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The Crystal Structures of Two Derivatives of 8-Hydroxyquinoline-5-sulfonic Acid, 2-Methyl-8-hydroxyquinoline-5-sulfonic Acid Monohydrate, and 7-Iodo-8-hydroxyquinoline-5-sulfonic Acid*

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(Received 27 November 1967 and in revised form 12 October 1968)

The crystal structures of 2-methyl-8-hydroxyquinoline-5-sulfonic acid monohydrate and 7-iodo-8-hydroxyquinoline-5-sulfonic acid have been determined by Fourier syntheses and refined by the method of least squares using three-dimensional photographic data. The 2-methyl derivative crystallizes from water as the monohydrate and the monoclinic unit cell has the dimensions $a = 13.35$, $b = 9.11$, $c = 17.84$ Å; $\beta = 90.3^\circ$. The space group is $C2/c$ with eight molecules in the unit cell. The molecule exists as a zwitterion and hydrogen bonds of lengths ranging from 2.65 to 2.94 Å link molecules together to form a three-dimensional hydrogen-bonded network in the structure. The final R was 0.087 for 1926 observed reflections. The 7-iodo derivative has a monoclinic unit cell of dimensions: $a = 9.55$, $b = 13.35$, $c = 8.83$ Å, $\beta = 109.2^\circ$, and the space group is $P2_1/c$ with $Z = 4$. The structure consists of sheets of molecules parallel to (010), the molecules being related by unit-cell translations in the a and c directions and linked by interactions of length 3.07 Å between iodine and oxygen atoms and hydrogen bonds of length 2.80 Å between oxygen atoms and quinoline nitrogen atoms. Sheets are bonded in pairs by hydrogen bonds between sulfonic acid oxygen atoms and hydroxyl groups, and distances between adjacent double sheets correspond to normal van der Waals interactions. The final R was 0.14 for 954 observed reflections.

Introduction

Structures of chelating organic molecules and the chelate complexes they form with inorganic ions, especially those complexes used by the analytical chemist, have long been of special interest to this laboratory.

The compound 8-hydroxyquinoline forms complexes with a large number of inorganic ions and so do most of its derivatives. However, substitution in the 2-position of the parent molecule prevents reaction with aluminum ions (Merritt & Walker, 1944) and it was felt desirable to determine the structures of derivatives with a 2-substituent and a 7-substituent, as these positions are adjacent to the chelate forming groups in the 1,8 positions of the 8-hydroxyquinoline molecule, in order to learn, if possible, what influences structure has on the formation and properties of the chelate

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molecule. In this article we report the structures of 2-methyl-8-hydroxyquinoline-5-sulfonic acid monohydrate (2-8-5 derivative) and 7-iodo-8-hydroxyquinoline-5-sulfonic acid (7-8-5 derivative).

2-8-5 DERIVATIVE

Experimental

2-Methyl-8-hydroxyquinoline-5-sulfonic acid was prepared by sulfonation of 8-hydroxyquinoline using Matsumura's (1927) method. Recrystallization of the product from hot water gives the monohydrate in the form of green diamond-shaped crystals. X-ray oscillation and Weissenberg photographs indicate a monoclinic unit cell of dimensions given in Table 1.

Table 1. *Crystal data*

2-Methyl-8-hydroxyquinoline-5-sulfonic acid monohydrate
Molecular formula: $C_{10}H_9O_4NS \cdot H_2O$

$$M = 257.3$$

Monoclinic; space group $C2/c$ or Cc
($C2/c$ confirmed by structure analysis)

$$a = 13.35 \pm 0.05 \text{ \AA}$$

$$b = 9.11 \pm 0.03 \text{ \AA}$$

$$c = 17.84 \pm 0.05 \text{ \AA}$$

$$\beta = 90.3 \pm 0.3^\circ$$

$$V = 2169.7 \text{ \AA}^3$$

$$d_{\text{obs}} = 1.565 \text{ g.cm}^{-3}$$

$$d_{\text{calc}} = 1.574 \text{ g.cm}^{-3}$$

$$Z = 8$$

7-Iodo-8-hydroxyquinoline-5-sulfonic acid
Molecular formula: $C_9H_6IO_4NS$

$$M = 351.1$$

Monoclinic; space group $P2_1/c$

$$a = 9.55 \text{ \AA}$$

$$b = 13.35 \text{ \AA}$$

$$c = 8.83 \text{ \AA}$$

$$\beta = 109.2^\circ$$

$$V = 1063.1 \text{ \AA}^3$$

$$d_{\text{calc}} = 2.19 \text{ g.cm}^{-3}$$

$$Z = 4$$

Using Cu $K\alpha$ radiation, equi-inclination multiple film Weissenberg photographs were taken of the levels Hkl for $0 \leq H \leq 6$ and hkl for $0 \leq K \leq 6$. A total of 1934 independent reflections were observed and their intensities were measured visually using calibrated scales. A further 276 reflections were below the minimum observed intensity M . Each of these latter reflections was given an intensity equal to the smallest $M/2$ on all films and a standard error of $0.7 M$. After scaling and correlating the data, Lorentz and polarization factors were applied but no correction was made for extinction or absorption.

The systematically absent reflections hkl with $(h+k)$ odd and $h0l$ with l odd show the space group to be either $C2/c$ or Cc .

The two independent groups of hkl data, those with h and k even and those with h and k odd, were placed on a common relative scale by Wilson's (1942) method. The standard errors of the observations were calculated from the agreement obtained in scaling reflections observed on more than one film in a pack and modified for the agreement between common reflections on different film packs.

In order to determine the correct space group, the statistical test of Howells, Phillips & Rogers (1950) was applied to the hkl data. This test indicated that $C2/c$ is the true space group, and the subsequent solution of the structure confirmed this choice.

Structure analysis

The structure determination commenced by examination of the three two-dimensional zones. Sharpened Patterson syntheses were computed from $hk0$, $h0l$ and $0kl$ data and the positions of the sulfur atoms in the unit cell were determined from the vector density distributions. Rows of peaks on the $h0l$ vector map indicated a possible molecular orientation and, together with consideration of van der Waals approaches, enabled a trial structure to be proposed for this projection.

An electron density projection onto (010), based on the phases calculated for the sulfur atom only, confirmed the trial structure and indicated the positions of the non-hydrogen atoms, although the water molecule position could not be determined at this stage. Structure factors were calculated for the $h0l$ zone using the new set of positional parameters and R , the usual reliability factor, was 0.53. The atomic scattering factors used were those given in *International Tables for X-ray Crystallography* (1962) with $B = 2.0 \text{ \AA}^2$ for all atoms. After three cycles of Fourier refinement, the agreement R for the $h0l$ data was 0.30.

Three-dimensional refinement

A three-dimensional electron density map based on the phases of the sulfur atom showed all the atoms (except hydrogen and the water oxygen) well resolved and confirmed the trial structure derived from the $h0l$ projection. Structure factors calculated for 518 hkl planes of greatest intensity, using the set of atomic coordinates obtained from the Fourier synthesis, gave an agreement R of 0.33, and a new electron density map located the position of the water oxygen atom.

