

An Accurate Determination of the Structure of Sodium Hydroxymethanesulphinic Acid (Rongalite).

By MARY R. TRUTER.

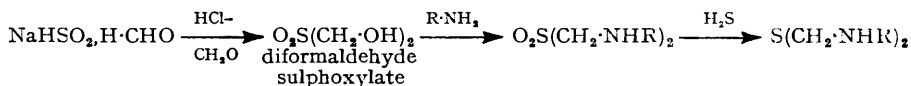
[Reprint Order No. 6161.]

A crystal-structure determination has shown that the compound of empirical formula $\text{NaHSO}_2 \cdot \text{H} \cdot \text{CHO} \cdot 2\text{H}_2\text{O}$ is sodium hydroxymethanesulphinic acid dihydrate. The bond lengths in the anion, $\text{HO} \cdot \text{CH}_2 \cdot \text{SO}_2$ are $\text{C}-\text{O} = 1.409 \text{ \AA}$, $\text{S}-\text{C} = 1.838 \text{ \AA}$, $\text{S}-\text{O} = 1.495 \text{ \AA}$ and 1.511 \AA , all with standard deviations of 0.01 \AA or less; the bonds to the sulphur atom are arranged pyramidally, the angles being $\text{O}-\text{S}-\text{O} 108^\circ 36'$ and $\text{C}-\text{S}-\text{O} 101^\circ 25'$ and $100^\circ 7'$, while the $\text{O}-\text{C}-\text{S}$ angle is $110^\circ 0'$.

WHEN a mixture of sodium hydrogen sulphite and formaldehyde is reduced by zinc dust in alkaline aqueous solution, a strongly reducing compound can be salted out. This compound is generally known as "Rongalite C" or "Formosul," the names under which it is sold as a reducing agent for vat dyeing. Although the empirical formula $\text{NaHSO}_2 \cdot \text{H} \cdot \text{CHO}$, sodium formaldehyde sulphonylate, is well established, the nature of the link between the inorganic and the organic portions of the compound has not hitherto been known. Two views are possible, each consistent with part of the chemical evidence but neither regarded, so far, as entirely acceptable. The parent compound, the hypothetical sulphonylic acid, may be formulated either (a) as $\text{S}(\text{OH})_2$ containing bivalent sulphur and analogous to SOCl_2 or (b) as $\text{H} \cdot \text{S} \cdot \text{O} \cdot \text{OH}$, a compound of quadrivalent sulphur analogous to the organic sulphinic acids. Accordingly, the formaldehyde sulphonylate ion may be (I) or (II).



The objection to the formulation (I) is that sodium formaldehyde sulphonylate does not react in the diagnostic manner with thiosulphate to form higher thionates. Moreover, the wavelengths of the K_α X-ray fluorescence spectrum are close to those of known quadrivalent sulphur compounds (Faessler and Goehring, *Naturwiss.*, 1943, 31, 567). The main objection to formulation (II) is evident from the reactions:



If formula (II) is correct, $\text{O}_2\text{S}(\text{CH}_2 \cdot \text{NHR})_2$ appears to be a sulphone, a type of compound which cannot usually be reduced by hydrogen sulphide. [This objection is not insuperable, however, since the amine might activate the methylene group; it would then be possible for the $\text{C}-\text{S}$ bond to break yielding a $\cdot(\text{CH}_2 \cdot \text{NHR})$ radical which would react with some of the sulphur present in the hydrogen sulphide solution.] Treatment of sodium formaldehyde sulphonylate with sodium hydrogen sulphite gives a mixture of sodium hydrosulphite (dithionite), $\text{Na}_2\text{S}_2\text{O}_4$, and formaldehyde-sodium hydrogen sulphite, $\text{NaHSO}_3 \cdot \text{CH}_2\text{O}$. Several lines of argument show that the latter almost certainly has the constitution $\text{Na}^+(\text{O}_3\text{S} \cdot \text{CH}_2 \cdot \text{OH})^-$; e.g., acetylation of the potassium salt gives the salt $\text{CH}_3 \cdot \text{CO} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{SO}_3\text{K}$ identical with the product obtained from potassium iodomethanesulphonate, $\text{I} \cdot \text{CH}_2 \cdot \text{SO}_3\text{K}$ (Lauer and Langkammerer, *J. Amer. Chem. Soc.*, 1935, 57, 2360). The dimeric formula $\text{Na}_2\text{S}_2\text{O}_4$ of the other product is supported by cryoscopic and magnetic measurements (Klemm, *Z. anorg. Chem.*, 1937, 231, 136); the ion may be $\text{O} \cdot \text{S} \cdot \text{O} \cdot \text{SO}_2$ or the symmetrical $\text{O}_2\text{S} \cdot \text{SO}_2$. Had formaldehyde-sodium hydrogen sulphite been the sole product of the reaction it could have been argued that formulation (II) was the more likely for the formaldehyde sulphonylate ion, but the existence of a second reaction product of unknown structure throws doubt on the validity of this argument.

