

## The Crystal Structure of the $\alpha$ Form of Anhydrous Copper 8-Hydroxyquinolate

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The crystal structure of the  $\alpha$  form of anhydrous copper 8-hydroxyquinolate,  $\text{Cu}(\text{C}_9\text{H}_6\text{NO})_2$ , has been determined by the Weissenberg equi-inclination X-ray method. The crystals, of bronze colored, fibrous morphology, were found to be monoclinic in the space group  $P2_1/c$ . The unit cell of dimensions  $a = 7.40 \pm 0.03$ ,  $b = 3.84 \pm 0.02$ ,  $c = 24.37 \pm 0.09$  Å, and  $\beta = 98^\circ 6' \pm 10'$ , contains two molecules. Intensities were measured visually, and the data refined by difference synthesis and least squares with a final  $R$  index of 12.2% including all observed reflections. Absorption corrections were neglected.

The copper atoms, which lie on symmetry centers, are six-coordinated. They are bound to the two hydroxyquinolate anions through the ring nitrogen atoms and the hydroxyl oxygen atoms in trans-planar configurations, and to the oxygen atoms from adjacent molecules; they reside at the centers of distorted octahedra. The anion rings are essentially planar with the planes of the opposing anions parallel but slightly displaced from each other. The copper and oxygen atoms are displaced from both of these planes.

### Introduction

Among known metal ion chelating agents is 8-hydroxyquinoline, which forms bidentate chelates with most of the divalent metals. Although these salts are well known, the nature of their anion-cation bonds is not well understood. Charles, Freiser, Fridel, Hillard & Johnson (1956) studied the infrared spectra of these complexes and found that they fell into two distinct groups when the positions of their carbon-oxygen stretching vibrations ( $9\mu$ ) were plotted against the atomic weights of the metals. One group, the transition metals, fell on a line of very steep positive slope while the other, the non-transition metals, resided on an almost horizontal line of slight negative slope. It was postulated that this result was due either to a difference in structure between the two groups, or to involvement of the  $3d$  orbitals in the metal-ligand bonding for the transition metal chelates. This question, however, was not resolved.

The cupric salt of 8-hydroxyquinoline,  $\text{Cu}(\text{C}_9\text{H}_6\text{NO})_2$ , has been shown to be dimorphic in both the anhydrous and dihydrate forms. Suito & Sekido (1957) described the  $\alpha$  and  $\beta$  forms of the dihydrate. The  $\alpha$  form, of fibrous morphology, was metastable and transformed into the  $\beta$  form which was plate-like, of tetragonal, hexagonal, or rhombohedral shape. X-ray powder diffraction patterns of the two forms indicated a probable difference in structure since the  $\beta$  form displayed many more lines. Merritt, Cady & Mundy (1954) investigated the  $\beta$  form and found it to be isomorphous with zinc hydroxyquinolate dihydrate. Jonassen (1962) has shown the anhydrous form to exist as a metastable  $\alpha$  form and a stable  $\beta$  form also. The anhydrous forms also exhibited a difference in their X-ray powder patterns and, in addition, an important difference in their infrared absorption spectra. When the positions of

their  $9\mu$  absorption peaks were plotted against atomic weight, it was found that the  $\alpha$  form fell into one of the groups described by Charles *et al.*, the transition metal group, whereas the  $\beta$  form fell into the other. A complete structure determination of the anhydrous  $\beta$  form has been accomplished by Palenik (1964). Further analysis of these complexes depends on the structure determinations of the remaining members of this family of compounds. In this regard the structure determination of the  $\alpha$  form of the copper salt was undertaken.

### Experimental

The  $\alpha$  form of anhydrous copper 8-hydroxyquinolate crystallizes in either lath-like or acicular crystals. Both types are essentially transparent with a yellowish gold tint, display well developed faces, and cleave normal to the needle axis. In addition transmitted light is polarized parallel to the needle axis.

Examination of single crystals of the compound with a Weissenberg camera using equi-inclination settings and copper radiation, revealed the following systematic absences:

$hkl$  no absences,  
 $h0l$  absent when  $l$  is odd,  
 $0k0$  absent when  $k$  is odd.

