The Crystal and Molecular Structure of 5-Chloro-7-iodo-8-quinolinol, Chinoform

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Isomorphous crystals of 5-chloro-7-iodo- and 5,7-dibromo-8-quinolinols have been examined by X-ray analysis. Both compounds crystallize in the monoclinic space group $P2/a$ with four formula units in the unit cell. The cell dimensions are: $a=16.98$; $b=4.16$; $c=14.84$ Å, and $\beta=112.0°$ for 5-chloro-7-iodo-8-quinolinol, and $a=16.34$, $b=4.02$, $c=15.52$ Å, and $\beta=115.6°$ for 5,7-dibromo-8-quinolinol. The structure of the former, chinoform, has been determined by the Patterson methods from data collected with Mo$K\alpha$ radiation on Weissenberg photographs, and refined by the block-diagonal least-squares method, with anisotropic temperature factors. The final R value is 0.081 for 836 observed reflections. The quinolinol molecule is nearly planar. In the crystals, the molecules related by two-fold axis are held together by hydrogen bonds to form bent dimers, which are stacked closely by van der Waals forces along the b axis.

The derivatives of 8-quinolinol are widely used as chelating agents in analytical chemistry and a number of their complexes are investigated, especially by Prout and his coworkers,[1] by means of X-ray diffraction structure analysis in connection with the Mulliken's "overlap and orientation" principle.[2] 5-Chloro-7-iodo-8-quinolinol is medically important as so-called "chinoform". In this study the cell dimensions and the space group of 5-chloro-7-iodo- and 5,7-dibromo-8-quinolinols were determined, and the structure of the former compound was studied by X-ray diffraction analysis.

Experimental

5-Chloro-7-iodo-8-quinolinol (prepared by Tanabe Seiyaku Co., Ltd.) was recrystallized from ethanol. Crystals obtained by slow evaporation from ethanol solution were monoclinic needles elongated along the b-axis. Cell constants were determined from Weissenberg and oscillation photographs taken with Cu$K\alpha$ radiation ($\lambda=1.5418$ Å). Crystal data are given in Table 1 along with those of 5,7-dibromo-8-quinolinol, which have been determined by the same way as those of chinoform. Since crystals of 5,7-dibromo-8-quinolinol gave no suitable photographic spots for intensity measurements, the structure analysis was not tried. A possible space group of these two compounds is determined to be Pa or $P2/a$ from the absent spectra: $h0l$ when h is odd. Structure analysis of chinoform was made on the basis of the latter space group symmetry and gave a reasonable structure. The space group of 5,7-dibromo-8-quinolinol may also be $P2/a$ because its molecular symmetry is the same as that of chinoform.

Intensity data of chinoform were initially collected with Cu$K\alpha$ radiation by means of the equi-inclination Weissenberg photographs, for the layers of $h0l$ to $h3l$. However, in view of the large absorption effect the data were recollected, after the structure was determined, with Mo$K\alpha$ radiation, for the layers of $h0l$ to $h4l$ using a crystal of $0.11\times0.12\times0.60$ mm³. A total of 836 independent non-zero reflections were measured visually. The inter-layer scaling was made according to the exposure time. Corrections were made for the Lorentz and polarization factors, and for the spot shape.

Table 1. Crystal data

	5-Chloro-7-iodo-8-quinolinol C_9H_5NOClI	5,7-Dibromo-8-quinolinol $C_9H_5NOBr_2$
MW	305.5	303.0
Mp	172°C	196°C
Crystal system	Monoclinic	Monoclinlic
a	16.98(2) Å	16.34 Å
b	4.16(1)	4.02
c	14.84(1)	15.52
β	112.0(2)°	115.6°
V	971.9 Å³	919.3 Å³
D_c	2.088 g cm^{-3}	2.189 g cm^{-3}
D_m	2.08$_4$ (by flotation)	
Z	4	4
Absent spectra	$h0l$ when h odd	$h0l$ when h odd
Space group	$P2/a$	$P2/a$
μ for Cu$K\alpha$	285.5 cm^{-1}	120.8 cm^{-1}
μ for Mo$K\alpha$	35.6	93.0
$F(000)$	576	576