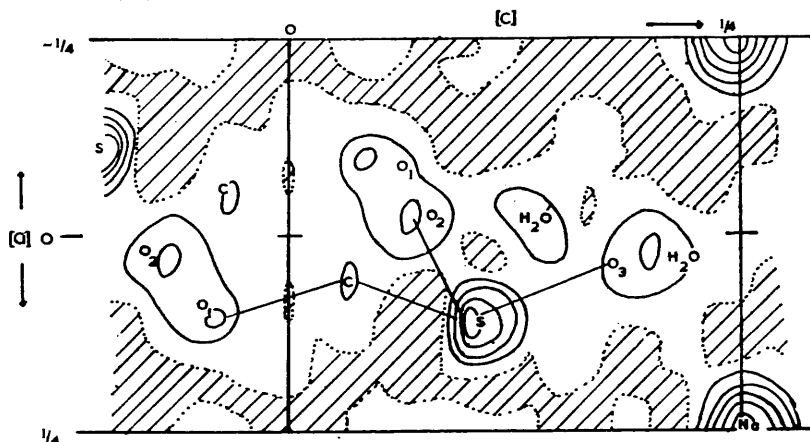
In order to explain all the chemical evidence it is necessary to postulate either

equilibrium between the two forms (I) and (II) in solution or a tendency for decomposition into formaldehyde and an unstable HSO_2^- ion. Evidence in favour of the second postulate is that the parent sulphonylate ion itself is unstable in solution, the only known compounds, ZnSO_2 and CoSO_2 , being insoluble, and that the full reducing power is only attained on warming the formaldehyde sulphonylate solution.

The structure analysis described below shows that $\text{NaHSO}_2 \cdot \text{H} \cdot \text{CHO} \cdot 2\text{H}_2\text{O}$ is, in the solid state, the dihydrate of sodium hydroxymethanesulphinate with the structure (II), and it also yields accurate values of bond lengths in a type of sulphur compound not previously studied.

Determination of Atomic Positions.—The orthorhombic unit cell has the constants $a_0 = 6.78$, $b_0 = 10.385$, $c_0 = 15.97$ Å; there are eight formula units in the general positions

FIG. 1. Fourier projection along [010]. Contour intervals are $2e/\text{Å}^2$ and negative areas shaded.



of the space group $Pbca-D_{2h}^{15}$. Absolute values of F^2 were obtained statistically from a set of relative three-dimensional intensities determined photographically.

Patterson projections along [100] and [010] proved intractable. Three-dimensional Patterson sections at $x = 0$, $x = \frac{1}{2}$, and $y = \frac{1}{2}$ showed symmetry-related peaks which could be identified as S-S and Na-Na vectors; the fractional co-ordinates obtained were S at 0.108, 0.273, 0.102, and Na at 0.00, 0.10, 0.25 or 0.25, 0.10, 0.25. The $(0kl)$ projection was considered first. Calculation of structure factors with sodium and sulphur only showed that at least some of the positions of the other six atoms (5 oxygen and 1 carbon) would have to be determined before Fourier synthesis was possible. By trial and error, and with the help of some weaker Patterson peaks, two atoms were located and designated $O_{(1)}$ and $O_{(2)}$, both being sufficiently near the sulphur to be part of the anion. The first value of $R = \Sigma|F_0 - F_c|/\Sigma|F_0|$ was 0.46; successive Fourier refinements reduced this to 0.22. The atomic arrangement viewed along [100] is shown in Fig. 3 and in Fig. 2 as a sketch on the $(0kl)$ difference projection; clearly formula (II) is correct and the compound is sodium hydroxymethanesulphinate.