Refinement continued by the method of least squares using the full-matrix program of Busing, Martin & Levy (1962). Three cycles, refining the two scale factors for data with h and k odd and with h and k even, positional parameters and isotropic temperature factors, reduced the reliability factor R from 0.33 to 0.15 for the 518 strongest reflections. The function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$, and the weights used during all refinement cycles were taken equal to the reciprocals of the squares of the standard errors of the obser-

Table 2. Observed and calculated structure factors for 2-methyl-8-hydroxyquinoline-5-sulfonic acid monohydrate

The three columns contain, from left to right, the values of I , $10F_0$ and $10F_c$. 8 low order reflections omitted from refinements because of extinction are marked with E , while the unobserved reflections are indicated by an asterisk.

0 0 L	0 963 918	-6 982 -1085	18 179 198	-8 226 -223	-2 289 266	-11 148 148	-15* 30 54	10 171 -182	6 486 549
2 739 783	2 339 338	-5 733 -756	19 280 -214	-7 122 111	-1 188 -213	-10 307 323	-14* 49 -55	11 219 227	7 50 2
4 1357 -1542	4 857 -847	-4 857 847	20 65 -49	-6* 33 -61	0 30 81	-9 175 158	-13 539 556	12 473 517	8 49 7
6 1377 -1479	6 241 194	-3 159 -187	9 1 L	-5 194 158	1 304 248	-8 913 -966	-12* 45 -37	13 108 -89	9 197 -206
8 92 98	8 332 361	-4 869 918	-19 78 78	-4 361 358	2 263 350	7 298 282	-11 109 27	14 104 -106	10 47 -18
10 1386 -1402	10 831 -223	-1 681 710	-18 58 -98	-3 93 81	3 564 616	-6 158 -136	-9 409 -395	15 155 -147	11 45 37
12 87 547	12* 75 -74	0 544 -359	-17* 34 -23	-2 60 -44	4 482 -554	-5 205 195	-10 388 -319	16 180 -203	12 272 289
14 589 -504	14* 68 -72	1 986 -377	-16 377 349	-1 74 78	5 718 749	-4 415 458	-8 254 271	17 71 69	13 165 -164
16 163 155	16 269 -269	2 2479 2744	-15 113 -180	0 150 -148	6 917 871	-3* 47 -77	-7 203 -159	18 198 201	14 129 -123
18 594 608	18 106 106	3 465 -348	-14 119 -130	1 124 126	7 115 86	-2 549 -554	-5* 29 50	19 119 -91	15 32 -27
20 346 -352	20 106 106	4 280 -205	-13 340 -351	2 151 164	8 757 739	-1 234 214	-5 415 480	20 202 230	16 70 -62
22 128 -161	22 106 106	5 447 417	-11 317 -318	3 36 47	9 271 245	0 263 263	-3 435 507	21 71 71	17 33 3
-20 187 173	-12 832 209	6 645 -571	-11 317 -318	4 125 -255	10 669 -669	1 242 228	-2 108 -76	22 107 -120	-12 456 -368
-18 575 -642	-8 162 96	7 154 -159	-10 103 98	5* 34 43	11 192 179	2 563 596	-1 253 192	-16 209 -216	-11 35 -33
-16 783 -362	-5 847 203	8 413 336	-9 441 -428	6 206 168	12 123 -116	3 467 -496	0 213 -265	-15 238 247	-10 852 -248
-14 940 -539	-4 294 -249	9 551 538	-8 352 -395	7 109 -181	13 341 336	4 566 -649	1 1023 -1075	-14 653 715	-9 153 135
-12 844 -867	-2 0 386 380	10 88 -148	-7 108 -148	8 184 -180	14 164 115	5 230 -225	2 106 -112	-13 50 -89	-8 61 75
-10 685 -640	-2 577 536	12 920 -844	-5 67 -9	10 97 -77	15 232 -240	6 150 155	3 359 347	-12 553 599	-7 86 60
-8 321 -179	4* 77 70	13 94 -95	-4 376 363	17 1 7	17 72 -44	8 127 115	4 432 459	-11 107 -94	-6 602 -567
-6 230 -279	6 363 324	14 534 574	-3 356 370	-2 141 -173	18 118 -116	9 106 73	5 384 364	-10 413 -118	-5 161 130
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-2K1386 1876	10* 61 34	16 126 -117	-1 364 331	1* 18 3	20 235 241	11 104 -91	7 3 61	-8 184 157	-2 216 210
0K 915 -1097	12* 64 48	17 121 117	0 493 -471	2 112 -143	21 74 60	12 333 119	8 223 -182	-7 201 397	-2 401 397
2 261 206	14 328 -207	18 168 -395	1 404 -407	0 2 2	22 127 124	9 153 -148	-5 372 355	-1 175 -152	0 136 -114
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22 274 288	6 127 -92	-15 205 -162	12 331 -346	10 246 211	-11 105 -1162	-11 129 -160	20 177 -164	5 252 -278	10 115 114
-22 143 136	8 139 -316	-14 269 -334	13 44 -27	11 108 -62	-10 1168 -1337	-10 177 -175	6 160 153	11 35 21	-11 35 21
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-18 233 -238	12 54 10	-12 1160 1154	15 40 -34	13 72 -61	-6* 41 3	-6 163 170	-26 315 320	13 25 23	13 25 23
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-12 436 408	-8 254 -311	-9 188 -173	18 101 -83	16 63 -88	-5 284 258	-5 284 258	11 288 104	-5 193 -142	-5 193 -142
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-4 1512 1915	2* 52 28	-4 767 742	-16 99 -99	20 64 -55	-1 792 804	-1 792 804	-12 771 -784	15 150 141	15 150 141
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Table 2 (cont.)

