39	8 15 -4
13 77 -80	1 25 32	6 114-107	11 75 -75	7 88 -93	5 84 85	17 23 -16	8 28 -18	9 16 6
14 49 51	2 74 69	7 39 -38	12 35 -43	8 83 81	6 58 59	H,L= 2 0	9 74 68	10 60 64

Table 2 (continued).

K	FO	FC
H,L= 3 -8		
0	32	-37
1	113	-119
2	20	23
3	45	46
4	20	-6
5	44	48
6	25	-26
7	95	-97
8	38	39
9	71	73
10	21	-13
11	24	-15
12	0	-4
H,L= 3 -7		
1	35	-33
2	102	-100
3	67	71
4	148	153
5	67	-78
6	95	-98
7	0	0
8	47	-41
9	0	7
10	69	67
11	33	-37
12	83	-80
13	22	35
H,L= 3 -6		
0	178	-179
1	171	-163
2	40	47
3	13	21
4	19	4
5	83	79
6	69	-61
7	90	-89
8	137	138
9	133	131
10	20	-25
11	6	-4
12	0	-10
13	38	-45
14	40	42
H,L= 3 -5		
1	28	-37
2	89	-89
3	182	179
4	160	163
5	110	-108
6	101	-101
7	38	35
8	28	-23
9	45	42
10	57	62
11	94	-97
12	70	-73
13	61	63
14	18	29
15	11	-12
H,L= 3 -4		
0	235	-227
1	168	-165
2	160	153
3	54	52
4	8	-19
5	82	82
6	135	-133
7	145	-136
8	148	145
9	82	79
10	73	-76
11	27	-15
12	27	-20
13	30	-33
14	33	47
15	80	74
H,L= 3 -3		
1	146	-136
2	95	-94
3	251	237
4	135	130
5	242	-239
6	65	-68
7	50	46
8	27	-24
9	99	100
10	85	81
11	151	-150
12	92	-99
13	107	110
14	23	-3
15	0	-5
16	0	-1
H,L= 3 -2		
0	344	-346
1	92	-87
2	196	196
3	82	82
4	69	67
5	77	75
6	163	-162
7	21	-22
8	242	236
9	50	44
10	106	-105
11	0	-5
12	22	-17
13	0	-4
14	105	104
15	39	39
16	85	-78
H,L= 3 -1		
1	39	-38
2	52	-41
3	295	295
4	68	61
5	307	-303
6	72	-47
7	59	61
8	48	-28
9	92	78
10	28	35
11	143	-150
12	28	-32
13	101	97
14	8	-3
15	28	-18
16	26	7
H,L= 3 0		
0	347	-344
1	6	-16
2	265	258
3	45	-43
4	60	47
5	31	24
6	263	-260
7	24	-32
8	215	207
9	36	26
10	158	-143
11	25	23
12	38	-39
13	14	-11
14	105	106
15	20	21
16	103	-109
H,L= 3 1		
1	141	-142
2	31	25
3	309	306
4	65	-58
5	244	-241
6	13	10
7	80	82
8	4	-15
9	126	118
10	57	-62
11	200	-205
12	19	16
13	106	109
14	29	-26
15	21	-2
16	21	3
H,L= 3 2		
0	310	-303
1	82	74
2	216	215
3	49	-50
4	11	-10
5	57	-60
6	178	-175
7	51	53
8	208	199
9	34	-29
10	55	-58
11	55	54
12	21	17
13	36	32
14	105	99
15	32	-21
16	89	-76
H,L= 3 3		
1	123	-127
2	60	58
3	218	208
4	82	-86
5	211	-220
6	95	96
7	47	45
8	4	-6
9	99	100
10	45	-37
11	143	-141
12	11	29
13	90	88
14	36	-31
15	15	-14
16	10	0
H,L= 3 4		
0	235	-230
1	117	119
2	156	146
3	60	-57
4	67	60
5	95	-93
6	118	-125
7	92	93
8	160	159
9	70	-71
10	103	-103
11	54	49
12	64	-63
13	49	43
14	54	63
15	43	-45
H,L= 3 5		
1	66	-67
2	108	105
3	135	133
4	129	-124
5	140	-133
6	93	93
7	36	38
8	17	-2
9	76	70
10	97	-98
11	42	-47
12	45	54
13	67	65
14	44	-44
H,L= 4 -6		
0	145	-146
1	0	5
2	143	146
3	16	-15
4	9	10
5	23	-18
6	103	-104
7	0	-5
8	137	138
9	21	-10
10	49	-50
11	35	13
12	21	-13
13	0	3
H,L= 4 -5		
1	105	-104
2	31	30
3	175	170
4	61	-58
5	174	-174
6	60	62
7	21	16
8	34	29
9	47	59
10	0	-6
11	108	-107
12	0	16
13	93	87
14	34	-30
H,L= 4 -4		
0	209	-206
1	92	88
2	114	108
3	14	-17
4	0	11
5	51	-46
6	118	-115
7	53	50
8	166	167
9	79	-79
10	74	-69
11	22	22
12	28	-31
13	40	45
14	48	50
H,L= 4 -3		
1	92	-96
2	87	85
3	211	206
4	113	-109