For the $(h0l)$ projection the Patterson-Harker section gave unambiguously the sulphur parameters only, so that the others had to be determined by trial and error. The correct model gave $R = 0.22$ and the electron-density projection shown in Fig. 1. It can be seen that the Na^+ ion is not exactly at $z = \frac{1}{4}$ and again there is an overlap of two glide-related ions giving an apparent value of $x_{\text{Na}} = \frac{1}{4}$. This projection shows the pyramidal shape of the anion.

This arrangement gave $R = 0.24$ for $(hk0)$ planes and the projection along [001] was computed; as expected, none of the oxygen atoms was resolved but the Na^+ ion appeared at $x = 0.276$, the previous approximate value of $\frac{1}{4}$ being due to the superposition of the two peaks at 0.27 and 0.23.

Refinement by Three-dimensional Methods.—All three-dimensional calculations were

carried out on the Manchester University digital computer with programmes devised by Ahmed and Cruickshank (*Acta Cryst.*, 1953, **6**, 765) and modified for *Pbca* by Dr. P. J. Wheatley.

Structure factors were calculated for all (*hkl*) planes, the initial value of *R* being 0.296. Co-ordinate shifts were determined by the method of differential synthesis, termination-of-series errors being corrected by the back-shift method. Successive refinements were carried out until the shifts were less than 0.01 Å, the agreement index for the observed planes then being *R* = 0.152. The final calculated structure factors, with those observed for comparison, are shown in Table 1; the indices of reflections not observed have been omitted, and the indices are arranged in groups first with *h* + *k* and *k* + *l* even, then *h* + *k* even and *k* + *l* odd, then *h* + *k* odd and *k* + *l* even, last *h* + *k* and *k* + *l* odd.

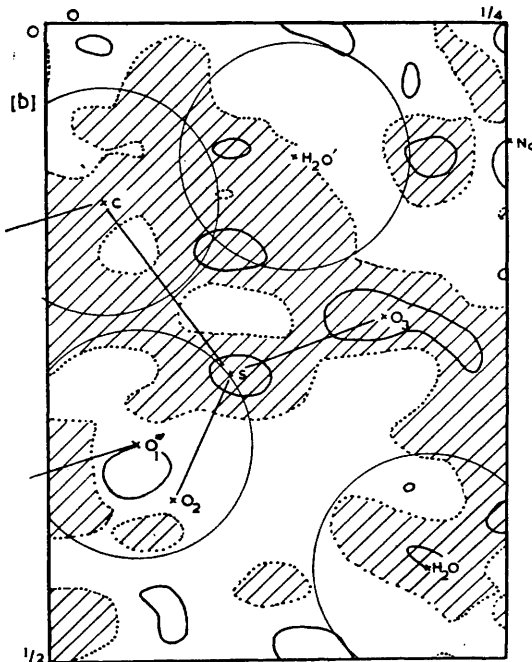


FIG. 2. Difference projection along [100] with contour intervals of $1e/\text{\AA}^2$ and negative areas shaded. Circles, radius 1 Å, are drawn about atoms which might be bonded to hydrogen atoms.

In Table 2 are given the final co-ordinates and their standard deviations calculated from Cruickshank's equation (*Acta Cryst.*, 1949, **2**, 65)

$$\sigma(x) = \frac{1}{V} \cdot \frac{2\pi}{a} [h^2(\Delta F)^2]^{1/2} / (\partial^2\rho/\partial x^2)$$

$\sigma(x)$ is the standard deviation in *x*, *V* is the volume of the unit cell, $\partial^2\rho/\partial x^2$ is the curvature of the atom in the *x* direction, and ΔF was taken as $|F_0 - F_c|$. In Table 2 are also shown the peak electron densities at the centres of the atoms, the ratio between these values and those obtained from an identical computation using the calculated instead of the observed structure factors (ρ_0/ρ_c), and similarly the ratio observed/calculated for the mean curvatures $\partial^2\rho/\partial x_i^2$ where $x_i = x, y, z$.