These absences are characteristics only of the space group  $P2_1/c$  ( $C_{2h}^5$ ). In addition, the unit-cell dimensions were found to be:

$$a = 7.40 \pm 0.03, \quad b = 3.84 \pm 0.02, \quad c = 24.37 \pm 0.09 \text{ \AA} \\ \beta = 98^\circ 6' \pm 10'.$$

Since the density, while not measured precisely, was found to be slightly greater than  $1.6 \text{ g.cm}^{-3}$ , it was concluded that there were two molecules per unit cell, as calculation based on this arrangement yields a density of  $1.71 \text{ g.cm}^{-3}$ .

In order to avoid the necessity of correcting for absorption, two very small crystals were used in making the photographs for the intensity measurements. An acicular crystal approximately  $0.050 \times 0.058$  mm in cross section was used for  $b$ -axis photographs, and a fragment about  $0.03 \times 0.03$  mm was cut from a larger crystal for rotation around the  $a$  axis. The crystals were mounted on a Weissenberg camera and their diffraction intensities recorded with exposures ranging up to 100 hours. Five films were exposed simultaneously in the multiple film technique. For Cu  $K\alpha$  radiation the transmission factor of the Kodak No-Screen film employed was approximately 23.3%. Intensities were measured visually by comparison with a standard scale prepared from the larger crystal.

Out of 2463 non-symmetry-related reflections accessible to film observation, 1144 were observed. All intensities were measured a minimum of three times and their average value taken as the best value. Approximate scale factors between layers were determined by comparing reflections common to layers of both axes. High order reflections were corrected for the  $\alpha_1 - \alpha_2$  split by multiplying partially resolved intensities by 1.2 and completely resolved intensities by 1.5 in a manner similar to that of Ghose & Fehlmann (1965). An additional 1319 reflections which were theoretically recorded on the film, but were too weak to be observed, were considered to be less than the minimum observable value at their respective angles. Contributions from these reflections were included in the final  $R$  value, but were excluded from the refinement process. Corrections for Lorentz and polarization factors were accomplished in the standard fashion.

The fact that there was a very short axis in the unit cell implied a planar molecule, generally lying in the  $x-z$  plane, and that the greatest information could be gained from projections parallel to this axis. Therefore, a two-dimensional Patterson projection map was constructed from the  $h0l$  data. Although examination of this Patterson projection suggested sites for all the heavy atoms, a more cautious approach was undertaken. A series of structure factor calculations of just the  $h0l$  reflections was embarked upon in which atoms, starting with copper only, and with estimated isotropic temperature factors, were added to the summations one at a time to observe their effect on the residual. Absolute structure factors were approximately obtained by multiplying the observed structure factors,  $F_o$ , by a scale factor such that the sum of the absolute values of  $F_o$  equalled the sum of the absolute values of the calculated structure factors,  $F_c$ . After each addition better agreement was achieved. The following atomic scattering factor curves were used in these calculations:  $\text{Cu}^{2+}$  from Watson & Freeman (1961), corrected for the real part of anomalous dispersion; oxygen and nitrogen from Hoerni & Ibers (1954); and carbon from McWeeny (1951). In addition, the isotropic temperature factor coefficients were assumed to be: 2.0 for copper and oxygen, 3.4 for nitrogen, and 4.0 for carbon.

After all but the hydrogen atoms were included, the method of successive Fourier synthesis was utilized to refine the  $x$  and  $z$  atom positions until no further sign changes were evident.

The  $y$  atom positions were determined by assuming that the atoms were in the  $x-z$  plane, and then estimating from a subsequent electron density projection around the  $[100]$  axis made from the  $0kl$  reflections. Again the successive Fourier synthesis technique was used and more accurate  $y$  positions ascertained. At this time the gross features of the structure of the molecule had been determined, and the  $R$  value was about 30% for all the observed reflections. A careful check of all observations revealed several errors which were corrected. In addition the 002 reflection appeared to be a victim of secondary extinction, and therefore was omitted from later refinement and residual calculations.