Structure Determination

Approximate positional parameters of all non-hydrogen atoms were easily determined from a three-dimensional Patterson map. The structure was then refined isotropically by the block-diagonal least-squares method.[3] An R value dropped from 0.24 for the trial structure to 0.18. The structure was refined anisotropically for the non-hydrogen atoms to the R value of 0.123 for the copper data. Using the positional parameters thus obtained and $B=5.35$ Å² from Wilson's method as initial parameters, an isotropic refinement was made with the molybdenum data. Thereafter the data of each layer were re-scaled on the basis of the ratio of $\Sigma|F_o|$ and $\Sigma|F_c|$. The refinement with anisotropic thermal parameters reduced the R value to 0.084. Three hydrogen atoms attached to a quinoline ring were located from a difference map, but the other two hydrogen atoms were not revealed. Assuming suitable geometries of the C–H bond (C–H=1.08 Å), the positional parameters of the four ring hydrogen atoms were computed. These parameters and an isotropic temperature factor, $B=4.5$ Å², were introduced as

1) E. Castellano and C. K. Prout, *J. Chem. Soc., A*, **1971**, 550.
2) R. S. Mulliken, *Rec. Trav. Chim.*, **75**, 845 (1956).
3) Y. Okaya and T. Ashida, "HBLS IV, The Universal Crystallographic Computing System (I)." The Crystallographic Society of Japan, Tokyo (1967) p. 65.

Table 2. Final atomic parameters

All values should be multiplied by 10^{-4}. The e.s.d.'s of atomic coordinates are shown in parentheses. The anisotropic thermal parameters are expressed as $\exp(-B_{11}h^2-B_{22}k^2-B_{33}l^2-B_{12}hk-B_{13}hl-B_{23}kl)$.

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I	7638(1)	6246(4)	1773(1)	43	663	82	22	54	85
Cl	4277(3)	990(18)	776(4)	35	1023	43	−11	12	−38
O	7698(8)	3544(43)	3840(10)	37	915	65	−83	34	−9
N(1)	6461(9)	360(45)	4352(11)	31	801	46	69	37	69
C(2)	5893(14)	−1441(63)	4600(15)	48	795	52	125	21	−5
C(3)	5089(14)	−2223(64)	3912(16)	42	1025	60	−91	49	109
C(4)	4848(11)	−1358(57)	2970(16)	32	617	85	−102	61	−164
C(5)	5288(10)	1719(50)	1703(13)	20	648	40	23	−13	−48
C(6)	5866(11)	3498(49)	1474(13)	31	491	42	63	13	4
C(7)	6700(11)	3977(52)	2167(15)	34	454	71	−42	32	−36
C(8)	6915(13)	2986(48)	3159(15)	34	544	56	−56	6	−163
C(9)	6261(10)	1324(55)	3419(14)	25	566	65	1	37	−61
C(10)	5444(13)	617(49)	2677(14)	41	578	48	−11	11	−80

fixed parameters, and the parameters for all non-hydrogen atoms were refined anisotropically, using the following weighting scheme:

$$\sqrt{w} = 1.0, \quad \text{if } 10.0 \leqq F_o \leqq 27.0,$$
$$\sqrt{w} = 27.0/F_o, \quad \text{if } F_o > 27.0,$$

and $\sqrt{w} = 0.0$ for unobserved reflections.

The final R value was 0.081 for the 836 non-zero reflections. The final atomic parameters are given in Table 2. A composite drawing of the final electron density map is shown in Fig. 1. The observed and calculated structure factors are listed in Table 3.

The atomic scattering factors used were those of Hanson, Herman, Lea, and Skillman.[4] The numerical calculations were performed with the aid of a HITAC 5020 E computer of the Computer Center of the University of Tokyo.

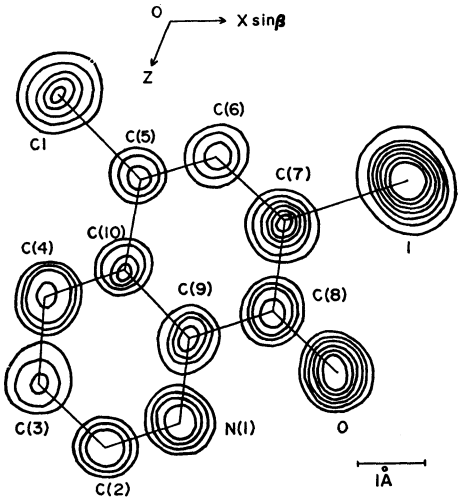

Fig. 1. Composite three-dimensional final electron-density map projected along the b axis. Contours are at intervals of 1 e Å^{-3} for C, N and O atoms, 5 e Å^{-3} for Cl atom and 10 e Å^{-3} for I atom, each starting at 3 e Å^{-3}.