The scattering factors used were those for Na^+ and neutral sulphur ("International Tables for the Determination of Crystal Structures," Borntraeger, Berlin, 1935) and those calculated by McWeeny (*Acta Cryst.*, 1951, **4**, 513) for oxygen and carbon. The original Wilson plot for (*Ok*l) had indicated that no temperature factor was required; however, the relation between the observed and the calculated values of the curvatures ($\partial^2\rho/\partial x_i^2$) of the atoms found in three-dimensional refinement showed that some modification should be made. Finally the scattering factors were multiplied by $\exp(-B \sin^2 \theta/\lambda^2)$ with $B = 0.8 \times 10^{-16} \text{ cm.}^2$ for Na^+ and sulphur, $1.2 \times 10^{-16} \text{ cm.}^2$ for carbon, and $1.6 \times 10^{-16} \text{ cm.}^2$ for

TABLE I.

<i>hkl</i>	$F_{\text{calc.}}$	$F_{\text{obs.}}$	<i>hkl</i>	$F_{\text{calc.}}$	$F_{\text{obs.}}$	<i>hkl</i>	$F_{\text{calc.}}$	$F_{\text{obs.}}$	<i>hkl</i>	$F_{\text{calc.}}$	$F_{\text{obs.}}$
000	(632)		0,2,10	-66	64	2,4,14	-43	39	086	-11	13
002	-17	9	0,2,12	-8	5	2,4,16	11	12	0,8,12	15	17
004	-4	9	0,2,14	61	59				0,8,14	-14	14
006	-116	103	0,2,16	26	21	440	-91	74			
008	-10	20	0,2,18	-24	21	444	27	29	280	26	23
0,0,10	-10	23	0,2,20	-24	23	446	65	73	282	21	21
0,0,14	-61	68							284	-16	16
0,0,18	-10	19	220	-61	50	151	27	23	2,8,10	-13	14
0,0,20	47	50	224	-9	14	153	-12	14	2,8,12	11	12
			226	13	14	155	13	19			
200	204	128	228	6	8	157	20	20	191	-64	56
202	63	57	2,2,12	-28	29	159	-60	55	193	9	8
204	-84	82	2,2,14	43	43	1,5,11	-30	32	195	47	37
206	58	64	2,2,16	-12	15	1,5,13	12	14	197	19	20
208	-99	84				1,5,15	40	39	199	-27	26
2,0,10	42	46	420	81	73	1,5,17	11	14	1,9,11	4	12
2,0,12	-61	67	424	-25	28	1,5,19	-24	21	1,9,15	12	13
2,0,14	29	30	426	-66	72						
2,0,16	-18	18	428	37	38	351	43	40	393	-14	13
			4,2,10	27	32	353	-34	33	3,9,11	28	26
400	70	63	4,2,14	-24	16	355	-30	26			
402	-93	71	4,2,16	-24	13	357	6	12	591	32	30
404	68	70									
406	24	30	620	32	31	551	35	32	0,10,2	-34	33