At this time a least-squares refinement program by Busing, Martin & Levy (1962) written for the IBM 7090 computer was adapted to the IBM 7044. Two cycles of this program on all the observed data assuming unit weighting factors, which were used throughout refinement, reduced  $R$  to about 18%. The function chosen to be minimized by this program was  $\Sigma|F_o - sF_c|/\Sigma|F_o|$  where  $s$  is a scale factor. From the atom positions derived from this process, a difference map about the  $[010]$  axis was calculated and plotted. Estimates of the possible positions of the six hydrogen atoms in the asymmetric unit were made from this projection. Their  $y$  positions were assumed to be the same as that of the carbon atom to which they were bound. This projection also served to call attention to the need for anisotropic temperature factors; therefore, anisotropic temperature coefficients were incorporated of the form:

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

Five more least-squares cycles were calculated and  $R$  fell to 12.3%, including contributions due to the hydrogen atoms whose positions were held constant. An isotropic temperature coefficient of 5.0 was assumed for the hydrogen atoms, and converted to anisotropic coefficients for the calculations. Difference maps about both axes were made from these positions, omitting the hydrogen atoms, so that new hydrogen positions could be determined. Probable positions were found for all six of the hydrogen atoms. With these new hydrogen positions,  $R$  was lowered to 12.2%, at which point refinement was terminated. However, when contributions from the unobserved reflections were added,  $R$  rose to 15.1%. A list of all the structure amplitudes together with their final calculated counterparts is given in Table 1.

The resulting atomic coordinates of the heavier atoms are given in Table 2 in fractions of the cell edge, and their temperature parameters in Table 3, along with their estimated uncertainties, which do not include the uncertainties in the lattice constants.

Table 1. Observed and calculated structure factors

Each group of three columns contains  $l$ ,  $10F_o$ , and  $10F_c$  respectively, and is headed by values of  $h$  and  $k$  common to the group. Minus signs in the  $F_o$  column denote unobserved reflections.

