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# Crystal and Molecular Structure of 2-Diazonium-4-phenolsulfonate Monohydrate, $C_6H_3.N_2^+.SO_3^-.OH.H_2O$

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The absorption spectra of a stable product of diazotization of 2-amino-4-phenolsulfonic acid exhibit characteristics of a diazonium salt; this is an exception to the generally established rule that a diazooxide structure is more stable than the corresponding diazonium salt. The monohydrate of the compound was therefore studied by the X-ray diffraction method. The crystal belongs to the monoclinic system with  $a=8.97\pm0.02$ ,  $b=11.63\pm0.02$ ,  $c=8.62\pm0.02$  Å,  $\beta=102.5^{\circ}$ ; the space group is  $P_{21/n}$ . The structure was determined from three-dimensional intensity data obtained with Cu Ka radiation. The observed bond distances and angles in the molecule established that the molecule possesses a zwitterion configuration, 2-diazonium-4-phenolsulfonate monohydrate,  $C_6H_3N_2^+SO_3^-$ . OH. H<sub>2</sub>O. The crystal structure is essentially ionic with short intermolecular N-O electrostatic attraction (2.88 Å) between the diazonium groups and the sulfonate groups. The water molecules connect the zwitterions by forming a three-dimensional network of O-H···O hydrogen bonds. The unusual stability of the diazonium structure is explained in terms of the zwitterion configuration and the crystal structure of the compound.

### Introduction

The diazo-oxides are stable compounds derived from *ortho*- and *para*-hydroxy substituted aromatic diazo-nium salts, sometimes through the action of alkali.





The structure of these compounds, once thought to be cyclic, is now generally accepted to be resonance hybrid of the type shown above, and the resultant resonance energy is held to be responsible for the stability of these compounds. Generally, whenever the diazonium salt and the diazo-oxide from a particular amine are isolable, the diazo-oxide is by far the more stable compound.

Morgan & Porter (1915) first diazotized 2-amino-4phenolsulfonic acid, I, and isolated an extremely stable product which they classified as a diazo-oxide, II, owing to its lack of the characteristic lability of diazonium compounds. The present X-ray work on the monohydrate crystal of this compound which was thought to be 2-diazo-1-oxide-4-benzenesulfonic acid monohydrate, the monohydrate of II, was undertaken when it was found that the visible and infrared absorption spectra of the crystal were characteristic of a diazonium salt and not of a diazo-oxide.



For example, a typical N–N absorption peak for a diazonium compound lies near  $4.40\mu$  and the corresponding peak for a diazo-oxide lies near  $4.75 \mu$  (Whetsel, Hawkins & Johnson, 1956); the N–N peak for the present substance taken in KBr lies at  $4.44 \mu$ . If the substance is indeed a diazonium compound, it must exhibit a rather interesting zwitterion configuration, III.

Table 1. Atomic coordinates in fraction of cell edges their standard deviations in  $10^{-3}$  Å and anisotropic temperature factors,  $\beta_{11}$  to  $\beta_{23}$  as used in the expression:

$$\exp\left[-\left\{h^{2}\beta_{11}+k^{2}\beta_{22}+l^{2}\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23}\right\}\right]$$

(a) Atom	ic coordinate	s				
	x	$\sigma(x)$	У	$\sigma(y)$	z	$\sigma(z)$
C(1)	0.3672	7	0.5500	7	0.1660	6
C(2)	0.3049	5	0.4666	6	0.2490	6
C(3)	0.3933	5	0.3814	7	0.3460	6
C(4)	0.5946	5	0.3861	4	0.3608	6
C(5)	0.6130	6	0.4732	7	0.2763	6
C(6)	0.5239	5	0.5532	6	0.1818	7
N(I)	0.1472	5	0.4698	6	0.2404	6
N(II)	0.0249	7	0.4708	7	0.2347	9
O(p)	0.2687	4	0.6225	5	0.0728	4
O(I)	0.8116	5	0.3430	6	0.5350	5
O(II)	0.6848	6	0.1876	6	0.3680	5
O(III)	0.5915	6	0.2460	6	0.5968	5
S	0.6688	1	0.2823	1	0.4750	1
O( <i>w</i> )	0.7127	5	0.2039	5	0.0400	5

(b) Thermal parameters

The standard deviations are of the order of 0.001.

	$\beta_{11}$	β22	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
C(1)	0:0141	0.0066	0.0136	0.0032	0.0002	0.0027
C(2)	0.0098	0.0060	0.0169	-0.0002	-0.0003	-0.0019
C(3)	0.0102	0.0068	0.0169	-0.0027	-0.0036	0.0003
C(4)	0.0112	0.0061	0.0167	0.0007	0.0037	0.0011
C(5)	0.0112	0.0062	0.0168	0.0022	0.0009	0.0010
C(6)	0.0107	0.0072	0.0188	-0.0021	0.0018	-0.0023
N(I)	0.0097	0.0061	0.0245	0.0016	0.0009	-0.0026
N(II)	0.0138	0.0096	0.0365	-0.0038	0.0056	-0.0031
O(p)	0.0130	0.0071	0.0211	0.0020	-0.0009	0.0044
O(I)	0.0092	0.0092	0.0240	0.0002	-0.0066	0.0038
(ÌÍ)O	0.0174	0.0073	0.0214	0.0078	-0.0069	-0.0004
O(III)	0.0188	0.0082	0.0222	0.0029	0.0036	0.0069
S	0.0121	0.0060	0.0166	0.0031	-0.0023	0.0004
O(w)	0.0162	0.0075	0.0204	-0.0003	0.0035	0.0017