4,0,10	-62	66	622	21	20				0,10,6	-19	17
4,0,14	31	34	624	-29	42	060	-119	95	0,10,8	41	56
4,0,16	44	67	626	-21	21	062	114	98	0,10,10	-24	32
4,0,18	-39	53	628	6	5	064	14	17	0,10,12	23	33
			6,2,10	24	26	066	42	42			
600	-26	40	6,2,12	-9	11	068	-58	69	2,10,0	-33	26
606	49	53	6,2,14	-7	8	0,6,10	-32	39	2,10,2	20	18
6,0,14	41	62				0,6,12	34	39	2,10,4	-41	33
			820	-15	10	0,6,14	26	23	2,10,6	23	18
800	39	35	822	-9	7	0,6,18	14	18			
806	-20	25	824	19	20				1,11,1	22	19
			826	12	14	262	6	8	1,11,3	5	8
111	-13	10				264	65	54	1,11,5	-47	41
113	20	17				266	-51	41	1,11,7	-22	20
115	99	72	131	-	-	268	29	27	1,11,9	22	22
117	-46	47	133	-52	48	2,6,10	-51	38	1,11,11	19	20
119	11	8	135	-60	50	2,6,12	25	22			
1,1,11	-8	10	137	-12	14	2,6,14	-26	26	3,11,1	-23	21
1,1,13	-25	24	139	41	44	2,6,16	12	10	3,11,3	17	15
1,1,15	-13	14	1,3,11	24	25				3,11,7	-2	10
1,1,17	-8	8	1,3,13	23	28				3,11,9	-14	8
1,1,19	7	10	1,3,15	9	12	460	-42	29			
			1,3,17	-4	8	462	50	47			
			1,3,19	11	14	464	-45	45	5,11,1	-34	36
311	-21	19									
315	45	45							0,12,2	-24	20
317	-22	22	331	8	7	666	-28	34	0,12,4	26	21
319	19	22	337	-14	15				0,12,8	11	19
3,1,11	17	17	339	-10	11	171	30	22	0,12,10	-23	37
3,1,13	-23	21	3,3,11	-18	10	173	27	25			
3,1,15	-10	7				175	-62	49	2,12,0	-21	18
			040	-71	66	177	27	27	2,12,4	-12	8
511	-14	13	042	-23	22	179	25	26	2,12,6	21	18
513	-11	13	044	-83	90	1,7,13	-20	18			
515	19	17	046	29	27	1,7,15	-45	45	1,13,5	33	36
517	-18	17	048	-15	13	1,7,17	-11	14			
519	27	30	0,4,10	124	129				3,13,1	21	22
5,1,11	11	13	0,4,12	10	10	371	-28	24	3,13,3	-12	18
5,1,15	-18	13	0,4,14	-39	41	373	28	26			
			0,4,16	-34	29	375	6	18			
			0,4,18	29	21	377	32	29	0,14,0	18	31
711	-11	10				379	-11	10			
713	-	-				379	-11	10	112	-94	57
7,1,11	12	17	240	-12	13	3,7,11	-26	22	114	-37	39
			242	-92	79				116	1	8
020	-116	72	244	38	38	571	-43	38	118	54	52
022	-90	86	246	-13	16				1,1,10	40	41
024	94	83	248	24	22	080	35	37	1,1,12	-70	72
026	15	14	2,4,10	23	33	082	29	29	1,1,14	-28	26
028	39	43	2,4,12	36	36	084	-36	43	1,1,16	28	27