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18 206 -213	5 107 88	-13 236 195	17 364 338	-2 118 228	6 147 -145	14 21 85	-10 253 -256	-12 118 70	20 1 1
19 93 100	6 275 -280	-12 197 188	18 298 272	-1 228 -244	7 177 152	15 1 1	-8 275 318	-11 138 135	21 1 1
20 117 -121	7 143 111	-11 48 -12	19 175 153	0 219 -212	8 417 461	-10 144 -139	-8 285 -286	-10 182 183	22 1 1
21 335 373	8 160 143	-10 536 -513	20 7 5	1 1 1	9 254 -221	-9 246 233	-7 498 514	-9 133 -122	23 1 1
L 4	9 224 239	-9 944 959	-17 242 -187	2 171 -175	10 248 -218	-8 89 95	-7 442 427	-8 135 98	24 1 1
-20 73 35	10 249 258	-8 151 64	-10 418 -313	3 171 176	11 358 402	-7 54 64	-3 329 344	-7 132 127	25 1 1
-19 76 -71	11 252 -280	-7 254 -238	-15 382 306	4 3 2	12 77 66	-4 110 65	-4 110 65	-4 110 65	26 1 1
-18 87 -83	12 252 -280	-4 98 107	-14 240 232	5 96 -84	13 136 110	-5 156 -128	-3 4 1	-3 4 1	27 1 1
-17 147 137	13 51 -47	-5 709 -717	-13 273 -274	-9 175 -175	14 140 149	-4 190 -179	-2 1 1	-2 1 1	28 1 1
-16 357 345	14 104 68	-4 658 -650	-12 327 290	7 38 4	15 395 -427	-3 240 337	-1 5 5	-1 5 5	29 1 1
-15 48 -27	15 117 96	-3 1033 1178	-11 51 30	8 36 -55	16 62 -58	-2 230 208	-1 138 109	-1 138 109	30 1 1
-14 494 -497	16 199 186	-2 53 43	-10 110 -89	9 147 137	17 212 197	-1 138 109	-1 281 235	-1 281 235	31 1 1
-13 651 651	17 351 351	-1 351 351	-8 307 287	10 223 216	18 6 6	2 111 100	3 58 -68	3 58 -68	32 1 1
-12 168 343	-16 217 244	1 519 501	-7 249 240	-5 86 -81	-17 282 -240	3 105 93	4 84 -80	4 84 -80	33 1 1
-11 467 549	-15 385 -379	1 548 -799	-6 124 -130	-4 384 354	-15 249 205	5 103 104	5 453 455	5 453 455	34 1 1
-10 317 276	-14 432 -381	2 243 251	-4 468 -436	-3 316 -311	-14 105 87	6 96 21	7 214 -234	7 214 -234	35 1 1
-9 550 -599	-13 38 -19	3 612 695	-5 209 156	-2 150 -149	-13 235 196	7 96 21	8 228 -228	8 228 -228	36 1 1
-8 355 -343	-12 123 -97	4 128 174	-4 468 -436	-1 27 27	-14 105 87	8 228 -228	9 337 -337	9 337 -337	37 1 1
-7 333 347	-11 50 42	5 257 287	-3 385 358	-1 27 27	-14 105 87	8 228 -228	10 337 -337	10 337 -337	38 1 1
-6 436 -425	-10 324 337	6 5 7	-2 173 350	-1 681 -681	-10 4 9	9 163 139	11 328 -342	11 328 -342	39 1 1
-5 495 53	-9 12 -51	7 50 -61	-1 681 -681	2 237 227	-9 284 292	10 158 137	12 204 211	12 204 211	40 1 1
-4 214 215	-8 335 -292	8 505 -517	1 197 -172	3 27 27	-7 372 315	11 285 282	13 121 -115	13 121 -115	41 1 1
-3 535 -558	-7 185 -174	1 1 1	2 27 -21	4 111 113	-7 372 315	12 285 282	14 121 -115	14 121 -115	42 1 1
-2 454 -511	-6 185 -174	1 1 1	3 27 -21	5 61 61	-8 485 -511	-5 1 1	15 121 -115	15 121 -115	43 1 1
-1 100 -95	-5 245 -324	1 1 1	4 111 113	6 61 61	-6 485 -511	-5 1 1	16 121 -115	16 121 -115	44 1 1
0 595 -628	-4 178 -182	12 42 -42	5 61 61	7 61 61	-5 1 1	-5 1 1	17 121 -115	17 121 -115	45 1 1
1 212 204	-3 2 2	13 42 -42	6 61 61	8 61 61	-4 34 -38	-2 1 1	18 121 -115	18 121 -115	46 1 1
2 746 812	-2 352 -311	14 312 -293	7 61 61	9 61 61	-3 222 212	1 1 1	19 121 -115	19 121 -115	47 1 1
3 788 877	-1 267 171	15 556 584	8 61 61	10 61 61	-2 274 252	2 132 13	20 121 -115	20 121 -115	48 1 1
4 982 1102	0 9 9	16 232 223	9 61 61	11 61 61	-1 131 -101	3 2 2	21 121 -115	21 121 -115	49 1 1
5 147 134	1 172 144	17 128 124	10 61 61	12 61 61	-2 274 252	4 2 2	22 121 -115	22 121 -115	50 1 1
6 34 142	2 1 1	18 328 373	11 61 61	13 61 61	-1 131 -101	5 2 2	23 121 -115	23 121 -115	51 1 1
7 139 -135	3 434 -441	19 274 -284	12 61 61	14 61 61	-2 274 252	6 2 2	24 121 -115	24 121 -115	52 1 1
8 209 204	4 428 -424	20 14 14	13 61 61	15 61 61	-1 131 -101	7 2 2	25 121 -115	25 121 -115	53 1 1
9 242 -254	5 189 141	3 1 1	14 61 61	16 61 61	-2 274 252	8 2 2	26 121 -115	26 121 -115	54 1 1
10 73 39	6 27 11	-2 42 42	15 61 61	17 61 61	-1 131 -101	9 2 2	27 121 -115	27 121 -115	55 1 1
11 214 203	7 13 13	-1 3 3	16 61 61	18 61 61	-2 274 252	10 2 2	28 121 -115	28 121 -115	56 1 1
12 114 102	8 281 27	-2 1 1	17 61 61	19 61 61	-1 131 -101	11 2 2	29 121 -115	29 121 -115	57 1 1
13 283 288	9 1 1	-1 1 1	18 61 61	20 61 61	-2 274 252	12 2 2	30 121 -115	30 121 -115	58 1 1
14 91 97	10 2 2	-2 1 1	19 61 61	21 61 61	-1 131 -101	13 2 2	31 121 -115	31 121 -115	59 1 1
15 242 -241	11 1 1	-1 1 1	20 61 61	22 61 61	-2 274 252	14 2 2	32 121 -115	32 121 -115	60 1 1
16 72 -47	12 1 1	-2 1 1	21 61 61	23 61 61	-1 131 -101	15 2 2	33 121 -115	33 121 -115	61 1 1
17 224 -23	13 2 7	-2 1 1	22 61 61	24 61 61	-2 274 252	16 2 2	34 121 -115	34 121 -115	62 1 1
18 89 85	14 1 1	-1 1 1	23 61 61	25 61 61	-1 131 -101	17 2 2	35 121 -115	35 121 -115	63 1 1
19 24 28	15 1 1	-2 1 1	24 61 61	26 61 61	-2 274 252	18 2 2	36 121 -115	36 121 -115	64 1 1
20 256 256	16 1 1	-1 1 1	25 61 61	27 61 61	-1 131 -101	19 2 2	37 121 -115	37 121 -115	65 1 1
L 4	17 1 1	-2 1 1	26 61 61	28 61 61	-2 274 252	20 2 2	38 121 -115	38 121 -115	66 1 1
-20 125 -133	-18 2 2	-1 1 1	27 61 61	29 61 61	-1 131 -101	21 2 2	39 121 -115	39 121 -115	67 1 1
-19 74 26	-13 32 2	-2 1 1	28 61 61	30 61 61	-2 274 252	22 2 2	40 121 -115	40 121 -115	68 1 1
-18 550 543	-12 14 134	-3 1 1	29 61 61	31 61 61	-1 131 -101	23 2 2	41 121 -115	41 121 -115	69 1 1
-17 167 -184	-11 115 -113	-4 1 1	30 61 61	32 61 61	-2 274 252	24 2 2	42 121 -115	42 121 -115	70 1 1
-16 343 -343	-10 44 -442	-5 1 1	31 61 61	33 61 61	-1 131 -101	25 2 2	43 121 -115	43 121 -115	71 1 1
-15 188 186	-9 258 27	-6 1 1	32 61 61	34 61 61	-2 274 252	26 2 2	44 121 -115	44 121 -115	72 1 1
-14 361 346	-8 209 178	-7 1 1	33 61 61	35 61 61	-1 131 -101	27 2 2	45 121 -115	45 121 -115	73 1 1
-13 411 434	-7 228 221	-8 1 1	34 61 61	36 61 61	-2 274 252	28 2 2	46 121 -115	46 121 -115	74 1 1
-12 293 278	-6 227 227	-9 1 1	35 61 61	37 61 61	-1 131 -101	29 2 2	47 121 -115	47 121 -115	75 1 1
-11 457 -438	-5 204 -200	-10 1 1	36 61 61	38 61 61	-2 274 252	30 2 2	48 121 -115	48 121 -115	76 1 1
-10 285 -246	-4 206 -202	-11 1 1	37 61 61	39 61 61	-1 131 -101	31 2 2	49 121 -115	49 121 -115	77 1 1
-9 198 158	-3 196 194	-12 1 1	38 61 61	40 61 61	-2 274 252	32 2 2	50 121 -115	50 121 -115	78 1 1
-8 516 -497	-2 192 -201	-13 1 1	39 61 61	41 61 61	-1 131 -101	33 2 2	51 121 -115	51 121 -115	79 1 1
-7 345 332	-1 192 -191	-14 1 1	40 61 61	42 61 61	-2 274 252	34 2 2	52 121 -115	52 121 -115	80 1 1
-6 96 85	0 231 -236	-15 1 1	41 61 61	43 61 61	-1 131 -101	35 2 2	53 121 -115	53 121 -115	81 1 1
-5 317 241	1 351 357	-16 1 1	42 61 61	44 61 61	-2 274 252	36 2 2	54 121 -115	54 121 -115	82 1 1
-4 522 -516	2 3 3	-17 1 1	43 61 61	45 61 61	-1 131 -101	37 2 2	55 121 -115	55 121 -115	83 1 1
-3 127 -122	3 1 1	-18 1 1	44 61 61	46 61 61	-2 274 252	38 2 2	56 121 -115	56 121 -115	84 1 1
-2 221 -165	4 240 -234	-19 1 1	45 61 61	47 61 61	-1 131 -101	39 2 2	57 121 -115	57 121 -115	85 1 1
-1 145 119	5 1 1	-20 1 1	46 61 61	48 61 61	-2 274 252	40 2 2	58 121 -115	58 121 -115	86 1 1
0 157 105	6 173 155	-21 1 1	47 61 61	49 61 61	-1 131 -101	41 2 2	59 121 -115	59 121 -115	87 1 1
1 402 -408	7 1 1	-22 1 1	48 61 61	50 61 61	-2 274 252	42 2 2	60 121 -115	60 121 -115	88 1 1
2 372 -374	8 1 1	-23 1 1	49 61 61	51 61 61	-1 131 -101	43 2 2	61 121 -115	61 121 -115	89 1 1
3 381 372	9 1 1	-24 1 1	50 61 61	52 61 61	-2 274 252	44 2 2	62 121 -115	62 121 -115	90 1 1
4 42 -27	10 205 194	-25 1 1	51 61 61	53 61 61	-1 131 -101	45 2 2	63 121 -115	63 121 -115	91 1 1
5 347 -331	11 1 1	-26 1 1	52 61 61	54 61 61	-2 274 252	46 2 2	64 121 -115	64 121 -115	92 1 1
6 551 -520	12 1 1	-27 1 1	53 61 61	55 61 61	-1 131 -101	47 2 2	65 121 -115	65 121 -115</	