# Table 2. Comparison of the observed and calculated structure factors $(\times 10)$

FO FC 4,K= 0, 0 1=2 126 91	F7 FC 4,K≥ 7, 13 3 59 54	FN FC H.K= 2, 1 1=0 9711012	FJ FC 4,X# 3, 3 6 42 41	FD FC H,K= 4, 7 L=1 119 88	FD FC 4,K= 6, 9 2 202 215	FD FC H,X= 7, 7 L=0 106 119	FD FC H,K= 13, 3 L=0 73 81	FD FC 4,K= -2, 2 3 376 533	FD FC H,K= -3, 7 L=1 334 354
4 216 259 8 44 45 9 97 58	5 16 20 4.Kz D. 14	1 179 191 2 598 639 3 242 259	7 142 116 8 47 39	2 130 89 3 172 152 4 165 162	4 321 349 6 70 59	1 104 103 2 21 9 4 91 83	1 57 43 2 46 37	4 85 110 5 47 49 6 198 178	2 342 317 3 80 66 4 195 195
10 91 90 4.x= 1, 1	L=0 46 40 1 55 56 2 142 132	4 746 235 5 36 43 6 74 62	H.K= 3, 4 L = 191 179 1 473 450	H,K= 4, 8 L=D 35 23	4,K= 6, 1 L=0 40 23 1 92 57	H.K. 7, 8 L=0 174 194	H,K= 10, 4 L=0 10 7 2 42 31	7 40 36 8 74 72	H,K= -3, 8 L=1 57 35
1 =1 07 87 7 383 300 3 261 292	-1,K= 1, 0 L=1 91 90	R 47 50	2 148 112 3 424 402 4 125 98	1 232 213 2 89 96 3 103 74	2 160 144 3 216 239 4 179 176	1 53 43 4 44 33	H.K. 10, 5 L=D 23 24	H.K= -2, 3 L=1 323 349 3 356 453	2 57 44 3 76 60 4 133 126
4 147 164 5 48 39 7 65 51	5 103 106 7 198 162	1 295 313 2 213 192	5 132 136 5 187 160 8 70 65	4 42 31 H,K= 4, 9	5 111 125 6 43 41 7 61 65	H,K= 7, 9 L=2 147 112 4 34 30	H,K= 10, 6 L=0 36 31	4 104 105 5 112 119 6 44 33	H,K= -3, 9 L=1 134 141
9 31 28 10 57 37	4 1×3 1/2 4.K= 1, 1	4 13 16 5 84 70	4.K= 3, 5 L=∩ 145 105	1 201 173 3 54 35	H.K= 6, 7 L=0 61 33	H.K. 7, 10 L.1 25 17	H,K= -1, 0 L=1 613 752	7 89 79 8 54 39 9 27 30	2 156 160 3 92 89 4 112 133
H,K= 0, 2 L=0 201 135 1 85 94	1 383 491 2 43 38 3 23 16	8 74 74 Hake 24 3	2 96 76 3 89 87 4 119 110	H,K= 4, 10 L=1 59 38 3 72 58	2 385 376 4 76 60 6 112 120	H,K= 7, 11	7 115 76	4,K= -2, 4 L=1 322 370 2 174 194	H,K= -3, 10 L=1 100 104 2 114 118
217031400 3 421 423 4 157 126	4 176 160 5 29 29 6 193 200	1 =0 462 491 1 281 264 2 615 726	-1,K= 3, 6 L=0 107 67	4 72 53	7 43 41	1 77 109 H.K. B. D	L=1 672 691 2 263 294 3 315 361	3 141 201 4 102 93 5 63 56	3 102 90 4 21 32
5 48 48 6 163 116 7 55 50	7 27 14 9 25 25 9 35 39	3 220 177 4 28 22 5 72 62	1 217 200 2 51 45 3 728 202	L=0 77 72 1 70 50 2 130 103	L=0 20 10 1 232 207 2 272 263	L=0 62 49 2 51 54 4 16 19	4 191 216 5 168 172 6 35 38	6 176 162 9 114 115 9 46 45	H,K= -3, 11 L=1 58 43 2 87 66
8 23 17 9 68 56 10 32 18	H.K.# 1. 7 L=0 252 303	6 81 65 7 87 69 8 81 77	4 37 35 4,K= 3, 7	3 132 86 4 74 67	3 108 93 4 89 71 5 155 168	6 19 12 4,K= 8, 1	7 190 204 9 129 121	H.K= -2, 5 L=1 299 342	4 50 34 H,K= -3, 12
4,K= 7, 3 1=1 514 571	1 638 732 2 17 18 3 80 72	H.K. 2, 4 L.N. 102 130	L=7 175 170 1 51 48 2 172 138	4,K= 4, 12 L=9 46 29 1 87 85	6 74 58 H,K= 6, 4	L=3 76 76 1 53 60 2 78 74	H.K= -1, 2 L=1 153 153 2 891 974	2 68 74 4 54 41	L=1 76 82 2 28 29 3 97 104
2 506 590 3 240 242 4 97 105	4 174 156 5 117 106 6 70 58	1 63 75 2 38 14 3 259 209	3 23 13 4 108 100	2 34 19 4 50 58	L=0 219 202 1 125 100 2 90 85	3 29 30 4 88 87 6 39 60	3 80 67 4 70 63 5 221 197	H.K= -2. 6 L=1 149 166 2 142 141	4 27 27 H,K= -3, 13
5 293 270 5 125 96 7 88 80	7 153 152 8 95 100 9 78 89	4 136 132 5 724 193 7 84 70	4.K= 3, 8 L=0 63 46 1 57 65	H,K# 4, 13 L=0 104 94 1 55 64	4 137 110 7 97 97	4,K= 8, 2 L=0 132 143	6 58 77 7 38 27 8 32 30	3 183 151 4 65 60	L=1 29 35 2 65 28 4 21 22