5	152	-152
6	58	57
7	53	54
8	0	4
9	65	65
10	46	-47
11	108	-104
12	63	56
13	67	66
14	37	-44
15	0	-9
H,L= 4 -2		
0	141	-138
1	135	132
2	203	201
3	165	-157
4	31	33
5	94	-91
6	156	-155
7	127	129
8	146	149
9	92	-87
10	70	-67
11	19	26
12	33	-23
13	24	32
14	71	84
15	63	-57
H,L= 4 -1		
1	228	-215
2	287	275
3	60	67
4	101	-92
5	135	-130
6	143	143
7	48	56
H,L= 4 -7		
8	12	2
9	102	99
10	130	-132
11	81	-88
12	0	-3
H,L= 4 -6		
0	18	
5	86	-86
6	95	-92
7	192	184
8	67	67
9	114	-111
10	56	-52
11	43	44
12	14	-20
13	46	45
14	43	44
15	68	-75
H,L= 4 1		
1	0	-9
2	164	163
3	127	128
4	246	-248
5	93	-93
6	135	129
7	19	19
8	15	11
9	63	64
10	102	-93
11	65	-70
12	107	104
13	29	30
14	57	-53
15	0	1
H,L= 4 2		
0	48	-40
1	254	252
2	55	53
3	28	-28
4	57	59
5	85	-82
6	48	-45
7	187	180
8	32	27
9	186	-186
10	39	-40
11	0	1
12	34	-29
13	50	59
14	21	29
15	82	-81
H,L= 4 3		
1	28	-29
2	147	144
3	44	-34
4	219	-210
5	65	-68
6	122	116
7	6	-15
8	32	34
9	0	18
10	91	-94
11	20	15
12	126	120
13	17	6
14	53	-47
H,L= 4 4		
0	0	1
1	184	182
2	5	16
3	86	-89
4	17	37
5	84	-84
6	6	4
7	139	136
8	21	-6
9	103	-101
10	20	2
11	22	31
12	18	-13
13	51	44
H,L= 5 -5		
1	34	-31
2	98	95
3	38	37
4	134	-138
5	47	-52
6	80	86
7	0	-1
8	13	16
9	27	20
10	77	-77
11	36	-23
12	70	76
H,L= 5 -4		
0	34	-33
1	182	184
2	12	8
3	65	-62
4	18	-3
5	62	-70
6	15	-20
7	144	140
8	16	18
9	96	-102
10	0	-7
11	26	16
12	23	-12
13	19	34
H,L= 5 -3		
1	8	10
2	6	6
3	162	-161
4	71	-69
H,L= 5 4		
5	41	43
6	114	113
7	0	-6
8	21	22
9	0	7
10	96	-92
11	0	9
12	108	113
13	24	0
H,L= 5 -2		
0	71	67
1	154	148
2	10	1
3	98	-98
4	21	-24
5	115	-114
6	9	-6
7	126	137
8	32	-34
9	115	-113
10	30	17
11	21	22
12	14	-15
13	38	40
14	0	-11
H,L= 5 -1		
1	23	-7
2	160	159
3	45	-50
4	200	-205
5	65	56
6	110	105
7	23	-23
8	25	15
9	32	-17
10	83	-93
11	71	27
12	105	104
13	35	-30
14	35	-30
H,L= 5 0		
2	6	-8
3	76	-74
4	17	-8
5	56	64
6	0	-4
7	35	-33
8	13	10
H,L= 5 8		
0	51	51
1	0	-6
2	50	-57
3	0	0
4	0	-3
5	14	-7
H,L= 6 -8		
0	11	20
1	58	66
2	18	-20
3	15	-17
4	0	0
5	27	-28
H,L= 6 -7		
1	29	21
2	49	51
3	33	-29
4	80	-83
5	35	35
6	44	43
7	0	1
H,L= 6 -6		
0	50	41
1	89	89
2	57	-55
3	27	-23
4	0	-6
5	13	-25
6	25	34
7	79	85
8	65	-62
9	41	-37
H,L= 6 -5		
1	41	39
2	59	65
3	83	-81
4	73	-73
5	76	72
6	33	33
7	8	-15
8	17	-12
9	13	-10
10	55	-59
H,L= 6 -4		
0	91	98
1	71	72
2	63	-62
3	19	-18
4	0	3
5	48	-44
6	67	68
7	53	68
8	81	-77
9	40	-39
10	38	37
11	18	4
H,L= 6 -3		
1	59	64
2	34	31
3	104	-101
4	92	-98
5	104	108
6	34	41
7	28	-31
8	24	19
9	46	-49
10	47	-41
11	71	74
H,L= 6 -2		
0	128	127
1	83	85
2	142	-147
3	62	63
4	42	-37
5	23	26
6	71	76
7	45	46
8	103	-103
9	37	-38
10	65	65
11	0	-11
12	26	15
H,L= 6 -1		
1	95	93
2	24	-25
3	92	-93
4	67	-71
5	133	135
6	0	-15
7	42	-41
8	27	24
9	71	-67
10	22	-7
11	70	69
12	25	26
H,L= 6 0		
0	158	160
1	8	20
2	93	-94
3	0	-14
4	0	-16
5	23	-18
6	95	106
7	0	8
8	105	-105
9	0	-8
10	59	61
11	0	-16
12	26	12
H,L= 6 1		
1	72	68
2	0	14
3	140	-141
4	29	29
5	122	126
6	16	-17