$h$	$k$	$l$	$10F_o$	$10F_c$	$h$	$k$	$l$	$10F_o$	$10F_c$	$h$	$k$	$l$	$10F_o$	$10F_c$	
0	0	1	864	928	-14	-46	29	-10	491	425	1	-4	0	-50	53
2	72	715	2 298	337	-18	191	231	0	37	-45	1	-20	29	2	37
4	101	-136	3 980	304	-22	166	182	1	170	140	1	-30	53	1	155
6	232	231	5 154	141	-26	61	63	2	64	44	1	-40	59	2	37
8	-32	-24	6 90	81	-28	-60	20	3	-51	58	1	-50	64	3	68
10	133	127	7 365	360	-30	89	49	4	172	154	1	-60	70	4	137
12	92	102	8 252	-220	-32	-48	42	5	222	161	1	-70	76	5	160
14	379	380	9 208	273	-34	63	91	6	-53	46	1	-80	81	6	158
16	149	155	10 39	-49	-36	71	86	7	117	86	1	-90	24	7	-47
18	265	257	11 115	145	-38	80	1	8	-53	-56	1	-100	25	8	158
20	476	462	12 -87	27	-40	89	1	9	103	50	1	-110	32	9	-48
22	76	83	13 183	190	-42	99	156	10	-43	-90	1	-120	37	10	148
24	-87	34	14 99	-84	-44	109	111	11	-42	7	1	-130	41	11	-51
26	96	36	15 217	225	-46	119	184	12	-40	18	1	-140	45	12	111
28	-47	21	16 -57	7	-48	129	77	13	-38	-11	1	-150	49	13	-54
30	-34	41	17 131	153	-50	139	204	14	-35	20	1	-160	53	14	238
			18 55	-65	-52	149	207	15	-33	-31	1	-170	57	15	159
			19 187	187	-54	159	284	16	-31	-34	1	-180	61	16	170
			20 359	169	-56	169	116	17	-28	28	1	-190	65	17	-28
			21 225	218	-58	179	40	18	-26	-6	1	-200	69	18	148
			22 85	86	-60	189	116	19	-24	3	1	-210	73	19	-46
			23 219	303	-62	199	234	20	-22	-15	1	-220	77	20	158
			24 316	363	-64	209	408	21	-20	43	1	-230	81	21	-51
			25 114	141	-66	219	86	22	-18	33	1	-240	85	22	248
			26 96	36	-68	229	190	23	-16	34	1	-250	89	23	166
			27 51	51	-70	239	344	24	-14	34	1	-260	93	24	-48
			28 79	220	-72	249	606	25	-12	33	1	-270	97	25	158
			29 137	279	-74	259	1045	26	-10	32	1	-280	101	26	-46
			30 234	41	-76	269	1489	27	-8	31	1	-290	105	27	170
					-78	279	2034	28	-6	30	1	-300	109	28	-44
					-80	289	2688	29	-4	29	1	-310	113	29	180
					-82	299	3451	30	-2	28	1	-320	117	30	-42
					-84	309	4324					-330	121		190
					-86	319	5307					-340	125		-40
					-88	329	6400					-350	129		200
					-90	339	7603					-360	133		-38
					-92	349	8926					-370	137		210
					-94	359	10369					-380	141		-36
					-96	369	11932					-390	145		220
					-98	379	13615					-400	149		-34
					-100	389	15428					-410	153		230
					-102	399	17371					-420	157		-32
					-104	409	19444					-430	161		240
					-106	419	21647					-440	165		-30
					-108	429	23980					-450	169		250
					-110	439	26443					-460	173		-28
					-112	449	29036					-470	177		260
					-114	459	31759					-480	181		-26
					-116	469	34612					-490	185		270
					-118	479	37595					-500	189		-24
					-120	489	40718					-510	193		280
					-122	499	43981					-520	197		-22
					-124	509	47384					-530	201		290
					-126	519	50927					-540	205		-20
					-128	529	54610					-550	209		300
					-130	539	58433					-560	213		-18
					-132	549	62406					-570	217		310
					-134	559	66529					-580	221		-16
					-136	569	70802					-590	225		320
					-138	579	75225					-600	229		-14
					-140	589	79808					-610	233		330
					-142	599	84551					-620	237		-12
					-144	609	89454					-630	241		340
					-146	619	94527					-640	245		-10
					-148	629	99770					-650	249		350
					-150	639	105283					-660	253		-8
					-152	649	111076					-670	257		360
					-154	659	117149					-680	261		-6
					-156	669	123502					-690	265		370
					-158	679	130135					-700	269		-4
					-160	689	137058					-710	273		380
					-162	699	144271					-720	277		-2
					-164	709	151784					-730	281		390
					-166	719	159597					-740	285		-1
					-168	729	167720					-750	289		400
					-170	739	176153					-760	293		-1
					-172	749	184906					-770	297		410
					-174	759	193979					-780	301		-1
					-176	769	203372					-790	305		420
					-178	779	213095					-800	309		-1
					-180	789	223148					-810	313		430
					-182	799	233531					-820	317		-1
					-184	809	244254					-830	321		440
					-186	819	255327					-840	325		-1
					-188	829	266750					-850	329		450
					-190	839	278523					-860	333		-1
					-192	849	290656					-870	337		460
					-194	859	303149					-880	341		-1
					-196	869	316002					-890	345		470
					-198	879	329225					-900	349		-1
					-200	889	342828					-910	353		480
					-202	899	356811					-920	357		-1
					-204	909	371184					-930	361		490
					-206	919	385947					-940	365		-1
					-208	929	401100					-950	369		500
					-210	939	416653					-960	373		-1
					-212	949	432616					-970	377		510
					-214	959	448989					-980	381		-1
					-216	969	465772					-990	385		520
					-218	979	482965					-1000	389		-1
					-220	989	500568					-1010	393		530
					-222	999	518581					-1020	397		-1
					-224	1009	537004					-1030	401		540
					-226	1019	555847					-1040	405		-1
					-228	1029	575110					-1050	409		550
					-230	1039	594793					-1060	413		-1
					-232	1049	614906					-1070	417		560
					-234	1059	635449					-1080	421		-1
					-236	1069	656432					-1090	425		570
					-238	1079	677865					-1100	429		-1
					-240	1089	699758					-1110	433		580
					-242	1099	722111					-1120	437		-1
					-244	1109	744934					-1130	441		590
					-246	1119	768237					-1140	445		-1
					-248	1129	792030					-1150	449		600
					-250	1139	816323					-1160	453		-1
					-252	1149	841126					-1170	457		610
					-254	1159	866439					-1180	461		

Table 1 (cont.)