9 38 33 10 88 56	4.K= 1. 3 L=9 55 59	4 3/ 7	4 63 45	2 57 55	L=0 209 192 1 31 6	2 40 45	4 44 106	L=1 72 79 2 202 193	H.K4, 0 L.Z. 293 353
4,K= 0, 4 L=0 447 495	2 238 240	1 210 158	L=0 209 215 1 115 103	3 133 66 5 110 117	4 63 56	L=0 29 17 1 77 73	2 40 20	4 118 104	6 81 73 8 53 50
2 208 194 3 142 114 4 342 364	5 171 114 6 95 83 7 68 62	4 186 193	4 125 111	H,K= 5, 1 L=0 74 71 1 259 287	L=0 85 80 1 89 66 2 32 23	4 95 84 5 42 30	5 129 125 6 123 81 7 173 171	L=1 329 307 2 100 82 3 129 115	H,K= -4, 1
5 111 101 6 66 69 7 161 150	A 66 56 9 38 23	L=0 163 177 1 459 462 2 133 122	H,K= 3, 10 L=0 47 38 1 99 54	2 99 95 3 312 318 4 117 124	3 27 33 4 32 28	H,K= 8, 4 L=2 31 27 3 65 57	H.K1, 4 L=1 103 152	4 104 98	2 99 22 3 82 89 4 68 66
8 58 45 9 32 20 10 16 13	H,K= 1, 4 L=0 11R 146 1 157 137	3 190 398 4 85 83	2 42 38 4 78 72	5 108 115 6 65 88	H,K= 6, 7 L=0 186 180 1 137 124	4 87 88 H.K.= 8. 5	2 44 52 3 132 124 4 635 641	L=2 129 113 3 159 146	6 103 104 7 100 102 8 59 56
H,K= ^, 5 L=1 389 367	2 299 287 3 498 499 4 24 28	H,K= 2, 7 L=0 129 107 1 205 187	H,K# 3, 11 L=7 134 152 2 95 92	H,K= 5, 2 L=3 74 73 1 53 29	3 66 77 4 13 7	L=0 57 41 2 32 25 4 161 138	5 121 116 6 70 75 7 213 205	H,K= -2, 10 L=1 182 172 2 42 38	H,K= -4, Z  =  126 102
2 125 109 3 530 558 4 95 64	5 200 169 6 121 91 7 80 66	2 224 187 4 76 67	4 54 38 4.K= 3, 12	2 25 3 3 34 27 4 224 220	H+K# 6, 8 L=0 134 127 2 99 62	H.K. 8, 6 L=0 29 26	8 82 69	3 111 108	2 70 58 3 160 157 4 183 159
5 161 169 6 183 171 7 72 45	9 59 62 4,K= 1, 5	H,K= 2, A L=0 51 39 1 258 262	2 87 69 3 50 40	5 35 39 6 110 130 7 47 52	3 58 68 4 13 16	1 48 31 2 76 41	L=1 235 270 2 142 130 3 16 15	L=1 88 84 2 39 44 3 48 51	5 97 93 6 63 48 8 59 54
10 15 14	1 498 510 2 61 36	7 103 125 3 244 728	4 57 54 4,K= 3, 13	H,K= 5, 3 L=0 34 21	L=0 62 72 1 137 119	L=1 21 16 2 57 21	4 99 87 4,K= -1, 6	H,K= -2, 12	10 39 36
L=0 38 39 1 87 87	4 174 179	L=1 72 69 2 157 149	1 39 33	2 219 211 3 119 103	3 46 73 4 28 27	4 51 20 4,K= 8, 8	2 197 168 3 157 158	4 38 49	2 35 11 3 171 172
3 175 140 4 137 118 5 439 424	L=0 152 179 1 91 120 2 97 85	H,K= 2, 10	1,K= 3, 14 1=0 23 19	5 117 89 6 76 55 7 106 99	H,K= 6, 10 L=0 19 4 1 63 42	1 103 101 2 57 42	H,K= -1, 7	L=1 97 92 2 121 87 3 73 48	5 191 184 6 100 103 7 63 53
6 57 44 7 48 29 8 15 18	3 77 67 4 46 36	1 129 108 2 20 3 3 92 65	1 50 66	H,K= 5, 4 L=0 66 49	3 34 50 4 31 22	H+K= 8+ 9 L=0 24 22 2 107 76	2 51 32 3 78 65 4 53 46	H,K= -2, 14 L=1 5 2	8 58 66 9 51 60
9 43 30 H,K= 0, 7	H,K= 1, 7 L=0 87 81 1 220 212	H.K. 2, 11 L=0 127 151	L=0 353 438 2 461 503 4 274 317	1 185 162 2 157 107 3 40 25	H.K= 6, 11 L=0 69 60 1 99 92	H.K= 8, 10 L=0 31 30	H.K1. 8 L=1 240 274	3 54 41 H,K= -3, O	H,K# -4, 4 L=1 55 32 2 80 64
L=1 224 212 2 21 21 3 348 329	2 98 82 3 161 143 4 210 213	1 48 31 2 97 87 4 165 145	6 182 195 8 153 125	4 198 157 6 50 55 8 43 50	2 69 61 H,K= 6, 12	1 61 81 H,K= 9, 0	2 80 60 3 51 47 4 326 266	L=1 183 193 3 55 49 5 294 327	3 95 93 4 44 32 5 59 46
4 112 106 5 69 70 6 66 53	H.K= 1, 8 L=0 141 152	H.K= 2, 12 L=0 48 46	H,K= 4, 1 L=0 156 153 1 104 75	H.K. 5, 5 L-7 108 80	L=0 50 41	4,K= 9, 1	H.K= -1, 9 L=1 130 108	7 129 91 9 55 52	6 73 55 H.K4, 5
9 78 22	3 264 768 4 50 30	2 17 16 3 97 66	2 191 209 3 89 74 4 156 152 5 85 83	1 35 12 2 27 11 3 204 158	3 276 321 5 74 57 7 36 41	1 43 36 3 35 41	4 174 147	L=1 235 242 2 130 101 3 296 347	2 157 176
