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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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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 $a=13{\cdot}35$, $b=9{\cdot}11$, $c=17{\cdot}84$ Å; $\beta=90{\cdot}3°$. 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: $a=9{\cdot}55$, $b=13{\cdot}35$, $c=8{\cdot}83$ Å, $\beta=109{\cdot}2°$, 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-hydroxyquinaldine 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: $C_{10}H_9O_4NS.H_2O$

$M = 257{\cdot}3$

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

$a = 13{\cdot}35 \pm 0{\cdot}05$ Å
$b = 9{\cdot}11 \pm 0{\cdot}03$ Å
$c = 17{\cdot}84 \pm 0{\cdot}05$ Å
$\beta = 90{\cdot}3 \pm 0{\cdot}3°$
$V = 2169{\cdot}7$ Å^3
$d_{obs} = 1{\cdot}565$ g.cm^{-3}
$d_{calc} = 1{\cdot}574$ g.cm^{-3}
$Z = 8$.

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

$M = 351{\cdot}1$

Monoclinic; space group $P2_1/c$

$a = 9{\cdot}55$ Å
$b = 13{\cdot}35$Å
$c = 8{\cdot}83$ Å
$\beta = 109{\cdot}2°$
$V = 1063{\cdot}1$ Å^3
$d_{calc} = 2{\cdot}19$ g.cm^{-3}
$Z = 4$.

Using Cu $K\alpha$ radiation, equi-inclination multiple film Weissenberg photographs were taken of the levels Hkl for $0 \le H \le 6$ and hKl for $0 \le K \le 6$. 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 $B = 2{\cdot}0$ Å^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 $\Sigma w(|F_o|^2 - |F_c|^2)^2$, 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 l, $10F_o$ 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.

Table 2 (*cont.*)

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 ($B=5{\cdot}0$ 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 ($B=5{\cdot}0$ 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 2-8-5derivative*

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

	x	y	z
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 ($\mu = 259$ 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(12*a*)	C(12)	0·342	0·050	−0·205	1·24
H(12*b*)	C(12)	0·417	−0·066	−0·189	0·93
H(12*c*)	C(12)	0·458	0·126	−0·180	0·98
H(16*a*)	O(16)	0·083	0·197	0·328	0·93
H(16*b*)	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 θ, however, showed an increase in R from 0·11 for the innermost reflections with sin $\theta \leq 0{\cdot}35$, to 0·21 for planes with sin $\theta \geq 0{\cdot}9$. 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.

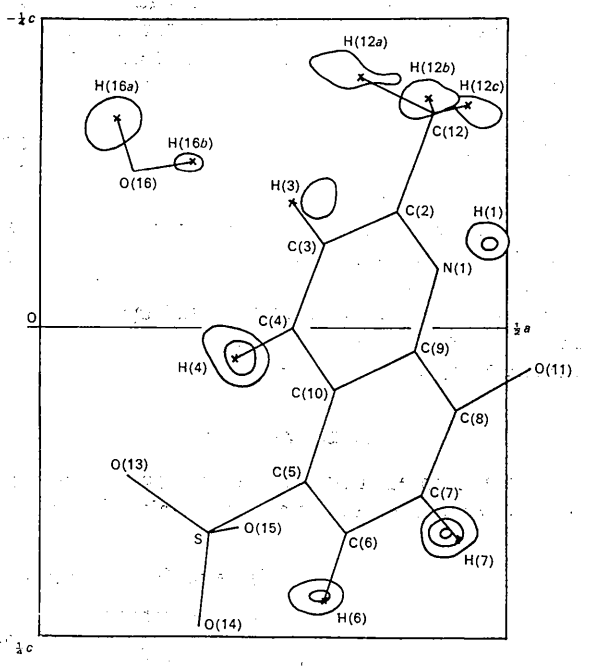

Fig. 1. 2-Methyl-8-hydroxyquinoline-5-sulfonic acid monohydrate. Composite sections of the final difference synthesis drawn through the centers of the hydrogen atoms. A skeleton of the molecule is also shown. Contours are drawn at intervals of 0·2 e.Å^{-3}, starting with 0·4 e.Å^{-3}.

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 $NH_3^+C_6H_4SO_3^-.H_2O$ (Rae & Maslen, 1962), $NH_3^+SO_3^-$ (Sass, 1960), and $K_2[NH(SO_3)_2]$ (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:

$$X - 1{\cdot}083\ Y + 0{\cdot}561\ Z - 3{\cdot}799 = 0\ ,$$

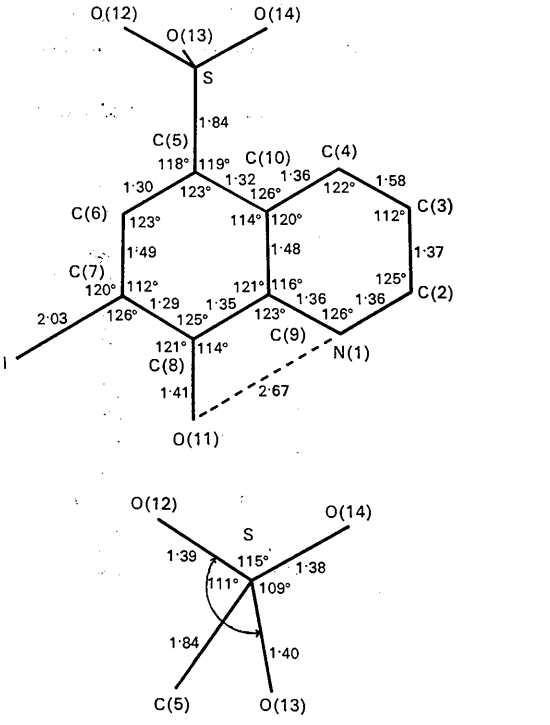

Fig. 2. Intramolecular bond lengths and angles in 7-iodo-8-hydroxyquinoline-5-sulfonic acid. Average e.s.d. = 0·04 Å (bond length), 3° (bond angle).