vations as determined from the scaling of films in a pack and correlation of different film packs.

At this stage it was seen that eight large, low order reflections were probably affected by extinction; these were omitted from subsequent refinement cycles.

A three-dimensional difference synthesis did not show the hydrogen atom positions but indicated anisotropic thermal motion for most of the heavier atoms. The positions of the four aromatic hydrogen atoms of the quinoline ring were calculated, assuming them to lie on the diagonals of the benzene rings at a distance of 1.05 Å from the carbon atoms. They were included as fixed atoms ($B = 5.0 \text{ Å}^2$) in three cycles of anisotropic refinement using all the observed data, and the reliability factor dropped from 0.18 to 0.094. A three-dimensional difference synthesis indicated the positions of the hydrogen atoms in the water molecule and methyl group and they were included as fixed atoms ($B = 5.0 \text{ Å}^2$) in a further refinement cycle. At this stage, the calculated shifts in parameters were less than the corresponding standard deviations and the refinement was terminated. The final reliability factor was 0.087 for the 1926 observed reflections.

Inclusion of the eight reflections affected by extinction and the 276 unobserved reflections gave an agreement factor R , of 0.100. The observed and calculated structure factors are listed in Table 2. At the end of refinement a difference Fourier synthesis was calculated (Fig. 1), for which the contributions of the hydrogen atoms were not included in the F_c 's. The final set of positional and thermal parameters for the non-hydrogen atoms are given in Tables 3 and 4 respectively, together with the standard deviations calculated from the diagonal terms of the inverse matrices. Hydrogen atom coordinates are presented in Table 5 with the distance to the atom to which the hydrogen atom is attached. The remaining intramolecular bond lengths and angles are given in Table 6.

Table 3. *Final atomic positional parameters in the 2-8-5 derivative*

The e.s.d.'s in parentheses correspond to the last significant digit.

	<i>x</i>	<i>y</i>	<i>z</i>
S	0.1807 (1)	0.0234 (1)	0.1673 (1)
N(1)	0.4286 (3)	0.1415 (3)	-0.0498 (1)
C(2)	0.3861 (4)	0.0457 (4)	-0.0947 (2)
C(3)	0.3052 (4)	-0.0377 (5)	-0.0679 (2)
C(4)	0.2703 (4)	-0.0185 (5)	0.0032 (2)
C(5)	0.2815 (3)	0.1214 (4)	0.1261 (1)
C(6)	0.3289 (3)	0.2323 (5)	0.1659 (2)
C(7)	0.4104 (3)	0.3087 (5)	0.1375 (2)
C(8)	0.4449 (3)	0.2808 (4)	0.0657 (2)
C(9)	0.3959 (3)	0.1698 (4)	0.0228 (2)
C(10)	0.3143 (3)	0.0885 (4)	0.0512 (2)
O(11)	0.5212 (2)	0.3479 (3)	0.0325 (1)
C(12)	0.4243 (5)	0.0313 (6)	-0.1741 (2)
O(13)	0.0932 (2)	0.0581 (3)	0.1206 (2)
O(14)	0.1720 (3)	0.0767 (4)	0.2434 (1)
O(15)	0.2080 (3)	-0.1317 (3)	0.1625 (1)
O(16)	0.0998 (3)	0.2476 (4)	0.3718 (2)

7-8-5- DERIVATIVE

Experimental

The compound 7-iodo-8-hydroxyquinoline-5-sulfonic acid crystallizes from water in the form of pale yellow needles elongated along the c crystallographic axis. A small crystal of suitable dimensions was mounted in a thin-walled glass capillary tube and X-ray oscillation and Weissenberg photographs indicated a monoclinic unit cell of dimensions given in Table 1.

Using Cu $K\alpha$ radiation, equi-inclination multiple-film Weissenberg photographs were taken of the levels $hk0$ to $hk4$. A total of 978 independent reflections were observed and their intensities were measured visually using a calibrated scale obtained from timed exposures of one of the crystal reflections.

Systematic absences ($h0l$ with l odd, $0k0$ with k odd)

Table 4. *Anisotropic temperature coefficients in the 2-8-5 derivative*

E.s.d.'s in parentheses.
All values have been multiplied by 10^5 .