L=0 65 44 1 134 113 2 35 25	H,K= 1, 9 L=0 104 115	4.K= 2, 13	6 68 80 8 21 24	H,K= 5, 6 L=7 285 278	H,K= 7, 1	4,K= 9, 2 L=1 84 89 2 42 48	L=1 82 74 2 283 287 3 125 136	4 23 19 5 264 325 7 178 189	4 119 100 H,K= -4, 6
3 268 286 4 74 74 5 73 52	2 198 195 3 55 72 4 190 169	1 59 68 3 62 60 4 82 86	H,K= 4, 7 L=0 266 254 L 337 325	2 108 72 3 61 61 4 25 21	1 296 325 2 40 25 3 40 30	3 77 71 4 23 23	H,K= -1, 11 L=1 87 83	9 48 56 4.K= -3. 2	2 85 89 3 88 81 4 42 36
6 78 77 7 152 132 9 31 29	H,K= 1, 10 L=0 110 127	H,K# 2, 14 L=0 39 47	2 498 524 3 61 48 4 232 224	H,K= 5, 7 L=0 195 190	4 55 47 5 28 28 6 27 30	H,K= 9, 3 L=0 77 57 3 24 24	2 76 64 3 81 69 4 39 34	L=1 167 167 2 274 279 3 58 63	H,K= -4, 7 L=1 117 108
H,K= 0, 9 L=1 217 223	1 159 155 2 55 42	1 39 30 2 39 35	5 31 20 6 99 98 8 43 54	1 31 4 3 35 32 4 54 37	4,K= 7, 2 L=0 72 65	H.K. 9. 4 L=0 23 I	H.K= -1, 12 L=1 54 51	4 239 257 5 72 67 5 123 114	2 54 49 4 130 150
2 39 40 3 53 48 4 32 24	H,K= 1, 11 L=0 112 113 1 95 93	H,K= 3, 0 L=1 157 188 3 70 61	4.K= 4, 3 L=0 171 192	4,K= 5, 8 L=0 78 64	1 201 169 2 168 155 4 73 76	1 69 60 2 55 31 3 44 51	2 50 42 3 38 45 4 65 67	7 156 171 4,K= -3, 3	H,K= -4, 8 L=1 180 174 3 193 199
5 123 107 6 32 23 7 134 97	2 158 110 3 73 71 4 51 50	5 62 68 9 54 34	1 292 276 2 198 159 3 65 62	1 168 151 2 89 76 3 24 26	5 125 129 6 51 50	4 17 13 H,K= 9, 5	H.K= -1, 13 L=1 29 13	L=1 141 109 2 145,112 3 296 322	4 50 58 H+K= -4+ 9
H,K= 0, 10 L=1 227 245	H.K= 1, 12 L=0 107 132	H.K. 3, 1 L=0 102 71 1 225 724	4 87 73 5 189 167 7 127 115	4 99 89 4,K= 5, 9	H,K= 7, 3 L=0 58 60 1 77 64	L=0 70 82 2 142 96	2 58 35 3 118 106 4 59 52	4 161 153 5 136 125 6 39 30	L=1 126 107 3 50 52 4 48 47
2 163 140 3 72 47 5 68 58	1 20 12 2 39 33 3 84 72	2 122 134 3 135 137 4 160 149	8 38 47 9 53 11	1 48 36 2 190 175	3 165 176 4 48 30 5 40 38	H,K= 9, 6 L=0 28 34 2 25 21	H,K= -1, 14 L=1 43 43	7 68 66 9 62 60 10 24 25	H.K= -4, 10 L=1 179 171
7 25 26	H.K= 1, 13 L=0 24 29	5 57 47 6 44 38 7 76 87	L=0 319 331 1 119 101	4 13 17	H,K= 7, 4 L=0 259 251	H,K= 9, 7 L=0 112 104	3 47 49	H,K= -3, 4 L=1 205 243	3 107 109
L=1 92 88 2 132 135	2 55 33 3 54 44	H,K= 3, 2	3 59 55 4 121 97 5 151 127	L=0 53 39 1 70 85 2 93 84	2 99 92 3 111 87	H,K= 9, 8	L=2 574 721 4 159 186 6 51 47	3 62 70 4 246 251	L=1 77 67 2 103 105
4 53 55 5 36 34 7 36 31	H,K= 1, 14	1 408 433 2 193 178 3 165 132	8 46 35	3 40 39 4 106 93	5 74 93 H.K. 7, 5	1 19 26	8 142 111 H.K2. 1	6 179 161 7 66 49 8 74 59	H.K= -4, 12 L=1 68 58
H,K= 0, 12 L=0 217 261	1 21 25 2 77 58	4 140 126 6 157 163 7 39 34	L=0 84 46 1 81 60 2 195 174	4,K= 5, 11 L=0 74 71 2 31 18	L=0 74 55 1 91 61 2 53 39	L=2 58 52 H,K= 10, 1	L=1 63 57 2 185 228 3 170 159	H.K= -3, 5 L=2 296 245	3 48 42 4 13 14
1 102 101 3 103 99 4 78 65	H,K= 2, 0 L=0 296 364 2 321 366	A 73 A5	3 232 214 4 97 69	4 28 18 H,K= 5, 12	4 48 46 H,K= 7, 6	L=0 42 50 1 65 51 2 17 20	4 141 144 5 288 374 6 32 18	3 38 30 4 293 251	H,K= -4, 13 L=1 65 62 2 32 46
5 43 33 6 36 30	4 158 152 6 134 128 8 84 61	L=0 240 265 1 95 65 2 193 131	H,K= 4, 6 L=0 59 41 1 253 212	L=0 121 122 1 99 97 2 103 77	L=0 53 34 1 87 67 2 159 136	3 51 63 H,K= 10, 2	7 40 36 8 25 21	H,K= -3, 6 L=1 88 73 2 95 78	4 34 36
H,K= 0, 13 L=1 65 50 2 73 63	10 69 61	3 197 145 4 13 10 5 51 43	2 59 34 3 353 305	H.K. 6, D L=0 250 269	4 98 78	L#1 34 25 2 39 28	H,K= -2, 2 L=1 134 182 2 68 41	3 103 102 4 182 146	