where X, Y, Z are orthogonal coordinates in Å in the directions of **a**, **b** and **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 devia-

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.

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

E.s.d.'s in parentheses.

	x	*y*	*z*
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. Nasanen & 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.

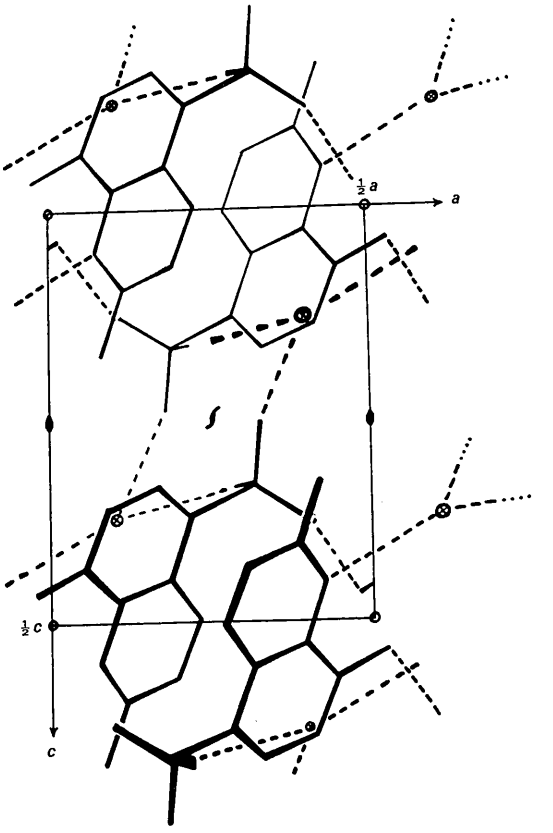

Fig. 3. 2-Methyl-8-hydroxyquinoline-5-sulfonic acid monohydrate. Projection of one-fourth the unit cell onto the (010) plane. Water molecules are shown by crossed circles and hydrogen bonds by broken lines.

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

Anisotropic temperature factors × 10⁴.

	β_{11}*	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Isotropic *B*
I	120	99	236	−10	46	−8	
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)							6·9
C(2)							5·3
C(3)							6·1
C(4)							4·3
C(5)							4·5
C(6)							5·5
C(7)							5·1
C(8)							5·5
C(9)							2·4
C(10)							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)···O(16) (I)	2·936 Å
O(16) (I)···O(15) (II)	2·860
O(11) (I)···O(13) (III)	2·654
O(16) (I)···N(1) (IV)	2·858
Atoms	**Angle**
O(14) (I)--O(16) (I)--O(15) (II)	74·8°
H(16*a*) (I)-O(16) (I)—H(16*b*) (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) $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$

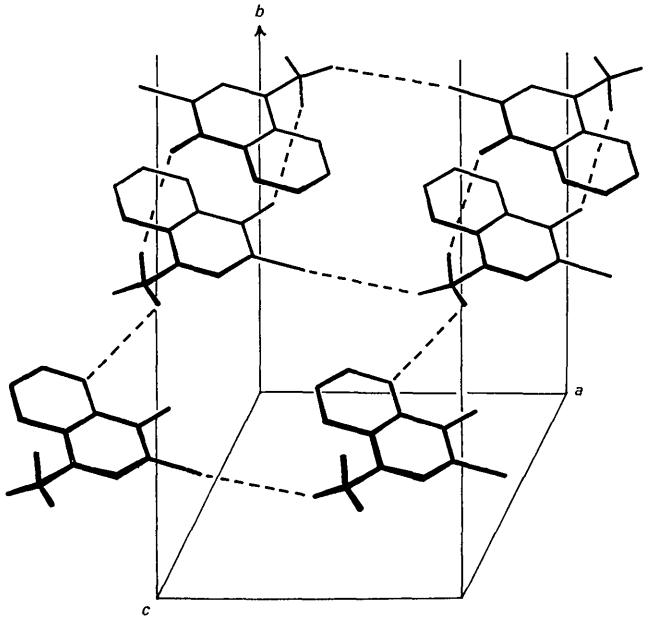

Fig. 4. 7-Iodo-8-hydroxyquinoline-5-sulfonic acid. View of part of the unit cell contents showing the hydrogen bonding and iodine–oxygen interactions.

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

$$X - 10{\cdot}299\ Y + 0{\cdot}313\ Z + 18{\cdot}323 = 0$$

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.

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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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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, $a=14{\cdot}16$, $b=12{\cdot}95$, $c=12{\cdot}09$ Å, $\beta=103{\cdot}0°$. 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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