TABLE I. (Continued.)

<i>hkl</i>	<i>F</i> _{calc.}	<i>F</i> _{obs.}	<i>hkl</i>	<i>F</i> _{calc.}	<i>F</i> _{obs.}	<i>hkl</i>	<i>F</i> _{calc.}	<i>F</i> _{obs.}	<i>hkl</i>	<i>F</i> _{calc.}	<i>F</i> _{obs.}
312	9	13	3,3,12	-18	28	172	36	33	0,14,1	-13	17
316	-61	69	3,3,14	-15	21	174	31	29			
318	-37	43				176	40	34	102	-44	40
3,1,10	36	43	534	-58	60	178	-26	30	106	53	52
3,1,14	16	17	536	24	34	1,7,10	-20	20	108	36	44
3,1,16	-4	11				1,7,12	20	23	1,0,12	-66	66
			041	-43	35	1,7,16	-22	25	1,0,18	34	34
512	37	44	043	-74	78						
514	11	15	045	-46	56	372	-13	13	302	-54	45
516	-67	71	047	86	103	374	-5	5	304	35	34
518	-51	54	049	-54	53	376	-29	28	306	25	28
5,1,10	17	18	0,4,11	34	38	3,7,10	-22	18	308	76	74
5,1,12	40	42	0,4,13	-37	30				3,0,10	-26	30
5,1,14	22	23	0,4,15	29	29	081	40	39	3,0,12	-62	73
			0,4,17	11	13	083	-75	88	3,0,14	-43	48
714	-7	4	0,4,19	20	21	085	23	22	3,0,16	31	35
716	-8	8				087	27	40	3,0,18	21	26
718	-4	4	241	66	63	089	52	53			
7,1,10	13	14	243	-94	84	0,8,11	-61	77	502	12	23
			245	40	43	0,8,13	-26	34	504	34	38
021	-34	41	247	-5	16	0,8,15	-25	32	506	-27	33
023	110	81	2,4,13	16	17				508	-18	26
025	48	49	2,4,15	-10	12	281	-18	15	5,0,12	-23	34
027	45	39	2,4,17	14	16	283	30	24			
029	-118	116				285	-52	41	702	32	39
0,2,11	28	22	441	15	13	287	43	38	704	35	38
0,2,13	-39	31	443	44	47	289	-21	18	706	-56	62
0,2,15	17	9				2,8,13	-32	33	708	-40	41
0,2,17	-36	36	641	33	10				7,0,12	20	34
0,2,19	23	24				481	60	59			
			841	-11	10				215	20	21
221	67	67				681	7	12	217	-21	23
223	-54	59	152	-34	30				219	12	12
225	122	93	154	-3	7	192	-30	30	2,1,13	15	16
227	-47	52	156	43	42	194	-10	12	2,1,15	-15	15
229	-21	20	158	9	16	196	-17	18			
2,2,11	-42	43	1,5,10	14	20				411	-47	40
2,2,13	13	14	1,5,12	-38	37	392	-20	16	413	24	22
2,2,15	-18	20	1,5,14	-7	11	396	-19	17	415	-26	26
			1,5,16	32	30				417	9	12
			1,5,18	9	8	0,10,1	18	14	419	-14	17
421	-53	42				0,10,3	43	58	4,1,11	10	11
445	-11	8	352	34	28	0,10,5	9	9	4,1,17	-14	17
447	33	38	354	38	35	0,10,7	-78	96			
449	-55	66	356	18	18	0,10,9	-14	12			
4,4,11	9	10	358	-25	21	0,10,11	-	-	613	-35	31
4,4,13	-29	28	3,5,10	-15	14	0,10,13	40	63	615	7	8
4,4,15	24	14							617	-24	23
			554	41	43	2,10,1	-25	20	619	18	17
623	-38	36				2,10,3	36	29	6,1,11	-20	19
625	24	22	061	57	56	2,10,7	-16	15	6,1,13	17	20
627	-11	10	063	19	17						
629	-1	4	067	-66	78	4,10,1	-23	23	811	-33	35
6,2,11	-14	14	069	26	25				815	-24	26
6,2,13	7	7	0,6,11	44	64	6,10,1	-22	22	817	8	10
			0,6,13	32	28						
821	11	8	0,6,15	1	7	1,11,2	-8	8	122	54	41
823	4	7	0,6,17	-34	40	1,11,4	-8	7	124	10	8
						1,11,6	-19	19	126	-35	39
132	128	89	263	13	16	1,11,8	15	19	128	-45	48
134	-93	73	265	-26	23				1,2,12	32	32
136	-34	40	267	-3	13	0,12,1	-43	46	1,2,14	24	26
138	-48	50	269	15	17	0,12,3	-19	20	1,2,16	-22	20
1,3,10	18	19	2,6,11	38	33	0,12,7	62	101	1,2,18	-12	15
1,3,12	50	46	2,6,13	-9	14	0,12,9	6	5			
1,3,18	-28	27	2,6,15	15	18				322	59	54
			2,6,17	-21	18	2,12,3	18	17	324	15	16
332	23	21				2,12,5	19	17	326	-53	57
334	-97	88	461	-9	8	2,12,7	10	13	328	-41	45
336	21	23	463	-54	47				3,2,10	-9	10
338	13	16				1,13,2	26	26	3,2,12	58	55
3,3,10	17	15	661	-15	25	1,13,4	26	28	3,2,14	19	22

TABLE I. (Continued.)