Main data table with multiple columns of numbers and some text labels like 'A C 22 - 3\*' at the bottom left.

Table 2. *Positional parameters of the heavy atoms in fractional coordinates and their estimated standard deviations*

	$x/a$	$y/b$	$z/c$	$\sigma_x$	$\sigma_y$	$\sigma_z$
Cu	0.0000	0.0000	0.0000	.....	.....	.....
O	-0.0876	0.2523	0.0599	0.0011	0.0025	0.0003
N	0.2284	-0.0592	0.0524	0.0012	0.0027	0.0003
C(1)	0.3858	-0.2060	0.0443	0.0017	0.0032	0.0005
C(2)	0.5349	-0.2137	0.0877	0.0016	0.0034	0.0005
C(3)	0.5105	-0.1063	0.1390	0.0017	0.0032	0.0005
C(4)	0.3433	0.0500	0.1494	0.0015	0.0030	0.0004
C(5)	0.3043	0.1760	0.2005	0.0018	0.0032	0.0005
C(6)	0.1417	0.3288	0.2045	0.0017	0.0033	0.0005
C(7)	-0.0008	0.3567	0.1574	0.0018	0.0033	0.0005
C(8)	0.0311	0.2296	0.1058	0.0015	0.0030	0.0005
C(9)	0.2031	0.0733	0.1030	0.0015	0.0029	0.0004

Table 3. *Least-squares thermal parameters and their estimated standard deviations*

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cu	0.0148 (0.0005)	0.1012 (0.0027)	0.0017 (0.0001)	0.0066 (0.0013)	0.0002 (0.0001)	-0.0033 (0.0004)
O	0.0162 (0.0018)	0.1295 (0.0101)	0.0015 (0.0002)	0.0019 (0.0035)	-0.0001 (0.0005)	-0.0040 (0.0011)
N	0.0181 (0.0021)	0.0891 (0.0104)	0.0012 (0.0002)	-0.0012 (0.0042)	0.0010 (0.0005)	-0.0017 (0.0011)
C(1)	0.0193 (0.0029)	0.0686 (0.0114)	0.0017 (0.0003)	0.0092 (0.0048)	0.0003 (0.0007)	-0.0007 (0.0014)
C(2)	0.0155 (0.0027)	0.0845 (0.0122)	0.0020 (0.0003)	0.0072 (0.0047)	0.0014 (0.0007)	-0.0028 (0.0015)
C(3)	0.0205 (0.0030)	0.0705 (0.0127)	0.0015 (0.0002)	0.0037 (0.0046)	-0.0004 (0.0007)	-0.0011 (0.0013)
C(4)	0.0216 (0.0025)	0.0548 (0.0108)	0.0013 (0.0002)	-0.0008 (0.0049)	0.0013 (0.0006)	0.0003 (0.0013)
C(5)	0.0228 (0.0032)	0.0775 (0.0011)	0.0014 (0.0003)	0.0010 (0.0047)	0.0006 (0.0007)	-0.0002 (0.0013)
C(6)	0.0170 (0.0029)	0.0831 (0.0117)	0.0017 (0.0003)	-0.0007 (0.0044)	0.0010 (0.0007)	-0.0006 (0.0014)
C(7)	0.0225 (0.0031)	0.0843 (0.0122)	0.0015 (0.0003)	-0.0001 (0.0045)	0.0024 (0.0007)	-0.0013 (0.0013)
C(8)	0.0171 (0.0026)	0.0565 (0.0106)	0.0018 (0.0003)	0.0093 (0.0046)	0.0009 (0.0006)	-0.0014 (0.0014)
C(9)	0.0164 (0.0024)	0.0519 (0.0110)	0.0015 (0.0002)	0.0062 (0.0042)	0.0004 (0.0006)	-0.0010 (0.0011)

Table 4. *Probable hydrogen atom positions in fractional coordinates and distance from the associated carbon atom (in brackets)*