F0 FC -6, 5 200 237 47 38 114 101 FC 290 102 180 47 145 FD FC H,X= -5, 5 4 189 164 FN -7, 66 FC 65 360 269 105 9 F0 293 111 194 50 133 FD -8 35 62 91 23 H,X= 6 10 FC 0 54 106 21 4,K= 3 4 6 9 4.K= -9 63 20 80 121 36 +,K= L=1 2 3 4 -7 99 29 24 74 7 79 23 31 68 H,K= L=1 2 3 4 -9; 20 88 65 -6. 6 31 40 29 62 5 33 68 17 145 113 63 44 12 -0 34 29 35 89 -8, 38 38 159 47 23 19 ×1234567810 52 77 11 86 67 83 61 25 142 13 93 69 74 57 28 29 167 40 36 24 -7, 32 51 141 26 26 46 123 42 101 52 42 27 53 115 53 44 25 42 227 76 175 -9; 34 47 -9 97 87 16 15 19 13 1 90 87 87 14 16 17 10 -7 95 134 84 35 58 81 65 50 -10 21 31 24 8 31 25 78 123 87 35 75 116 68 30 47 76 59 45 116 82 36 63 H,K= L=1 2 3 4 -8, 82 57 39 119 9 80 51 32 60 4 75 54 43 114 -9, 41 39 36 7 -5, 8 106 130 152 113 24 19 96 104 69 46 40 88 L=1 2 3 4,K H.K. L=1 24 567 -6 95 102 91 141 39 55 , 2 95 95 94 89 136 40 58 8 78 98 103 -7, 25 92 32 38 -8, 51 42 28 0 48 30 12 H,K= L=1 2 3 4 5 40 43 24 H,K= L=2 3 4 10 19 70 26 25 87 50 63 20 27 31 -5, 35 91 140 135 9 24 91 123 68 35 13 4 6 -7 157 29 163 149 81 47 21 31 , 3 148 29 166 156 84 39 21 35 9 108 60 37 H,K L=1 2 3 4 6 -5 23 73 136 185 126 42 63 54 38 34 -8, 35 55 34 H,K= L=1 2 3 4 5 8 -10, 27 70 65 53 47 H, <= -6 L =1 111 2 74 3 123 4 187 6 63 7 23 8 27 9 29 10 32 H,K= L=2 3 4 6 15 55 31 1 22 67 56 56 41 3 82 56 140 35 46 33 73 37 13 11 46 34 20 -9 44 38 36 76 38 20 -7. 151 61 47 13 143 73 42 18 H,K= L=1 2 4 10 57 33 30 65 35 36 66 24 28 123 34 73 200 65 17 25 27 31 7 15 30 33 12 -8 21 38 31 13 H,K=-10, L=1 23 2 25 3 32 6 32 101 40 62 217 -7. H,K= L=2 - A. 4,K= L=1 3 4 -5, 72 69 74 -6, 89 63 17 11 59 67 62 11 66 49 22 118 39 70 221 4 114 8 157 98 91 -9, 42 61 84 13 50 35 4 25 62 81 17 52 35 123456 HşK L≡1 3 4-H,K= L=1 2 3 4 6 7 9 = -6 171 142 137 55 46 51 39 -8 81 20 47 8 56 11 38 H,K= L=1 2 3 4 5 ₹ -5, 25 107 5 108 138 115 91 12 25 85 4,K= -6, 12 L=4 15 17 -7, -101 77 46 24 58 42 H,K 3 55 42 48 44 149 103 62 53 65 135 115 54 54 50 39 23456 27 21 29 42 42 10 20 31 35 41 -7, 21 102 183 125 -11, 34 10 H.K= l=î 3 5 7 0 5 76 158 91 125 -5, 40 68 13 37 64 9 52 82 36 5 35 100 26 -9, 42 97 -5, 5 38 45 258 277 44 38 -7, 6 111 90 340 357 50 36 H,K= -8, 2 L=1 69 70 2 121 104 H.K=-10, L=1 65 2 28 41 H,K= -6, 0 H,K= -6, 5 L=2 127 138 L=1 175 193