Table 2 (continued).

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC
7	54	-54	4	31	30	3	76	-76	4	19	-8	3	86	-88	6	44	-39	8	25	-23	2	21	8	0	24	-27
8	14	-10	5	112	113	4	63	64	5	19	4	4	19	22	7	7	-12	9	50	-50	3	24	21	1	65	-56
9	65	-65	6	45	-41	5	47	48	H,L=	7	-5	5	57	56	8	7	-9	H,L=	7	2	4	24	-8	2	29	22
10	0	-11	7	0	-9	6	45	-50	1	36	36	6	47	-44	9	26	-28	0	51	46	5	22	30	3	0	29
11	83	85	8	0	-6	7	11	-16	2	10	-6	7	24	-22	H,L=	7	0	1	93	-88	6	0	8	H,L=	8	1
12	0	-11	9	41	-49	8	17	-1	3	83	-83	8	19	4	0	55	65	2	33	-22	H,L=	7	5	1	26	-38
H,L=	6	2	10	10	18	H,L=	6	6	4	31	21	H,L=	7	-2	1	91	-94	3	26	24	1	17	-6	2	51	-54
0	102	102	11	47	59	0	5	10	5	74	70	0	67	68	2	37	-32	4	0	-3	2	40	-45	3	22	25
1	61	-59	H,L=	6	4	1	53	-53	6	17	-11	1	49	-42	3	31	29	5	27	28	3	11	2			
2	116	-120	0	111	115	2	54	-54	7	30	-11	2	55	-65	4	15	-6	6	28	30	H,L=	8	-3			
3	11	1	1	55	-53	3	21	21	H,L=	7	-4	3	39	47	5	28	25	7	78	-89	1	0	-1			
4	38	-40	2	71	-72	4	0	-3	0	101	100	4	18	-12	6	41	43	8	10	-11	2	26	-28			
5	0	4	3	18	18	5	18	31	1	35	-32	5	38	35	7	47	-53	H,L=	7	3	H,L=	8	-2			
6	81	81	4	5	-6	6	47	53	2	60	-54	6	70	69	8	17	-31	1	0	1	0	21	-6			
7	17	-3	5	23	25	H,L=	6	7	3	22	18	7	45	-50	9	77	80	2	62	-69	1	79	-86			
8	56	-85	6	64	66	1	52	43	4	8	10	8	64	-64	H,L=	7	1	3	25	-9	2	8	22			
9	56	51	7	30	-35	2	35	-30	5	24	15	9	47	42	1	29	22	4	86	93	3	9	-12			
10	68	64	8	69	-73	3	31	-29	6	58	66	H,L=	7	-1	2	46	-54	5	15	0	H,L=	8	-1			
11	0	2	9	35	33	H,L=	7	-6	7	24	-31	1	39	32	3	26	-38	6	47	-41	1	23	-11			
H,L=	6	3	10	32	35	0	43	55	8	58	-62	2	58	-59	4	96	94	7	0	-5	2	45	-46			
1	56	55	H,L=	6	5	1	0	-7	H,L=	7	-3	3	74	-71	5	26	28	H,L=	7	4	3	0	7			
2	18	-23	1	33	31	2	62	-65	1	23	34	4	90	89	6	52	-50	0	9	2	4	71	79			
3	75	-78	2	33	-43	3	0	5	2	56	-63	5	58	68	7	0	-18	1	58	-70	H,L=	8	0			