	$x/a$	$y/b$	$z/c$	Distance
H(1)[C(1)]	0.357	-0.246	0.000	1.08 Å
H(2)[C(2)]	0.615	-0.367	0.068	1.00
H(3)[C(3)]	0.613	-0.030	0.175	1.12
H(5)[C(5)]	0.407	0.198	0.236	1.07
H(6)[C(6)]	0.066	0.349	0.241	1.12
H(7)[C(7)]	-0.101	0.501	0.163	0.95

Probable hydrogen positions designated by the number of the carbon atoms to which they are attached, and their calculated bond lengths to the associated carbons are given in Table 4. From the atomic positions in Table 2, all the intramolecular distances and angles

of interest were computed, and are given in Fig. 1. Their maximum probable error in bond length was 0.018 Å, and 1.2° in bond angle. Their average probable error in bond length was 0.015 Å and in bond angle 1.0°.

### Discussion

Fig. 1 illustrates the final calculated bond lengths and angles for the molecule. Since there were no unusual intermolecular or intramolecular distances involved, the resulting structure is stereochemically sound and may be regarded as a molecular structure with only weak bonding, as signified by the relatively long bond length of 3.324 Å between the copper and oxygen atoms of adjacent molecules. Thus, the copper atoms in this

crystal, unlike those of the  $\beta$  form investigated by Palenik (1964) which were fivefold coordinated in distorted tetragonal pyramidal forms, are sixfold coordinated. The existence of four short bonds and two long bonds in the distorted octahedral arrangement around the copper make this compound one more example of Jahn–Teller distortion in a  $\text{Cu}^{\text{II}}$  complex. The two hydroxyquinolate anions that are bound through the hydroxyl oxygen and ring nitrogen atoms essentially form two planes parallel to each other, but displaced by a small distance. The best least-squares planes through various atoms of the asymmetric unit have been calculated following Scho-

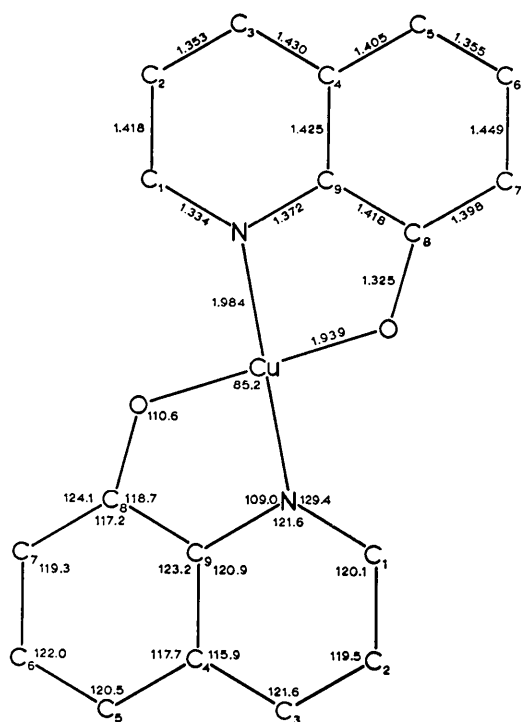


Fig. 1. Intermolecular distances and angles.

maker, Waser, Marsh & Bergman (1959) and are given in Table 5. Both the copper and oxygen atoms are slightly displaced from the planes of the quinoline rings.

The copper–oxygen distance of 1.939 Å found in this study is in agreement with that of the  $\beta$  form and those found in other studies. This distance is slightly shorter than the copper–nitrogen bond which was 1.984 Å and was discussed by Palenik in a similar situation for the  $\beta$  form. He pointed out that this difference, in this case 0.045 Å, can be accounted for by the Schomaker and Stevenson correction to the additivity of single-bond radii, and that the contention of Lingafelter, Simmons, Morosin, Scheringer & Freiburg (1961), that this inequality ought to be attributed to steric hindrance, should be re-examined. Although the agreement with the Schomaker and Stevenson correction is better for the  $\alpha$  form than the  $\beta$  form, the molecule also appears to be sensitive to steric repulsion and no conclusions can be reached in regard to this question.

A comparison of the ring structures of the  $\alpha$  and  $\beta$  forms reveals that they are essentially the same; the largest difference in the chemically equivalent bond is 0.023 Å with an average difference of 0.012 Å. This average difference is of the same order as the estimated standard deviations for the bond, and it is felt that this represents a good estimate of the accuracy of the structure.