	β_{11}^*	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	311 (6)	606 (15)	77 (3)	-96 (6)	88 (3)	-13 (3)
N(1)	344 (20)	775 (46)	66 (7)	-5 (24)	80 (9)	-13 (12)
C(2)	428 (27)	848 (54)	75 (9)	-51 (29)	69 (12)	-78 (16)
C(3)	489 (31)	1015 (63)	138 (10)	-230 (35)	34 (14)	-138 (18)
C(4)	451 (29)	814 (57)	150 (11)	-108 (31)	64 (14)	-69 (18)
C(5)	353 (23)	665 (47)	67 (8)	-115 (26)	50 (11)	-12 (14)
C(6)	330 (24)	845 (55)	97 (8)	-93 (27)	80 (11)	-62 (16)
C(7)	410 (27)	833 (54)	118 (9)	-188 (31)	44 (12)	-107 (18)
C(8)	304 (23)	693 (48)	109 (8)	-83 (27)	30 (11)	-43 (16)
C(9)	299 (21)	533 (43)	78 (8)	1 (25)	58 (10)	-3 (14)
C(10)	345 (23)	553 (46)	98 (8)	-37 (27)	68 (11)	11 (16)
O(11)	462 (20)	1186 (50)	166 (8)	-386 (25)	128 (10)	-75 (15)
C(12)	656 (40)	1713 (91)	101 (10)	-287 (44)	156 (15)	-185 (22)
O(13)	335 (19)	820 (40)	241 (9)	-89 (22)	32 (11)	22 (14)
O(14)	608 (24)	1321 (50)	109 (7)	-230 (27)	171 (10)	-113 (14)
O(15)	534 (21)	605 (38)	198 (8)	68 (23)	141 (10)	34 (12)
O(16)	506 (27)	1478 (64)	300 (10)	-66 (28)	176 (13)	-258 (18)

* The anisotropic thermal parameters are in the form: $\exp \{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$.

among the reflections indicate unambiguously the space group $P2_1/c$. The calculated density for four molecules in the unit cell is 2.19 g.cm^{-3} , which seems reasonable for this type of compound. No experimental density was determined.

After applying the usual Lorentz and polarization corrections, the intensities were corrected for absorption ($\mu = 259 \text{ cm}^{-1}$ for Cu $K\alpha$ radiation) using the values given in *International Tables for X-ray Crystallography* (1959) and assuming a cylindrical crystal. No correction was made for extinction and reflections thought to be affected were omitted from the final cycles of refinement. These reflections are marked with an asterisk in the list of F_o and F_c (Table 7).

Structure analysis

The data from each of the five hkl levels were placed on a common relative scale by Wilson's (1942) method

and a three-dimensional Patterson synthesis was computed. The positions of the iodine and sulfur atoms in the asymmetric unit were determined from the Patterson map and were used in a structure factor calculation to assign phases to the Fourier coefficients. The first three-dimensional electron density map confirmed the coordinates of the iodine and sulfur atoms and showed the positions of all the other atoms (except hydrogen) in the molecule. The packing of molecules in the unit cell appeared reasonable with regard to hydrogen bonding and van der Waals close approaches and a structure factor calculation based on the atomic coordinates derived from the first three-dimensional Fourier synthesis gave an agreement factor, R , of 0.29. The scattering factor curves used were those of Hoerni & Ibers (1954) for carbon, nitrogen and oxygen atoms, the values given by Dawson (1960) for sulfur and those of Thomas & Umeda (1957) for iodine. No correction was made for anomalous dispersion.

Table 5. *Hydrogen atom coordinates in the 2-8-5 derivative*

Atom	Attached to	x	y	z	Distance
*H(1)	N(1)	0.480	0.203	-0.070	0.94 Å
H(3)	C(3)	0.270	-0.116	-0.102	1.05
H(4)	C(4)	0.209	-0.076	0.023	1.04
H(6)	C(6)	0.303	0.254	0.220	1.05
H(7)	C(7)	0.446	0.389	0.170	1.05
H(12a)	C(12)	0.342	0.050	-0.205	1.24
H(12b)	C(12)	0.417	-0.066	-0.189	0.93
H(12c)	C(12)	0.458	0.126	-0.180	0.98
H(16a)	O(16)	0.083	0.197	0.328	0.93
H(16b)	O(16)	0.163	0.303	0.363	1.00

* Coordinates taken from the final difference map (Fig. 1) and not included in the least-squares refinement.

Table 6. *Intramolecular bond lengths and angles in the 2-8-5 derivative*

E.s.d.'s in parentheses.*

Length		Angle	
S—O(13)	1.466 (3) Å	O(13)—S—O(14)	113.2 (2)°
S—O(14)	1.447 (3)	O(13)—S—O(15)	111.9 (2)
S—O(15)	1.462 (3)	O(14)—S—O(15)	113.6 (2)
S—C(5)	1.777 (4)	O(13)—S—C(5)	105.0 (2)
N(1)—C(9)	1.387 (4)	O(14)—S—C(5)	106.5 (2)
N(1)—C(2)	1.334 (5)	O(15)—S—C(5)	105.8 (2)
C(2)—C(12)	1.514 (5)	C(2)—N(1)—C(9)	122.4 (3)
C(2)—C(3)	1.406 (6)	C(3)—C(2)—C(12)	122.3 (4)
C(3)—C(4)	1.365 (5)	C(3)—C(2)—N(1)	119.2 (3)
C(4)—C(10)	1.422 (5)	C(12)—C(2)—N(1)	118.5 (4)
C(5)—C(10)	1.440 (4)	C(4)—C(3)—C(2)	120.9 (4)
C(5)—C(6)	1.386 (5)	C(10)—C(4)—C(3)	120.4 (4)
C(6)—C(7)	1.386 (5)	S—C(5)—C(6)	119.9 (2)
C(7)—C(8)	1.388 (4)	S—C(5)—C(10)	120.9 (3)
C(8)—O(11)	1.330 (5)	C(6)—C(5)—C(10)	119.1 (3)
C(8)—C(9)	1.425 (5)	C(5)—C(6)—C(7)	122.3 (3)
C(9)—C(10)	1.413 (5)	C(6)—C(7)—C(8)	120.7 (3)
		C(7)—C(8)—C(9)	118.1 (3)
		C(7)—C(8)—O(11)	126.0 (4)
		O(11)—C(8)—C(9)	115.9 (3)
		C(8)—C(9)—C(10)	122.1 (3)
		C(8)—C(9)—N(1)	118.1 (3)
		C(10)—C(9)—N(1)	119.8 (3)
		C(9)—C(10)—C(5)	117.5 (3)
		C(9)—C(10)—C(4)	117.4 (3)
		C(5)—C(10)—C(4)	125.1 (4)

* The e.s.d.'s were computed using the full variance-covariance matrix from the least-squares refinement.

The structure was refined by the least-squares method using the Busing, Martin & Levy (1962) full-matrix program. Two cycles of isotropic refinement reduced the R factor to 0.19. At this stage it was seen that several low order planes of strong intensity were making too large a contribution, probably because of extinction; these were omitted from subsequent cycles. Weighting of the observations during the refinement was based on the standard errors determined from the scaling of films in a pack.

It was now thought justified to do anisotropic refinement of the heavier atoms (I, S and O), although the scaling procedure precludes meaningful discussion of the resulting parameters (Lingafelter & Donohue, 1966). The isotropic temperature factors of the lighter atoms were kept fixed as it was not possible to refine both anisotropic and isotropic temperature factors in the same refinement cycles with the program used. Three cycles of refinement reduced the reliability factor R to 0.14; at this stage the calculated shifts in atomic parameters were all less than their standard errors and refinement was considered complete. An analysis of the reliability factor for different ranges of $\sin \theta$, however, showed an increase in R from 0.11 for the innermost reflections with $\sin \theta \leq 0.35$, to 0.21 for planes with $\sin \theta \geq 0.9$. This is probably due to the application of an inexact absorption correction curve. Including the 24 planes affected by extinction gave an overall reliability factor R of 0.17.