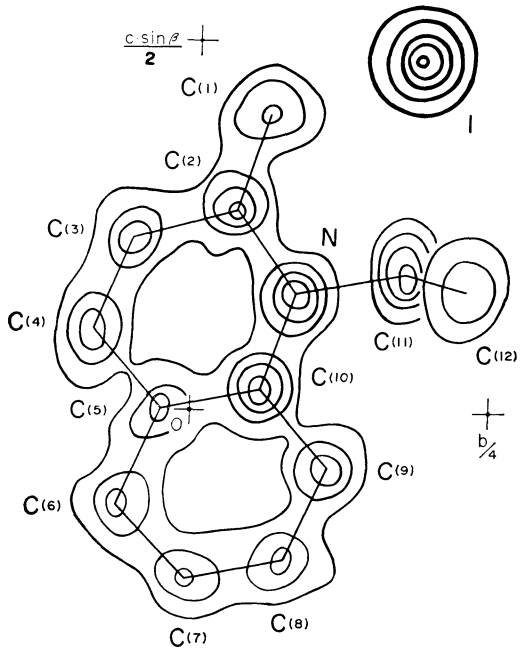

Fig. 1. A composite drawing of the electron density distribution, projected along the *a* axis. Contours at intervals of 1 eÅ^{-3} for the lighter atoms and of 10 eÅ^{-3} (thick lines) for the iodide ion.

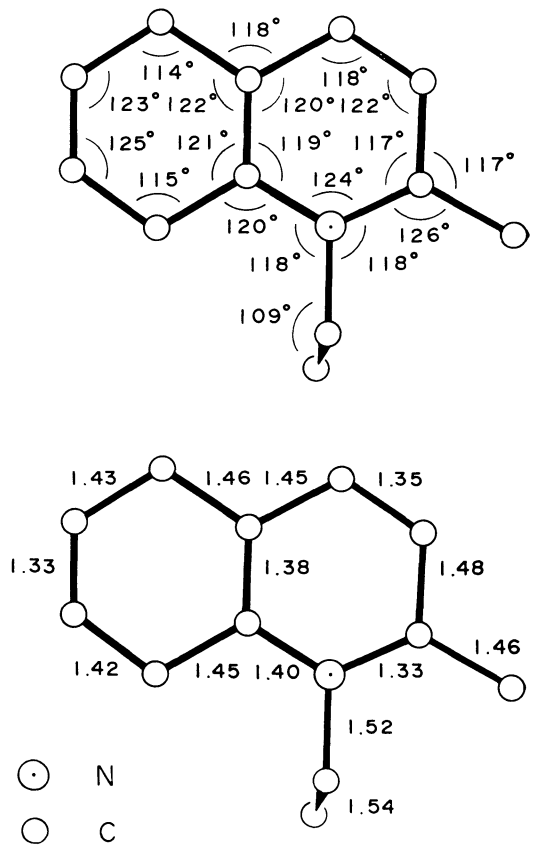

Fig. 2. Bond distances and angles in 1-ethyl-2-methylquinolinium cation. E.s.d.'s are about 0.028 Å and 1.6° respectively.

procedure, and anisotropic thermal parameters were considered. In the refinement, the function minimized was $\sum w(|F_o|-|F_c|)^2$, and the weight, w was taken as unity for all reflections. Using the HBLS IV (UNICS) program,[6] the calculation was done on a HITAC 5020E computer at the University of Tokyo. After 7 cycles of refinement, the R factor was reduced to 0.073 for non-zero reflections (R=0.082 for all reflections). The final atomic co-ordinates and thermal parameters, along with their estimated standard deviations, are listed in Table 1. The observed and calculated structure factors are listed in Table 2. In the calculation the neutral atomic scattering factors used were taken from those of Hanson and his co-workers.[7]

6) "Universal Crystallographic Computation Program System," ed. by Tosio Sakurai, Crystallographic Society of Japan, Tokyo (1967).