#### Structure determination

Crystals of the compound were prepared by the method of Morgan & Tomlins (1917) and have the following crystallographic constants:  $a=8.97\pm0.02$ ,  $b=11.63\pm$ 0.02,  $c=8.62\pm0.02$  Å,  $\beta=102.5^\circ$ ,  $g_{obs}=1.66$  g.cm<sup>-3</sup>. The space group for this choice of axes is  $P2_1/n$  with four chemical units in a unit cell.

Every attempt to make crystalline alkaline salts of the acid was unsuccessful; the products possessed crystallographic data identical with those of the free acid monohydrate, as well as identical acidimetric equivalent weights.

Complete sets of intensity data for crystal mountings about the *b* and *c* axes were collected with a Weissenberg camera with filtered Cu  $K\alpha$  radiation. The intensities of 1488 independent reflexions were recorded and estimated by visual comparison with a calibrated scale. No correction for absorption was made.

The structure analysis was initiated by locating the position of the sulfur atom with the b and c projections of the Patterson function and the Harker section at  $y=\frac{1}{2}$ . The position thus obtained was later confirmed by a three-dimensional Patterson function. With the use of known bond lengths and angles, a theoretical intramolecular vector map of the planar part of the molecule was made and the direction of the planar part was sought by a systematic search of peaks around the origin of the Patterson function to have maximum coincidence between the peaks and the theoretical vector map. The direction thus obtained was combined with the already obtained sulfur position; the ambiguity in the actual positions of the atoms in the planar part of the molecule was resolved by comparing these positions to the electron density projections obtained by the use of the phases based on the sulfur positions. The positions of the sulfonate oxygen atoms and the water molecule were also obtained in the course of successive refinement of the projections of electron density functions. The atomic coordinates thus arrived at were then subjected to least-squares refinement using a diagonal approximation with isotropic temperature factors. After several cycles of refinement, with an R value  $\Sigma ||F_0| - |F_c||/\Sigma |F_0|$  of 0.19, the refinement ceased to proceed; a study of the electron density function revealed marked anisotropy of the vibrations of the majority of atoms, especially the two nitrogen atoms of the diazonium group. A more detailed account of the structure determination and the isotropic refinement is given elsewhere (Greenberg, 1962).

At this stage of the refinement procedures the leastsquares treatment with anisotropic temperature factors



Fig. 1. Numbering of atoms used in the discussion.

## Table 2 (cont.)

was started by the use of the full-matrix method on an IBM 7094 at the IBM Research Center, Yorktown Heights, New York; the number of parameters to be refined was 127. The weighting factor for the leastsquares method was  $\omega = 1.0/|F_{obs}|$  when  $|F_{obs}| \ge 35$ ;  $\omega = 2.0/|F_{obs}|$  when  $10 \le |F_{obs}| < 35$ ; and  $\omega = 1.5/|F_{obs}|$ when  $|F_{obs}| < 10$ ; the non-observed reflections were given zero weights. After the introduction of anisotropic thermal factors, the structure refined rather smoothly, and after five cycles the convergence was observed through smallness of the improvement in the residuals (less than one-tenth of the standard deviations), the final R value being 0.128. At no time was the contribution of hydrogen atoms included in the computation since the intensity data, collected photographically, were not considered to be of sufficient quality. The atomic scattering factors used in the computation were those for neutral atoms listed in International Tables for X-ray Crystallography (1962).

The positional and thermal parameters for all nonhydrogen atoms are given in Table 1; the designation of the atoms to be used hereafter is shown in Fig. 1. The estimated standard deviations of the atomic coordinates are calculated in the usual manner and are also in Table 1. The observed and calculated structure factors are listed in Table 2.

As shown from Table 1, there exists a marked anisotropy in the thermal motion of each atom. In order to interpret the thermal motion, the temperature factors  $\beta_{11} \dots \beta_{23}$  were decoded into the amplitudes and directions of thermal vibration ellipsoids by a program on the 7094; some typical examples are listed in Table 3. Since no absorption correction was made to the observed intensity data, the values of amplitudes in Table 3 have only relative significance. Even so, it is quite clear that the nitrogen atoms of the diazonium group, especially the terminal nitrogen, N(II), show marked anisotropy, the latter with amplitudes of 10.7, 5.6 and  $3.7 \times 10^{-16}$  cm<sup>2</sup> \* for the three principal axes of the ellipsoid. Since the molecules are connected to each other by a complicated combination of forces, no quan-

\* These values are expressed in the same unit as the conventional isotropic temperature factor to facilitate the comparison between the two different schemes. titative analysis of the thermal motion was made other than the evaluation of the principal directions of the ellipsoids.

# Discussion of the results

The atomic coordinates and their standard deviations thus determined were used in the calculation of all interatomic distances shorter than  $5 \cdot 0$  Å. Important bond angles as well as the equation of the least-squares plane passing through the benzene ring are obtained in the normal fashion. These values will be used in the discussions of the structure.