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

Results and Discussion

Bond lengths and angles are shown in Fig. 2. The average C–C bond length within the quinoline ring is 1.42 Å. Although the average standard deviation of the bond lengths amounts to 0.03 Å, the shortening of the C(3)–C(4) and C(5)–C(6) bonds and the lengthening of the C(4)–C(10) and C(8)–C(9) bonds may be significant. The results of semi-empirical SCF-MO calculation[5] and X-ray crystallographic studies[1,6,7] of quinoline and its derivatives have shown the similar shortening and lengthening of the corresponding bonds as compared in Table 4. The C–O bond length (1.36 Å) is almost the same as those

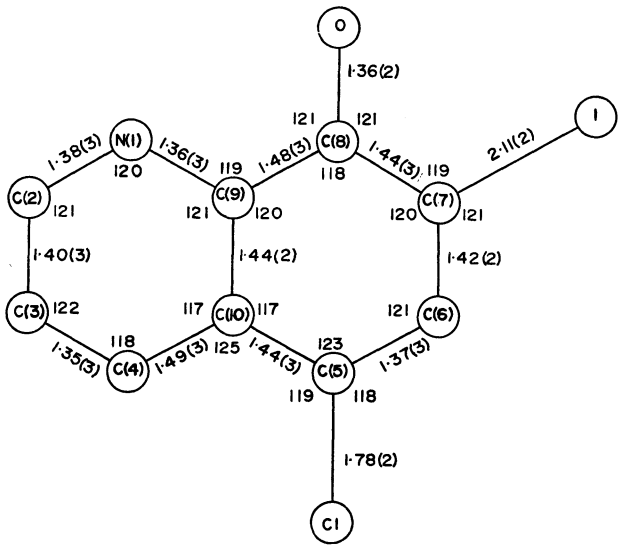

Fig. 2. Bond lengths(Å) and angles(°). The e.s.d.'s are shown in parentheses for bond lengths, and are 2° for all the bond angles.

5) M. J. S. Dewar and G. J. Gleicher, *J. Chem. Phys.*, **44**, 759 (1966).

6) M. Sax and R. Desiderato, *Acta Crystallogr.*, **23**, 319 (1967).

7) L. L. Merritt, Jr and B. Duffin, *ibid.*, **B26**, 734 (1970).