In light of the difference in structure between the  $\alpha$  and  $\beta$  forms of anhydrous copper 8-hydroxyquinolate, it is very evident that this is the cause of the difference between their infrared spectra. Since the  $\beta$  form (Palenik, 1964) and the zinc complex (Merritt, 1953) have both been shown to have a tetrahedral structure, and are in one of the groups studied by Charles *et al.* (1956), whereas the  $\alpha$  form is in the other, it seems reasonable to predict that future studies will show that the reason for the differences in the two groups of divalent metal chelates is a difference in structure.

Table 5. Least-squares planes

Atom	Plane and deviations ( $\times 10^3$ ) from the plane			Distance from origin	Description of plane
	I	II	III		
Cu	−093	−156	−112		
O	095	049	090		
N	−020	−052	−032		
C(1)	−017	−045	−035		
C(2)	071	068	060		
C(3)	005	018	003		
C(4)	−009	−001	−005		
C(5)	−051	−027	−038		
C(6)	−019	−002	−001		
C(7)	007	−000	018		
C(8)	029	005	030		
C(9)	002	−014	−001		
Direction cosines ( $\times 10^4$ ) with respect to					
Plane	<i>a</i>	<i>b</i>	<i>c</i> *		
I	3836	8919	−2397	0.0933	Asymmetric unit
II	3909	8927	−2242	0.1562	Hydroxyquinoline anion
III	3821	8943	−2329	0.1117	Quinoline ring only

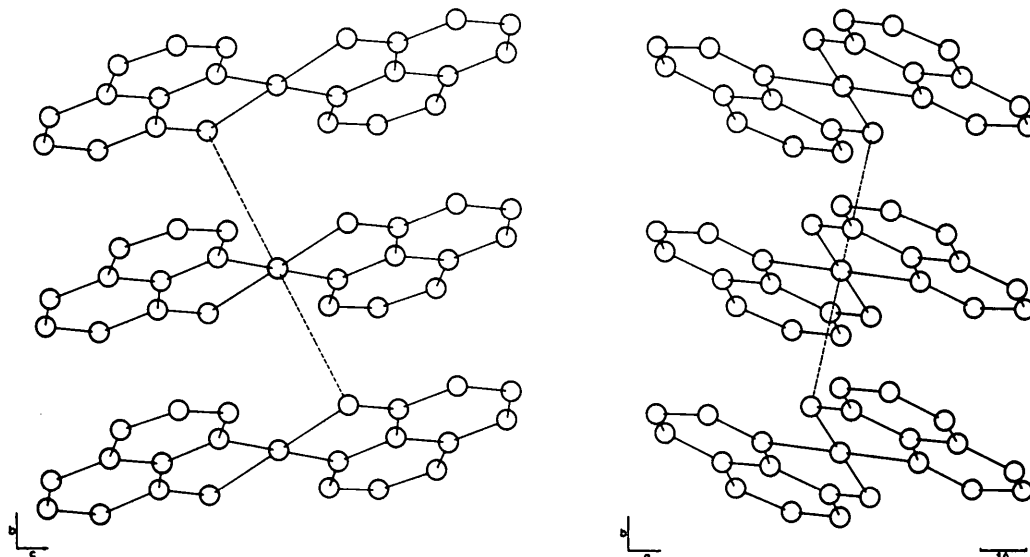


Fig. 2. Views of the structure along [100] and [001].

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## The Crystal Structure of 10,10'-Dianthranyl

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The crystal structure of 10,10'-dianthranyl has been determined from three-dimensional X-ray data. The atomic coordinates and anisotropic temperature factors have been refined by the method of least squares. The dimer has twofold symmetry perpendicular to the C(10)–C(10') bond and the planes of the two half-molecules make an angle of 145°18' with each other. The thermal vibrations indicate libration of the two half-molecules about C(10)–C(10').

#### Introduction

In the course of studies of the diamagnetic anisotropy of organic crystals Lasheen (1963, 1964) crystallized

anthrone from acetic acid and from ethyl alcohol, and in both cases he obtained two types of crystal, which he assumed to be two modifications of anthrone. Srivastava (1957*a,b*, 1961) had determined a crystal