#### (a) The molecular configuration

The bond distances and angles in the molecule are shown in Figs. 2, 3 and 4; their standard deviations are also listed in these Figures.

The purpose of this study was to substantiate the results of the infrared and visible spectroscopic examinations and to seek a possible explanation of this apparently anomalous circumstance, *i.e.* that the supposedly unstable modification is, in reality, the only stable form. Translated into crystallographic terms, this means that, first, it had to be shown that the molecular structure of the compound was a diazonium-benzenoid structure, III, with little or no contribution of the imino-quinoid structure such as II, and second that some plausible mechanism existed which stabilized the normally unstable diazonium-benzenoid structure. A systematic study of the observed bond lengths in Fig.2 reveals that it has a diazonium-benzenoid structure. Therefore, the molecule is a zwitter-ion in the crystal containing a negatively charged sulfonate group and a positively charged diazonium group. The apparent contradiction arising out of the stability of the diazotized product of 2-aminophenol-4-sulfonic acid is reconciled with existing ideas on molecular structure when one considers the existence of the strongly acidic sulfonate group and the intermolecular interactions within the monohydrate crystal, which are described in the following section.

The benzene ring is a slightly distorted hexagon with C-C distances varying from 1.37 to 1.43 Å (average, 1.39 Å) and the bond angles are all around the expected value of  $120^{\circ}$  (117 to  $124^{\circ}$ ). The observed C(3)-C(4)

Table 3. Interpretation of the anisotropic thermal parameters for C(2) and the diazonium nitrogen atoms

	Temperature factor	Directior	o cosines with	respect to
	in 10 <sup>-16</sup> cm <sup>2</sup>	а	b	с
C(2)	5.59	- 0.299	-0.142	0.833
- (/	2.63	0.970	0.257	0.553
	3.22	0.288	-0.956	0.025
N(I)	7.83	-0.191	-0.145	0.887
- ()	2.67	0.932	-0.337	0.372
	3.28	0.308	0.931	0.273
N(II)	10.74	-0.035	-0.069	0.953
	3.70	0.880	0.471	0.291
	5.58	0.473	-0.880	0.082

and C(5)-C(6) distances discourage the conclusion that the molecule exists as a resonance hybrid of the diazonium-benzenoid and imino-quinoid forms; this can be substantiated by the bond distances in chloranil (Chu, Jeffrey & Sakurai, 1962), a typical structure where single and double bonds exhibit separations of 1.49 and 1.29 Å respectively. The planar part of the molecule is studied by evaluating the best plane through the six carbon atoms of the ring; the equation of the plane obtained by the least-squares method is:

### 0.0851X + 0.6124Y + 0.7860Z = 4.7618,

where  $X=ax+cz \cos\beta$ , Y=by, and  $Z=cz \sin\beta$ . The shifts of the atoms from this plane are shown in Fig. 5; a negative value of the shift means that the atom and the origin of the coordinate system lie on the same side of the plane. The atoms in the ring are coplanar within experimental error; however, the shifts of C(2), N(I) and N(II) indicate that the linear diazonium group is inclined from the plane by about  $3\cdot4^\circ$ . The inclination of the diazonium group as a whole from the plane bears some relationship to the thermal vibration of those three atoms; comparison of the three ellipsoids in Table 3 reveals that from C(2) to N(II), the amplitudes of the vibration increase regularly, while the directions of the maximum amplitude remain almost the same.

The observed distances in the C(2)-N(I)-N(II)grouping further preclude the resonance hybrid of the diazonium-benzenoid and the imino-quinoid structures. The C(2)–N(I) distance of 1.41 Å can be compared with those of 1.47 and 1.27 Å which are the expected pure single and double bond distances, respectively. The corresponding distance in benzenediazonium chloride as determined by a three-dimensional crystal structure analysis is 1.39 Å (Romming, 1962). It is then rather obvious that the C(1)-O(p) bond should be close to a single bond. The observed separation of 1.35 Å is again compared with similar aromatic C-O bond distances, e.g. 1.35 Å in resorcinol (Bacon & Curry, 1956) and others, whereas C=O bond distances are around 1.2 Å [1.195 Å for chloranil (Chu, Jeffrey & Sakurai, 1962)]. The N(I)–N(II) distance of 1.08 Å compares with that of 1.10 Å for benzene diazonium chloride (Rømming, 1962) and a figure of 1.10 Å for the pure triple bond (Pauling, 1960).

The sulfonate group is a distorted tetrahedron and the C(4)–S distance of 1.76 Å can be compared with those of 1.74 Å in magnesium and zinc *p*-toluenesulfonates (Hargreaves, 1960) and of 1.76 Å in similar benzenesulfonates (Broomhead & Nicol, 1948). The S–O distances, as shown in Fig.2, are all normal and comparable with the values in other substances: 1.47 to 1.41 Å in the above mentioned sulfonates; 1.43 to 1.45 Å in sulfamic acid (Osaki, Tadokoro & Nitta, 1955); 1.448 to 1.465 Å in taurine, NH<sub>3</sub><sup>+</sup>–CH<sub>2</sub>–CH<sub>2</sub>– SO<sub>3</sub><sup>-</sup> (Okaya, 1966). The average C–S–O and O–S–O angles for the present structure are 105 and 113°, respectively. It has been well established that the C–S–O angles in sulfonate groups are always smaller than the tetrahedral angles whereas the oxygen atoms tend to have larger separations with each other by making O-S-O angles of  $110^{\circ}$  or more. [See for an example of aromatic sulfonates, recent accurate data (Okaya, 1967) on ammonium acid *o*-carboxybenzenesulfonate,



Fig. 2. Bond distances in the zwitterion molecule. Separations for the ionic contact and the hydrogen bond approaches are also shown.