TABLE 3. OBSERVED AND CALCULATED STRUCTURE FACTORS

H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC	H	FO	FC
K,L=	0	0	-4	108	121	-2	23	26	0	142	118	-17	19	21	4	36	-35	-4	23	-22	-1	33	29	0	44	-46	-9	1/	-18
2	151	-112	-2	205	-179	2	24	26	1	157	128	-16	33	-34	5	18	-16	-3	155	-147	1	42	-42	1	52	54	-8	29	-28
4	202	165	0	88	77	4	13	-16	2	78	-78	-15	45	-45	7	23	20	-2	14	11	3	25	23	2	35	35	-7	36	33
6	184	-150	2	82	-83	K,L=	0	15	3	97	-93	-14	31	27	K,L=	1	12	-1	133	130	K,L=	2	10	3	33	-33	-6	36	33
8	72	75	4	78	78	-16	23	-21	4	141	119	-13	36	35	-15	15	-18	1	70	-77	-17	25	21	4	37	-27	-4	13	-20
10	63	-63	6	17	-17	-14	20	23	5	20	26	-12	49	-49	-14	25	26	2	13	17	-15	35	-33	5	33	31	-3	24	24
12	55	55	8	24	25	-10	31	35	6	33	-36	-11	43	-43	-13	24	24	3	90	96	-13	19	17	6	31	29	-2	20	19
K,L=	0	1	K,L=	0	7	-8	29	-30	7	63	-60	-10	27	30	-12	25	-27	4	16	15	-11	36	-33	7	31	-32	-1	32	-30
-18	32	-35	-20	29	29	-4	30	-29	8	22	25	-9	71	68	-11	53	-45	5	74	-74	-9	47	43	8	20	-20	0	14	-15
-16	37	38	-18	38	-38	2	19	14	9	12	13	-8	15	-28	-10	14	19	7	32	28	K,L=	2	11	9	25	22	1	17	17
-14	55	-57	-16	35	33	K,L=	1	0	10	39	-39	-7	38	-40	-9	34	34	9	40	-41	-9	18	-18	K,L=	3	4	2	17	18
-12	100	105	-14	70	-64	2	220	198	K,L=	1	4	-6	65	66	-8	35	-34	11	18	18	-5	24	-23	-15	24	23	3	18	-14
-10	88	-96	-12	44	47	3	85	85	-18	27	-26	-5	29	32	-7	19	-20	K,L=	2	4	-3	37	35	-14	24	21	K,L=	4	0
-8	89	92	-10	63	-69	4	135	-123	-17	20	-24	-4	10	-12	-6	23	24	-19	22	-21	-1	56	-51	-13	21	-19	2	29	34
-6	207	-178	-8	61	70	5	109	-98	-15	50	49	-3	51	-52	-5	43	40	-17	31	31	3	37	-31	-12	22	-23	4	31	-31
-4	91	99	-6	26	-24	6	69	71	-14	59	-54	-2	12	17	-4	26	-25	-15	41	-37	K,L=	2	12	-11	31	30	6	35	33
2	71	-69	-4	46	54	7	92	85	-13	43	-44	1	13	19	-3	16	-19	-13	62	60	-15	27	25	-10	28	25	8	19	-20
4	21	25	-2	13	14	8	68	-64	-12	66	60	2	19	-24	-2	42	42	-11	48	-46	-13	36	-31	-9	29	-29	K,L=	4	1
6	22	-27	6	42	42	9	21	-25	-11	68	62	5	51	52	-1	17	20	-9	58	61	-11	30	28	-8	27	-29	-12	19	-23
8	105	-101	10	24	28	10	25	29	-10	52	-51	7	13	-13	1	14	-15	-7	94	-87	-9	47	-40	-6	55	52	-10	21	25
10	24	27	12	19	-27	11	45	47	-9	68	-64	8	24	28	3	15	11	-4	24	21	-7	48	43	-5	53	-49	-8	19	-22
12	37	-40	K,L=	0	8	12	19	-26	-8	78	74	9	14	16	K,L=	1	13	-3	54	-61	-5	25	-23	-4	12	-16	-6	32	33
14	45	43	-20	17	16	14	23	27	-6	98	-94	11	19	-23	-14	27	24	-1	45	47	-3	35	32	-3	25	28	-4	22	-23
K,L=	0	2	-16	23	20	K,L=	1	1	-5	77	-74	K,L=	1	8	-11	21	-19	2	27	27	-1	23	-18	-2	19	20	-2	16	16
-18	32	-32	-14	14	-19	-17	19	21	-4	50	51	-12	16	-21	-10	18	19	7	39	-44	1	22	23	-1	12	-15	K,L=	4	2
-12	51	55	-6	62	64	-16	22	-25	-3	23	27	-11	22	24	-8	17	-19	11	25	-22	3	23	-17	1	19	21	-4	16	15
-4	116	-116	-2	61	66	-15	28	-30	-2	81	-82	-8	21	22	-3	17	19	13	31	28	K,L=	2	13	K,L=	3	5	-2	16	-18
0	177	-136	0	111	-107	-14	35	35	0	36	36	-7	44	42	K,L=	1	14	K,L=	2	5	-13	20	-21	-8	21	22	0	24	26
2	274	185	2	48	49	-13	18	21	2	19	20	-5	67	-66	-9	26	-22	-13	25	28	-9	19	-21	-6	17	-20	2	28	-27