The list of observed and calculated structure factors is presented in Table 7 and the final atomic coordinates and their standard deviations are given in Table 8. The atomic thermal parameters are shown in Table 9. Values for intramolecular bond distances and angles are shown in Fig. 2.

RESULTS AND DISCUSSION

2-8-5 Derivative

The molecular dimensions of the hydroxyquinoline group of the 2-8-5-derivative agree well with those obtained by Palenik (1964*a,b*) for the molecule in its copper and zinc salts respectively and with the values reported by Datta (1959) for 2,2'-biquinolyl. None of the bond distances differs significantly from its mean value observed in the four determinations.

The mean S—O bond length of 1.458 Å agrees with the values reported for $\text{NH}_4^+\text{C}_6\text{H}_4\text{SO}_3^- \cdot \text{H}_2\text{O}$ (Rae & Maslen, 1962), $\text{NH}_4^+\text{SO}_3^-$ (Sass, 1960), and $\text{K}_2[\text{NH}(\text{SO}_3)_2]$ (Cruickshank & Jones, 1963), and the slight flattening of the sulfur tetrahedron (average O—S—O = 112.9°, average C—S—O = 105.8°) has also been reported in these previous investigations. The C—S distance of 1.777 Å is in good agreement with the value given by Rae & Maslen (1962).

The equation of the best plane through the atoms in the quinoline ring was calculated by the method of least-squares and is given by:

$$X - 1.083 Y + 0.561 Z - 3.799 = 0,$$

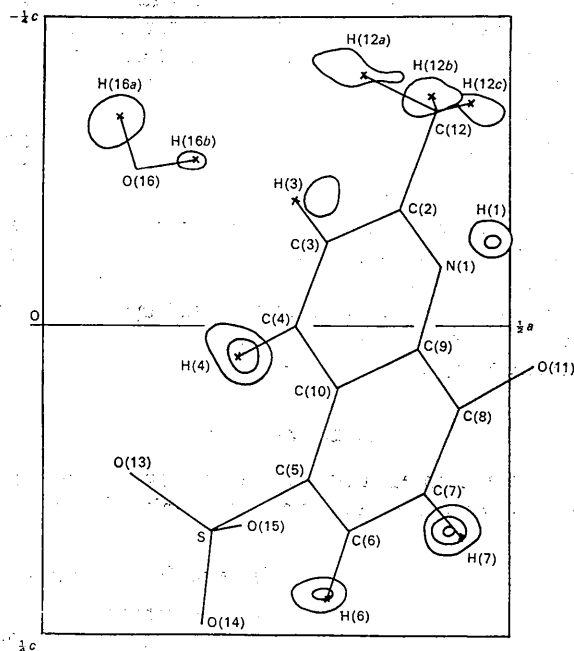


Fig. 1. 2-Methyl-8-hydroxyquinoline-5-sulfonic acid monohydrate. Composite sections of the final difference synthesis drawn through the centers of the hydrogen atoms. A skeleton of the molecule is also shown. Contours are drawn at intervals of 0.2 e.Å⁻³, starting with 0.4 e.Å⁻³.

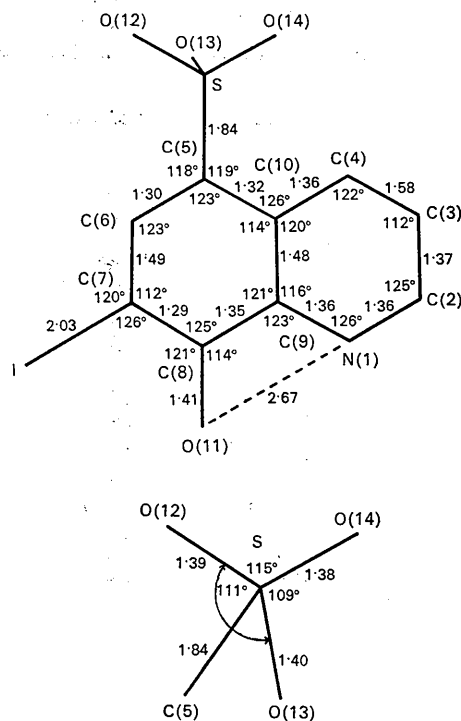


Fig. 2. Intramolecular bond lengths and angles in 7-iodo-8-hydroxyquinoline-5-sulfonic acid. Average e.s.d. = 0.04 Å (bond length), 3° (bond angle).

where X, Y, Z are orthogonal coordinates in Å in the directions of \mathbf{a}, \mathbf{b} and \mathbf{c}^* . The atom deviations from the plane are: $S=0.025$, $N(1)=-0.002$, $C(2)=-0.021$, $C(3)=-0.016$, $C(4)=0.015$, $C(5)=0.007$, $C(6)=-$

-0.035 , $C(7)=-0.005$, $C(8)=0.013$, $C(9)=0.023$, $C(10)=0.020$, $O(11)=0.031$, $C(12)=-0.107$ Å. Although some of the deviations appear to be significant in terms of the individual positional standard deviation.

Table 7. Observed and calculated structure factors for 7-iodo-8-hydroxyquinoline-5-sulfonic acid

The three columns contain, from left to right, the values of h , $10F_o$ and $10F_c$. Reflections omitted from refinements are marked with an asterisk.

0	0	0	12	0	0	3	260	-370	12	1	0	5	222	3	342	3	397	0	4	251	3	260
1	772	1541	1	250	1	39	7	318	7	318	4	414	4	186	4	186	10	345	4	251	4	260
2	1541	1541	2	250	2	39	8	318	8	318	5	414	5	186	5	186	20	345	5	251	5	260
3	1541	1541	3	250	3	39	9	318	9	318	6	414	6	186	6	186	30	345	6	251	6	260
4	1541	1541	4	250	4	39	10	318	10	318	7	414	7	186	7	186	40	345	7	251	7	260
5	1541	1541	5	250	5	39	11	318	11	318	8	414	8	186	8	186	50	345	8	251	8	260
6	1541	1541	6	250	6	39	12	318	12	318	9	414	9	186	9	186	60	345	9	251	9	260
7	1541	1541	7	250	7	39	13	318	13	318	10	414	10	186	10	186	70	345	10	251	10	260
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9	1541	1541	9	250	9	39	15	318	15	318	12	414	12	186	12	186	90	345	12	251	12	260
10	1541	1541	10	250	10	39	16	318	16	318	13	414	13	186	13	186	100	345	13	251	13	260
11	1541	1541	11	250	11	39	17	318	17	318	14	414	14	186	14	186	110	345	14	251	14	260
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15	1541	1541	15	250	15	39	21	318	21	318	18	414	18	186	18	186	150	345	18	251	18	260
16	1541	1541	16	250	16	39	22	318	22	318	19	414	19	186	19	186	160	345	19	251	19	260
17	1541	1541	17	250	17	39	23	318	23	318	20	414	20	186	20	186	170	345	20	251	20	260
18	1541	1541	18	250	18	39	24	318	24	318	21	414	21	186	21	186	180	345	21	251	21	260
19	1541	1541	19	250	19	39	25	318	25	318	22	414	22	186	22	186	190	345	22	251	22	260
20	1541	1541	20	250	20	39	26	318	26	318	23	414	23	186	23	186	200	345	23	251	23	260
21	1541	1541	21	250	21	39	27	318	27	318	24	414	24	186	24	186	210	345	24	251	24	260
22	1541	1541	22	250	22	39	28	318	28	318	25	414	25	186	25	186	220	345	25	251	25	260
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43	1541	1541	43	250	43	39	49	318	49	318	46	414	46	186	46	186	430	345	46	251	46	260
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52	1541	1541	52	250	52	39	58	318	58	318	55	414	55	186	55	186	520	345	55	251	55	260
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54	1541	1541	54	250	54	39	60	318	60	318	57	414	57	186	57	186	540	345	57	251	57	260
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60	1541	1541	60	250	60	39	66	318	66	318	63	414	63	186	63	186	600	345	63	251	63	260
61	1541	1541	61	250	61	39	67	318	67	318	64	414	64	186	64	186	610	345	64	251	64	260
62	1541	1541	62	250	62	39	68	318	68	318	65	414	65	186	65	186	620	345	65	251	65	260
63	1541	1541	63	250	63	39	69	318	69	318	66	414	66	186	66	186	630	345	66	251	66	260