Fig. 3. Bond angles in degrees.



Fig. 4. Bond angles in the sulfonate group in degrees.



Fig. 5. Planarity of the molecule. The deviations of atoms from the least-squares plane are indicated (Å).



Fig. 6. Projection of the structure along the b axis. Short intermolecular approaches are given by broken lines. Shaded circles represent water molecules.



Fig.7. Drawing of the structure projected down the c axis.

 $NH_4C_6H_4COOHSO_3$ : C-S, 1.775 Å C-S-O, 106.3° and O-S-O, 112.3°.

# (b) The crystal structure, hydrogen-bond system

The crystal structure of this aromatic zwitterion compound is essentially ionic with electrostatic interaction between positive diazonium groups and negative sulfonate groups; the water molecules are involved in a hydrogen-bond system connecting these zwitterions together through sulfonate-water-hydroxyl linkages. The general feature of the structure is illustrated in Figs.6 and 7 as its projections along the b and c axes, respectively. The ionic interaction is found between N(I) of the diazonium group of one molecule and O(II) of the sulfonate group of another molecule related to the first by an n-glide; N-O distance is 2.88 Å. Since no proton is available from the sulfonate group, this short distance is a result of the ionic interaction and not a hydrogen bond. The interaction results in the shift of the linear diazonium group out of the plane of the benzene ring towards the indicated sulfonate oxygen atom; the exact nature of the shift was discussed earlier. The molecules are then connected by a three-dimensional hydrogen-bond system, the water molecules being active as intermediaries. As shown in Figs. 6 and 7, the water molecule connects two sulfonate groups related by an *n*-glide forming a sheet-like hydrogen-bond system perpendicular to the b axis. The OH group makes a hydrogen bond to the water molecule, through which two aromatic molecules related by a twofold screw axis are connected; thus infinite spiral chains along the baxis are formed. These two hydrogen-bond systems therefore form a three-dimensional network of hydrogen-bonds. The hydrogen bonds made by the water molecules are 2.71 and 2.72 Å, respectively, and are of medium strength as compared with the O-H...O bonds in similar substances; the six hydrogen-bond distances in zinc and magnesium *p*-toluenesulfonate hexahydrates (Hargreaves, 1960) vary from 2.72 to 2.82 Å, the average being 2.78 Å. The third hydrogen-bond of 2.56 Å formed by the OH group to the water molecule is stronger than the other two hydrogen-bonds but comparable with other hydrogen-bond distances involving hydroxyl groups and water molecules. The water molecule is surrounded by three oxygen atoms, the quartet forming a distorted pyramid with the water molecule sitting at the apex. The arrangement is quite common among the structure of various hydrates of organic compounds.

An observed red shift of the visible absorption maximum, from  $388 \mu$  in acid solution to  $488 \mu$  in basic solution, in the course of base titration favors the conclusion that the proton is associated with the phenolic oxygen and substantiates the above assignment of proton donors and acceptors in the last hydrogen bond around the water molecule. In this connection it can be safely assumed that the molecule does not make a 'double zwitterion' salt of a hydronium ion (see Fig.8). However, it would be desirable to confirm the above conclusion directly by the neutron diffraction method.

This rather fully developed system of hydrogen bonds together with the ionic interaction between positive diazonium nitrogen atoms and sulfonate oxygen atoms in all probability provides the necessary minimization of the energy to make the diazonium form so stable. Also the zwitterion character of the molecule and the electrostatic attraction in the crystal structure account for the infeasibility of preparing alkaline salts of the compound.

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(a) 2-Diazonium-4-phenolsulfonate monohydrate



(b) The less likely hydronium 2-diazonium-4-sulfophenolate

Fig. 8. Possible chemical formulas.

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# Crystal and Molecular Structure of 3-Hydroxy-5-phenylisoxazole (β form)

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The crystal structure of the  $\beta$  form of 3-hydroxy-5-phenylisoxazole has been determined from threedimensional X-ray data. The crystals, which are obtained either by sublimation or by slowly cooling the melt in the atmosphere, are monoclinic, space group  $P2_1/c$ , with four molecules in the unit cell. The cell dimensions are: a=8.75, b=5.64, c=16.10 Å,  $\beta=95.9^{\circ}$ . The structure was refined by the block-diagonal least-squares method to a final R value of 0.084 for 1116 observed reflexions. The molecule is present in the hydroxyl form and the values of bond distances suggest a conjugation effect between isoxazole and benzene rings. Pairs of molecules form dimers linked together by two hydrogen bonds across a centre of symmetry.

## Introduction

In the course of the investigation of the crystal structure of 3-hydroxy-5-phenylisoxazole (Fig. 1), two crystalline forms were identified. One ( $\alpha$ ) is obtained when an n-hexane solution is allowed to crystallize; the crystals are colourless prisms, space group  $P2_1/c$ . The crystal structure has already been reported in a short communication (Cannas & Mocci, 1965) and the refinement, based on three-dimensional data, is now being completed. A second type of crystallization ( $\beta$ ) was detected during the determination of the melting point of the  $\alpha$  form with a hot stage microscope. It was noticed that at a temperature around 140 °C the compound sublimes