4	164	-141	4	75	-77	-12	53	-48	4	33	35	-4	55	54	-7	14	15	-6	13	12	-1	23	22	-5	11	14	4	27	25
6	55	57	6	37	36	-11	64	-63	5	29	-33	-3	44	44	-6	18	-23	-5	52	-55	K,L=	2	14	-4	20	20	8	19	28
8	98	-101	8	23	-23	-10	89	86	6	13	15	-2	44	-40	-3	18	17	-4	20	-20	-7	25	-18	-3	26	-26	10	39	-18
10	48	50	10	32	34	-9	41	43	7	11	13	-1	68	-65	-2	18	-19	-3	36	38	-5	26	23	-2	28	-28	12	18	17
12	57	-55	12	17	-17	-8	91	-87	8	15	-17	0	11	17	0	19	21	-1	56	-55	-1	23	19	-1	23	23	K,L=	4	3
14	43	42	K,L=	0	9	-7	93	-92	9	23	-27	1	46	48	1	15	12	1	75	78	K,L=	2	15	0	42	39	-10	16	-20
K,L=	0	3	-18	30	26	-6	43	43	11	17	22	2	59	-59	K,L=	1	15	2	25	-22	-7	26	-20	1	11	-11	-8	22	22
-14	38	43	-16	16	-16	-5	73	70	12	24	-28	3	33	-30	-15	20	19	3	43	-44	-1	17	13	2	46	-40	-6	33	-30
-12	42	-45	-14	42	45	-4	53	-53	K,L=	1	5	4	36	36	-14	23	-19	5	61	60	K,L=	3	0	3	33	32	-4	32	34
-10	100	114	-12	72	-66	-3	129	-119	-20	17	14	5	44	44	-12	19	20	7	71	-65	2	56	-70	4	34	32	-2	29	-32
-8	78	-73	-10	50	50	2	49	49	-18	22	-28	6	36	-35	-11	19	17	9	20	18	3	40	43	5	27	-24	0	32	37
-6	105	104	-8	94	-96	5	13	-22	-15	14	14	7	45	-39	-9	15	-15	11	35	-31	4	42	41	6	35	-32	2	35	-36
-4	189	-161	-6	106	109	6	25	-28	-14	13	-17	8	17	22	-6	19	-25	13	28	24	5	50	-50	7	17	18	4	29	26
-2	152	134	-4	74	-74	7	30	-23	-8	17	11	K,L=	1	9	-5	15	-13	K,L=	2	6	6	39	-37	8	18	18	K,L=	4	4
0	211	-161	-2	67	74	8	17	-15	-7	13	-15	-17	19	-22	K,L=	2	0	-17	24	-24	7	41	39	9	38	-34	-12	17	22
2	214	160	0	81	-76	10	51	-47	-6	39	39	-16	21	20	3	121	-121	-15	22	22	8	23	19	10	23	-23	-10	28	-29
4	68	-69	4	93	-90	12	30	30	-5	32	33	-15	27	24	4	19	-18	-13	28	-28	10	20	-20	K,L=	3	6	-8	24	23
6	171	136	6	26	22	13	25	25	-4	58	-56	-14	24	-23	5	65	73	-11	63	59	11	20	21	-13	15	19	-6	23	-23
8	63	-63	K,L=	0	10	16	31	26	-3	61	-60	-13	39	-35	7	56	-57	-9	53	-51	K,L=	3	1	-12	31	29	-4	25	22
12	39	-40	-20	25	-23	K,L=	1	2	-2	41	42	-12	32	29	9	87	91	-7	62	65	-14	16	-17	-10	29	-29	-2	10	-10
K,L=	0	4	-18	48	45	-19	17	-15	-1	41	44	-11	43	42	K,L=	2	1	-5	102	-104	-13	19	21	-9	37	38	0	11	10
-20	20	-19	-16	20	-25	-17	19	22	0	126	-106	-10	57	-57	-15	40	40	-3	72	75	-12	28	30	-8	25	23	K,L=	4	5
-18	30	31	-14	43	45	-16	18	-21	1	62	-63	-9	39	-36	-13	51	-53	-1	76	-76	-11	34	-34	-7	25	-23	-4	11	-11
-16	73	-70	-12	54	-57	-15	17	-21	2	59	56	-8	64	59	-11	26	25	0	18	-21	-10	31	-33	-6	50	-48	-2	30	31
-14	24	25	-10	34	31	-14	24	26	3	77	78	-7	68	66	-9	83	-81	1	91	93	-9	24	26	-5	42	36	0	20	-21
-12	79	-75	-8	45	-49	-13	50	49	4	65	-60	-6	50	-47	-7	68	73	3	33	-35	-8	36	36	-4	40	40	2	28	27
-10	109	114	-6	34	39	-10	26	26	5	41	-41	-5	33	-33	-5	89	-94	5	47	45	-7	36	-35	-3	48	-50	4	32	-30
-8	152	-130	-2	22	26	-6	13	-17	6	79	79	-4	64	61	-3	125	117	7	38	-35	-6	32	-35	-2	40	-41	K,L=	4	6
-6	123	118	2	41	-43	-4	32	-30	7	35	38	-3	50	52	1	34	43	9	21	20	-5	36	38	-1	47	44	-12	15	-15
-4	197	-173	4	29	33	-3	157	134	8	40	-37	-2	49	-48	3	41	-47	K,L=	2	7	-4	28	30	0	28	27	-10	20	19
0	111	-90	8	25	27	-2	183	-142	9	47	-47	-1	50	-50	4	14	16	-19	18	16	-3	23	-24	1	26	-27	-8	41	-39