Table 8. *Final atomic coordinates and their standard deviations in the 7-8-5-derivative*

E.s.d.'s in parentheses.			
	<i>x</i>	<i>y</i>	<i>z</i>
I	0.3107 (2)	0.1691 (1)	0.1206 (2)
S	−0.2324 (7)	0.0979 (5)	0.2432 (12)
N(1)	−0.2170 (24)	0.1178 (17)	−0.3318 (31)
C(2)	−0.3667 (28)	0.1108 (17)	−0.3958 (39)
C(3)	−0.4610 (26)	0.1034 (18)	−0.3082 (34)
C(4)	−0.3747 (25)	0.1072 (16)	−0.1218 (33)
C(5)	−0.1431 (28)	0.1205 (16)	0.0910 (34)
C(6)	−0.0015 (26)	0.1408 (17)	0.1398 (36)
C(7)	0.0911 (29)	0.1358 (18)	0.0333 (40)
C(8)	0.0113 (27)	0.1337 (17)	−0.1165 (46)
C(9)	−0.1373 (19)	0.1224 (12)	−0.1730 (30)
C(10)	−0.2240 (30)	0.1146 (20)	−0.0624 (38)
O(11)	0.0765 (17)	0.1408 (13)	−0.2377 (24)
O(12)	−0.2841 (14)	−0.0004 (11)	0.2209 (17)
O(13)	−0.3499 (22)	0.1658 (14)	0.2140 (31)
O(14)	−0.1315 (21)	0.1175 (11)	0.3933 (28)

tions, it is thought that these latter values may have been underestimated.

In the structure hydrogen bonds, of length 2.94 and 2.86 Å between water molecules and sulfonic acid oxygen atoms O(13) and O(14) respectively in hydroxyquinoline molecules related by twofold screw axes, form a spiral of hydrogen-bonded molecules parallel to the *b* crystallographic axis. Molecules related by the $(a+b)/2$ translation are linked by hydrogen bonds of length 2.65 Å between the sulfonic acid oxygen atoms O(12) and the hydroxyl oxygen atoms O(11). These bonds serve to connect molecules in adjacent hydrogen-bonded spirals.

An interesting feature of the structure is that the molecule exists as a zwitterion in the solid state. Nansen & Ekman (1952) had proposed that 8-hydroxyquinoline-5-sulfonic acid exists as a zwitterion in acidic solutions, the proton being transferred from the sulfonic acid group to the quinoline nitrogen atom. More recent work, however, has shown that the hydroxyl group is more acidic than the sulfonic acid group

(Ballard & Edwards, 1964). Only ten of the eleven hydrogen atoms in the asymmetric unit have been located in this present determination, the remaining proton being associated with either the sulfonic acid group or the hydroxyl oxygen atom.

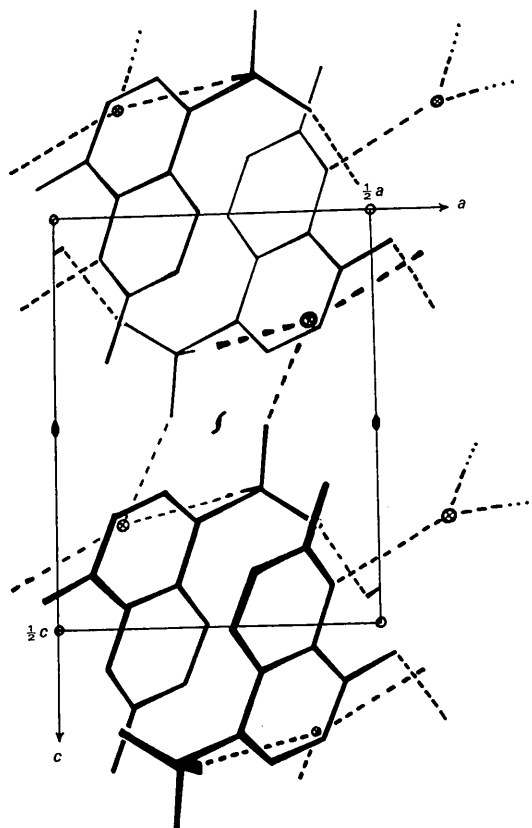


Fig. 3. 2-Methyl-8-hydroxyquinoline-5-sulfonic acid mono-hydrate. Projection of one-fourth the unit cell onto the (010) plane. Water molecules are shown by crossed circles and hydrogen bonds by broken lines.

Table 9. *Final atomic thermal parameters in the 7-8-5 derivative*

Anisotropic temperature factors $\times 10^4$.							Isotropic <i>B</i>
	β_{11}^*	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	
I	120	99	236	−10	46	−8	6.9
S	120	92	164	−19	17	9	
O(11)	177	72	206	−21	−10	−50	
O(12)	133	91	100	0	−11	18	
O(13)	133	177	244	25	86	−79	
O(14)	230	65	357	11	158	2	
N(1)							
C(2)							
C(3)							
C(4)							
C(5)							4.3
C(6)							4.5
C(7)							5.5
C(8)							5.1
C(9)							5.5
C(10)							2.4
							5.5

* The anisotropic thermal parameters are in the form: $\exp \{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$.

The NH^+ group takes part in hydrogen bonding and acts as a proton donor in forming a hydrogen bond of length 2.86 Å to the water oxygen atom O(16) in a direction which completes a distorted trigonal planar environment for the water molecule. A close approach of length 3.00 Å between N(1) and the sulfonic acid oxygen atom O(13) of a hydroxyquinoline molecule in an adjacent hydrogen-bonded spiral is not in a direction suitable for the formation of a hydrogen bond and may be due to electrostatic interaction. The closing of the O(11)–C(8)–C(9) angle of 115.9° must also be ascribed to an electrostatic attraction of O(11) to N(1). The distance N(1)–O(11) is 2.66 Å. Bond lengths and angles between atoms involved in hydrogen bonding are presented in Table 10 and the *b* axis projection of the structure is shown in Fig. 3.