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

A composite diagram of the final electron density distributions along the a axis is shown in Fig. 1.

Description and Discussion of the Structure

The skeleton of the 1-ethyl-2-methylquinolinium cation, together with the bond distances and angles, is illustrated in Fig. 2. The estimated standard deviations of the bond distances and angles are about 0.028 Å and 1.6° respectively.

The quinoline ring is planar within the limit of experimental error. The mean plane of the ring is expressed by:

$$-0.9680X + 0.2188Y + 0.1228Z + 4.2243 = 0,$$

where

$$X = ax + cz \cdot \cos\beta,\ Y = by, \text{ and } Z = cz \cdot \sin\beta.$$

The views along the a and c axes of the crystal structure are both shown in Fig. 3. The main feature is that the iodide anions and the planar 1-ethyl-2-methylquinolinium cations lie roughly on a plane. Each iodide anion is surrounded by three cations. The planar cations are stacked approximately parallel to the a-plane, forming an endless column along the a axis. The interplanar spacings of these cations along the column are alternately 3.4 and 3.6 Å; there thus seem to be the usual van der Waals contacts. The iodide ions are located in the spaces between these columns and the ethyl groups of the cations. The closest contact between an iodide ion and the carbon atoms of

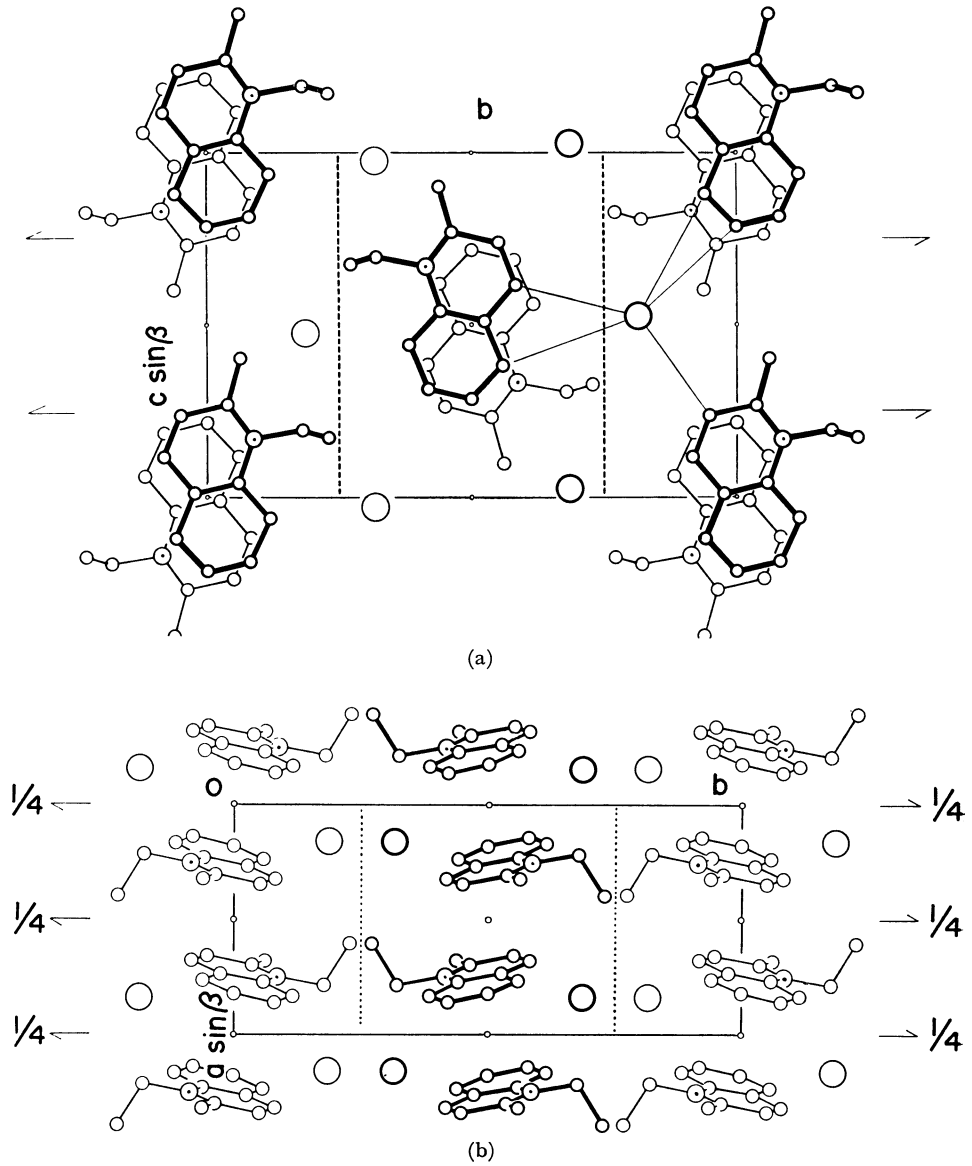

Fig. 3. The crystal structure viewed along the a axis (a) and the c axis (b).

TABLE 3. SHORT NON-BONDED DISTANCES LESS THAN 4.0 Å ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS WITHIN PARENTHESES EACH MULTIPLIED BY 10^2

C(5) ···C(5^{i})	3.50 (4) Å
C(7) ···C(3^{i})	3.59 (3)
C(3) ···C(7^{i})	3.59 (3)
C(4) ···C(8^{i})	3.45 (3)
C(6) ···C(10^{i})	3.54 (3)
C(4) ···C(9^{i})	3.54 (3)
C(2) ···C(7^{i})	3.47 (3)
C(10)···C(6^{i})	3.54 (3)
C(5) ···C(9^{i})	3.53 (3)
C(7) ···N	3.45 (3)
C(6) ···N	3.51 (3)
I ···C(9^{iii})	4.00 (2)
I ···C(3^{i})	3.93 (2)
I ···C(4^{ii})	3.95 (2)

Codes for superscripts:

i	$-x$,	$-y$,	$-z$;
ii	$-x$,	$0.5+y$,	$0.5-z$;
iii	x,	$0.5-y$,	$0.5+z$.