2	68	70	K,L=	0	11	0	113	99	10	31	33	0	39	39	11	22	18	-17	35	-32	-2	17	-16	2	24	-21	-6	27	26
4	50	51	-10	54	-59	1	117	104	12	33	-33	1	25	25	13	21	-18	-15	39	33	1	10	-13	3	38	37	-4	26	-24
10	54	-56	-8	15	17	2	31	-33	K,L=	1	6	2	61	-59	15	21	19	-13	52	-52	2	11	-11	K,L=	3	7	-2	32	28
12	14	17	-6	49	-50	3	83	-81	-18	16	17	6	24	-25	17	33	-22	-11	64	59	10	28	29	-15	26	-24	0	28	-25
K,L=	0	5	-4	49	58	4	68	68	-16	14	-18	8	18	20	K,L=	2	2	-9	50	-49	K,L=	3	2	-13	27	25	2	19	20
-20	20	-17	-2	32	-32	5	67	66	-15	17	-26	K,L=	1	10	-15	39	34	-7	47	50	-3	31	29	-11	27	-23	4	16	-17
-18	18	17	0	55	59	6	89	-84	-13	34	31	-17	19	-16	-13	20	-21	-5	50	-50	-2	32	34	-10	21	-22	K,L=	4	7
-16	48	-47	2	23	-25	7	111	-100	-12	43	-46	-16	42	37	-11	33	33	-1	25	-28	-1	10	-11	-9	30	31	-12	15	-17
-14	17	18	4	21	22	8	33	33	-11	48	-44	-15	22	22	-9	17	-18	3	22	22	0	33	-36	-8	13	12	-8	13	-16
-12	20	-25	6	39	-38	9	72	70	-10	82	78	-14	28	-28	-7	16	-17	7	40	41	1	33	33	-7	20	-21	-6	10	14
-8	67	73	8	16	19	10	70	-61	-9	62	62	-13	30	-30	-5	53	56	9	22	-20	2	31	32	-6	15	-17	-4	15	-17
-6	16	-17	K,L=	0	12	11	41	-37	-8	56	-54	-12	25	24	-4	16	-16	K,L=	2	8	3	48	-49	-4	12	-9	K,L=	4	8
-4	52	54	-18	17	-22	12	39	33	-7	79	-73	-11	32	27	-3	18	16	-9	30	29	4	41	-39	-3	30	-31	-6	11	-14
-2	158	-154	-16	33	33	13	45	42	-6	108	106	-10	34	-32	-2	21	-19	-7	32	-29	5	23	22	K,L=	3	8	-4	13	14
0	108	90	-14	28	-28	15	25	-26	-5	61	54	-8	15	19	-1	66	83	-5	48	47	6	50	45	-8	16	-16	0	22	21
2	151	-124	-10	47	-46	K,L=	1	3	-4	77	-75	-7	23	24	1	57	-64	-3	69	-67	7	59	-50	-5	16	-21	2	14	-14
4	167	148	-8	43	40	-17	15	-13	-3	119	-110	-6	29	-30	3	79	80	-1	44	41	9	26	24	-4	13	-15	4	17	19
6	53	-52	-6	56	-58	-16	15	10	-2	43	45	-4	29	31	5	110	-109	1	58	-60	10	27	25	-3	15	14	K,L=	4	9
8	84	83	-4	44	41	-15	33	31	-1	59	61	1	16	-17	7	67	67	3	55	57	K,L=	3	3	-2	36	38	-12	15	15
10	61	-63	0	39	39	-12	44	43	0	122	-106	K,L=	1	11	9	76	-72	5	26	-25	-12	20	-24	-1	32	-31	-10	18	-17
12	35	34	K,L=	0	13	-11	43	40	1	44	-45	-11	17	-18	11	59	55	7	41	37	-11	17	20	0	22	-20	-8	21	21
14	31	-31	-18	14	-17	-10	29	-26	2	54	55	-8	55	-49	13	32	-30	9	42	-35	-10	16	20	1	22	21	-6	24	-23
K,L=	0	6	-16	21	25	-9	79	-75	3	79	76	-7	22	-23	15	29	25	K,L=	2	9	-9	33	-38	2	26	26	-4	20	18
-20	17	15	-14	12	-16	-8	87	87	4	31	-31	-6	23	24	17	26	-21	-17	24	18	-8	39	-38	4	20	-20	-2	22	-24
-18	13	-12	-12	49	50	-7	85	82	5	29	-31	-5	30	33	K,L=	2	3	-15	33	-30	-7	36	37	5	29	28	0	16	17
-16	20	24	4	16	-13	-6	121	-110	6	43	44	-4	13	-18	-13	41	41	-13	35	33	-6	33	33	K,L=	3	9			
-14	63	-66	K,L=	0	14	-5	154	-129	7	27	26	-3	30	-31	-11	47	-49	-11	52	-45	-5	57	-56	-14	16	16			
-12	63	66	-14	16	17	-4	33	32	9	20	-22	-2	44	40	-9	58	61	-9	64	62	-4	36	-34	-13	23	-19			
-10	48	-56	-8	23	-28	-3	160	133	K,L=	1	7	-1	13	17	-7	90	-89	-7	27	-24	-3	50	50	-12	19	-17			
-8	180	165	-6	14	12	-2	105	-99	-19	20	-21	1	59	-56	-6	22	-24	-5	78	79	-2	43	44	-11	23	23			
-6	111	-108	-4	42	-46	-1	146	-125	-18	25	25	2	34	33	-5	144	114	-3	58	-56	-1	33	-34	-10	22	22			