Table 10. Bond lengths and angles between atoms involved in hydrogen bonding in the 2-8-5 derivative

Bond		Length
O(14) (I) \cdots O(16) (I)		2.936 Å
O(16) (I) \cdots O(15) (II)		2.860
O(11) (I) \cdots O(13) (III)		2.654
O(16) (I) \cdots N(1) (IV)		2.858
Atoms		Angle
O(14) (I)–O(16) (I)–O(15) (II)		74.8°
H(16 <i>a</i>) (I)–O(16) (I)–H(16 <i>b</i>) (I)		108.6
C(8) (I)–O(11) (I)–O(13) (III)		110.1
O(14) (I)–O(16) (I)–N(1) (IV)		146.0
O(15) (II)–O(16) (I)–N(1) (IV)		133.9
S(I)–O(14) (I)–O(16) (I)		159.7
S(II)–O(15) (II)–O(16) (I)		127.5
(I)	x, y, z	(III) $\frac{1}{2}+x, \frac{1}{2}+y, z$
(II)	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$	(IV) $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$

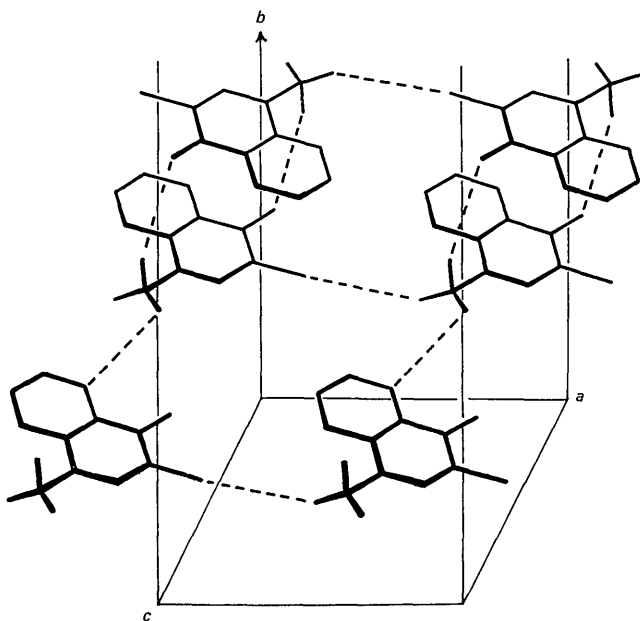


Fig. 4. 7-Iodo-8-hydroxyquinoline-5-sulfonic acid. View of part of the unit cell contents showing the hydrogen bonding and iodine-oxygen interactions.

All other distances less than 4.0 Å between non-bonded atoms have been calculated and none are less than normal van der Waals contacts.

7-8-5 Derivative

The average bond length within the quinoline ring of the 7-8-5 derivative is 1.39 Å and all bonds in the ring except C(2)–C(3) differ from this value by less than three times the average standard deviation. Two of the quinoline bond angles, C(2)–C(3)–C(4), and C(6)–C(7)–C(8) differ significantly, by the criterion of Cruickshank & Robertson (1953), from 120° , but the difficulty in obtaining accurate light atom coordinates in the presence of an iodine atom may explain these differences. In the sulfonic acid group, the average S–O bond length is 1.39 Å, which is somewhat, but not significantly, shorter than the corresponding value in the 2-8-5 derivative, and there is also a slight flattening of the sulfur tetrahedron (average O–S–O angle = 111° , average C–S–O angle = 107°). The C–S and C–I bond lengths agree well with average values reported by Sutton (1958).

The hydroxyquinoline group is planar within experimental error, the average deviation from the least-squares plane being 0.03 Å. The equation for the plane, referred to a set of orthogonal axes, is given by

$$X - 10.299 Y + 0.313 Z + 18.323 = 0$$

where $X = x + z \cos \beta$, $Y = y$, $Z = z \sin \beta$. Individual deviations from the plane are: N(1) = 0.01, C(2) = –0.03, C(3) = –0.02, C(4) = 0.01, C(5) = 0.03, C(6) = –0.10, C(7) = 0.05, C(8) = 0.01, C(9) = 0.02, C(10) = 0.04, O(11) = –0.02, I = –0.19, S = 0.25 Å.

In the structure, a hydrogen bond of length 2.80 Å links the sulfonic acid oxygen atom O(3) in one molecule to the quinoline nitrogen atom N(1) in the equivalent molecule displaced one unit cell in the *c* direction. Between molecules related by a unit-cell translation in the *a* direction, an I–O(13) distance of 3.07 Å suggests a strong interaction; similar iodine-oxygen distances of 2.72 and 2.87 Å have been reported by Archer (1948) in *p*-chlor-iodoxybenzene and distances of 2.94 and 2.95 Å by Groth & Hassel (1965) in the 1:1 addition compound of cyclohexane-1,4-dione and diiodoacetylene. The structure thus consists of sheets of molecules perpendicular to the *b* axis and a second hydrogen bond, of length 2.70 Å between the third oxygen atom O(12) of the sulfonic acid group and the hydroxyl oxygen atom O(11) of a molecule in an adjacent sheet, forms a double layer of hydrogen-bonded molecules. Forces between adjacent double layers are due solely to van der Waals interactions, which is consistent with the observation that the crystal is most easily cleaved in a direction parallel to the *c* crystallographic axis. A view of the structure showing the hydrogen bonds and iodine-oxygen interactions is given in Fig. 4. The hydrogen bond angles at atoms O(11), O(12) and O(14) are 114, 115 and 121° respectively, while the

interaction angle S-O(13)-I' is 140° . No attempt has been made to locate the hydrogen atoms in the structure.

The authors wish to thank the U.S. Atomic Energy Commission for financial support under contract AT(11-1)-120, the staff of the Indiana University Research Computing Center for assistance in performing the computations, and Kirsten Folting Streib for modification of some of the programs used in these determinations.

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The Crystal Structure of Bis-(2-methylpentane-2,4-dioxydimethyltitanium), $[(CH_3)_2TiO_2C_6H_{12}]_2$

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(Received 3 July 1969)

The crystal structure of bis-(2-methylpentane-2,4-dioxydimethyltitanium), $[(CH_3)_2TiO_2C_6H_{12}]_2$, has been determined by the X-ray diffraction method. The crystals are monoclinic with space group $P2_1/n$ and the unit-cell dimensions are, $a = 14.16$, $b = 12.95$, $c = 12.09$ Å, $\beta = 103.0^\circ$. There are four formula units, $[(CH_3)_2TiO_2C_6H_{12}]_2$, per unit cell. The atomic parameters were refined by the block-matrix least-squares method allowing for anisotropic thermal vibration. The final R value for 1107 observed structure factors was 0.158.

The structure of the complex molecule was found to consist of two units with essentially the same structure, 2-methylpentane-2,4-dioxydimethyltitanium, joined together by a shared oxygen atom at the 4-position to form a binuclear dimer molecule. Each of the two titanium atoms coordinates three oxygen and two methyl carbon atoms forming a trigonal bipyramidal pentacoordinated group. The lengths of the titanium-methyl-carbon bonds range from 2.11 to 2.19 Å.

Introduction

During the last decade a number of organometallic complexes containing titanium have been synthesized and their structures and catalytic activities in polymerization reactions of ethylene and other olefins have

been investigated (Natta & Mazzanti, 1960). Most of these compounds, however, involve the cyclopentadienyl groups which are bound to titanium by means of σ - π bonds and only a few compounds have been reported in which the alkyl groups are bound to the titanium atom through σ bonds. Among the latter type of compound, dicyclopentadienyl dimethyltitanium (Piper & Wilkinson, 1956) is the only substance which is stable at room temperature.

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