an 1-ethyl-2-methylquinolinium ring is 3.93 A (Fig. 3). Some close inter-ionic atomic contacts are shown in Table 3.

In the study of the solvent effects on the charge-transfer absorption band of 1-alkylpyridinium iodide complexes, Kosower[1] assumed that the complexes exist in the form of ion-pairs in non-polar solvents, and to explain the effects he proposed a model in which an iodide ion is in contact with a 1-alkylpyridinium ion, with the line joining the centers of charge perpendicular to the plane of the ring.

In the structure of the tropylium iodide crystal, it was found that the iodide ion is located on the center of the tropylium ring.[8] This finding gives evidence for a weak charge-transfer bond between the iodide ion and the tropylium ion, such a bond as might be expected to persist in an ion-pair.[9] In the *N*-methylacridinium iodide[10] and the quinolinium salt of 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide,[4] it was again found that the crystal structures of these salts persist in having ion-pairs.

Unlike these, the obtained crystal structure of the present crystal (Fig. 3) seems not to be so useful in explaining the charge-transfer absorption band, although the yellowish-green color of the crystal may be due to weak interionic interaction. The differences in structure between the 1-ethyl-2-methylquinolinium iodide and the tropylium iodide may be due to the facts that the electron affinity of the tropylium ion is larger than that of the 1-ethyl-2-methylquinolinium ion and that the bulky ethyl and methyl groups of the 1-ethyl-2-methylquinolinium ion affect the packing of ions in the crystal.

The authors wish to express their deep thanks to Professor Hiroshi Mikawa of this University for supplying materials and for his continued interest.

8) A. I. Kitaigorodski, Yu. T. Struchkov, T. L. Khotsyanova, M. E. Vol'pin and D. N. Kursanov, *Izvest. Akad. Nauk S. S. S. R., Otdl. Khim. Nauk.*, **1**, 32 (1960).

9) K. M. Harmon, F. E. Cummings, D. A. Davis and D. J. Diestler, *J. Amer. Chem. Soc.*, **84**, 3349 (1962).

10) K. Nakamura, N. Yasuoka, N. Kasai and M. Kakudo, unpublished data.