found in 8-hydroxyquinoline–1,3,5-trinitrobenzene[1] and 8-hydroxyquinoline–chloranil[8] complexes (1.353 and 1.38 Å, respectively), and in phenols such as *p*-hydroxybenzoic acid monohydrate (1.359 Å),[9] α- and β-modifications of *p*-nitrophenol (1.351 and 1.361 Å, respectively).[10,11] No bond angles in a quinoline ring differ significantly from 120°.

As is shown in Table 5, the planes of a benzene ring, P(2), and a pyridine ring, P(3), are planar within 0.050 and 0.013 Å, respectively. The dihedral angle between these planes is only 3.2°, and the quinoline

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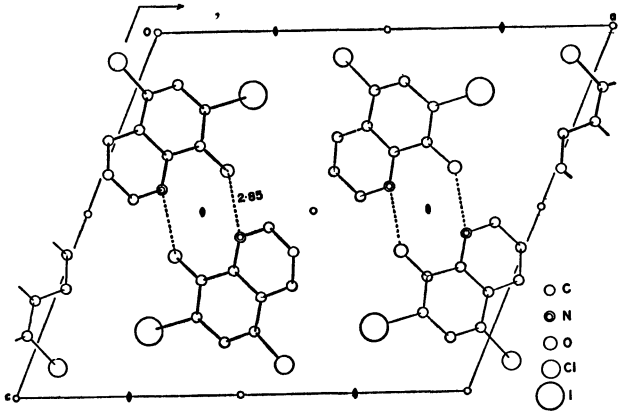
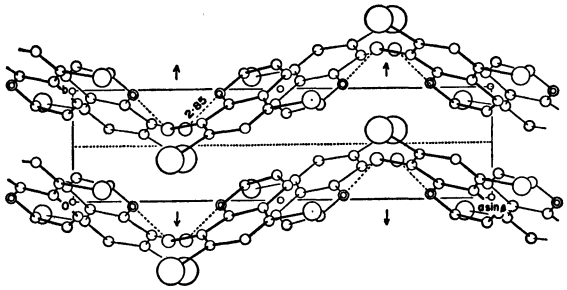
Table 4. The comparison of bond lengths (Å) of quinoline and its derivatives

	CIQ[a]	AMNQ[b]	HQSA[c]	HQTNB[d]	Quinoline[e] (Theoretical)
N(1)–C(2)	1.38	1.314	1.334	1.318	1.314
C(2)–C(3)	1.40	1.408	1.406	1.411	1.424
C(3)–C(4)	1.35	1.365	1.365	1.352	1.374
C(4)–C(10)	1.49	1.416	1.422	1.426	1.424
C(10)–C(5)	1.44	1.422	1.440	1.418	1.429
C(5)–C(6)	1.37	1.379	1.386	1.364	1.373
C(6)–C(7)	1.42	1.410	1.386	1.429	1.426
C(7)–C(8)	1.44	1.371	1.388	1.380	1.370
C(8)–C(9)	1.48	1.416	1.425	1.411	1.436
C(9)–C(10)	1.44	1.423	1.413	1.431	1.409
C(9)–N(1)	1.36	1.370	1.387	1.372	1.352

a) 5-Chloro-7-iodo-8-quinolinol, this work. b) 5-Acetoxy-6-methoxy-8-nitroquinoline, Ref. 6. c) 2-Methyl-8-hydroxyquinoline-5-sulfonic acid monohydrate, Ref. 7. d) 1 : 1 complex of 8-hydroxyquinoline and 1,3,5-trinitrobenzene, Ref. 1. e) Ref. 5.



(a)



(b)

Fig. 3. (a) The projection of the crystal structure along the *b* axis. (b) The projection of the crystal structure along the *c* axis. Hydrogen bonds are shown by broken lines.

Table 5. Distances from the least-squares plane (Å)

	P(1)	P(2)	P(3)
I	−0.218*	−0.138*	
Cl	0.041*	−0.032*	
O	−0.088*	−0.029*	
N(1)	0.047	0.040*	0.007
C(2)	−0.005		−0.006
C(3)	−0.022		0.010
C(4)	−0.041	−0.113*	−0.013
C(5)	0.005	−0.029	−0.017*
C(6)	0.052	0.050	
C(7)	−0.060	−0.030	
C(8)	−0.038	−0.009	−0.125*
C(9)	0.035	0.029	−0.011
C(10)	0.026	−0.012	0.013

P(1), the plane of quinoline ring; P(2), the plane of benzene ring; P(3), the plane of pyridine ring. The atom with asterisk is not included in the plane evaluation.

Table 6. Intermolecular distances

From molecule (I)	To atom	Of molecule	Translation			Distance (Å)
I	I	(I)	0	−1	0	4.16
I	C(7)	(I)	0	1	0	3.73
I	Cl	(II)	0	1	0	3.79
O	C(2)	(IV)	1	0	1	3.35
O	C(2)	(IV)	1	1	1	3.36
N(1)	N(1)	(IV)	1	0	1	3.33
C(2)	C(3)	(III)	1	0	1	3.57
C(3)	C(9)	(I)	0	−1	0	3.58
C(4)	C(10)	(I)	0	−1	0	3.56
O	N(1)	(IV)	1	0	1	2.85[a]

a) Hydrogen bond.
Key for molecules (I) x/a, y/b, z/c (given in Table 2) (II) $x/a+1/2$, $-y/b$, z/c (III) $-x/a$, $-y/b$, $-z/c$ (IV) $-x/a+1/2$, y/b, $-z/c$

ring as a whole is substantially planar within the limit of experimental errors. Among three substituents, only iodine atom deviates significantly from the quinoline ring plane, P(1).

The arrangements of the molecules viewed along the *b* and *c* axes are shown in Fig. 3. In the crystals, the molecules related by the two-fold axis are held together by the hydrogen bonds between oxygen and nitrogen atoms to form bent dimers, which are stacked closely by van der Waals forces along the *b* axis. The hydrogen bond length is 2.85 Å, which is comparable to the intermolecular O–H···N hydrogen bond lengths in 8-hydroxyquinoline dimers in 8-hydroxyquinoline–chloranil[8] and 8-hydroxyquinoline–1,3,5-trinitrobenzene[1] complexes (2.80 and 2.914 Å,

respectively). The intramolecular N···O distance is 2.82 Å, close to the corresponding distances in the complexes (2.74 and 2.745 Å).[8,11]

Some intermolecular distances are shown in Table 6. The intermolecular contacts are at the normal van der Waals distances. The dimension of the *b* axis is governed by the contact between atoms I and I (0 −1 0). In fact, in 5,7-dibromo-8-quinolinol, the lattice constant *b*, 4.02 Å, corresponds to the Br···Br van der Waals contact.

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