<i>hkl</i>	<i>F</i> _{calc.}	<i>F</i> _{obs.}	<i>hkl</i>	<i>F</i> _{calc.}	<i>F</i> _{obs.}	<i>hkl</i>	<i>F</i> _{calc.}	<i>F</i> _{obs.}	<i>hkl</i>	<i>F</i> _{calc.}	<i>F</i> _{obs.}
524	-15	15	473	-46	31	321	-41	33	650	28	29
526	7	8				323	-46	41	656	-19	32
528	16	16	671	14	13	325	-22	23			
						327	28	31	161	32	29
722	-30	29	182	-13	12	329	36	38	165	-35	31
724	-21	20	184	-11	12	3,2,11	35	36	167	-9	12
726	26	32	1,8,12	-10	10	3,2,13	-6	13	169	18	19
728	44	53	1,8,16	10	13				1,6,11	20	21
7,2,10	-9	12				521	-26	20	1,6,13	-13	15
			384	-16	13	523	-27	28	1,6,15	-16	17
231	-27	22	291	26	24	525	12	10	1,6,17	-9	12
233	-40	40	293	-25	22	527	7	10			
235	-23	27	297	-58	44	529	23	31	361	48	47
237	19	20	299	-20	17	5,2,11	-8	10	365	-40	33
2,3,11	-12	16	2,9,11	28	25	5,2,13	12	13	367	-25	26
2,3,15	12	16	2,9,13	39	33				369	32	30
2,3,17	24	26				721	-17	12	3,6,11	15	15
			691	-12	13	725	13	12			
831	18	18				727	9	10	561	7	7
			1,10,10	9	10	729	-4	5			
142	-59	53				7,2,11	-11	14	761	-13	17
144	-22	25	2,11,1	-11	11				274	-39	36
146	7	10	2,11,3	-37	29	230	114	84	278	13	17
148	38	37	2,11,5	19	16	232	-13	14	2,7,10	41	36
1,4,12	-12	14	2,11,7	41	30	234	-33	35	2,7,16	-17	16
1,4,14	-16	17	2,11,9	24	20	236	-65	68			
1,4,16	24	21	2,11,11	-26	22	238	14	14			
1,4,18	6	10				2,3,10	49	52	670	-20	20
			4,11,1	-12	8	2,3,12	20	23	676	32	44
342	-73	65				2,3,14	-40	42	181	-40	33
344	-36	36	1,12,2	9	8	2,3,16	-16	18	183	7	11
346	25	29				2,3,18	11	13	185	26	28
348	33	32	3,12,2	9	8				187	19	18
3,4,10	21	33				430	25	25	189	-28	23
3,4,12	-32	40	2,13,1	17	17	434	-38	47	1,8,15	32	31
			2,13,3	31	30						
						634	53	41	381	-53	49
744	25	21	210	-134	99				385	49	39
			212	-66	62	830	-31	36	389	-17	20
251	24	25	214	64	72	836	32	48	3,8,11	-17	10
253	80	78	216	35	40				3,8,13	26	29
257	-19	22	2,1,10	-46	49	143	10	12			
259	-24	23	2,1,12	9	13	145	42	38	781	24	28
2,5,11	28	26	2,1,14	52	48	147	-15	16			
2,5,17	-32	31	2,1,16	33	26	149	-19	24	290	-21	17
			2,1,18	-19	16	1,4,11	-36	36			
451	43	41				1,4,13	10	12	690	-15	31
			410	-79	76	1,4,15	6	10			
651	-29	29	414	3	5	1,4,17	12	12	1,10,1	26	20
			416	14	15	1,4,19	-15	14	1,10,5	-33	26
162	32	30	418	-12	15				1,10,9	15	15
164	28	26	4,1,14	41	44	341	10	8	1,10,11	16	18
168	-7	12				343	17	18	1,10,13	-14	16
1,6,10	-12	14	610	46	39	345	44	43			
1,6,12	26	23	614	-16	27	349	-45	40	3,10,1	31	26
1,6,14	-10	12	616	-59	66	3,4,11	-27	29	3,10,5	-42	34
1,6,16	-4	10	618	20	20	3,4,13	-11	17	3,10,11	24	22
1,6,18	-23	19	6,1,10	20	20						
			6,1,12	16	19	541	22	21	5,10,1	-18	15
362	50	41	6,1,14	-15	16						
364	17	18				741	21	24	2,11,0	4	10
366	13	13	810	18	25				2,11,2	9	12
368	-35	30	812	26	30	250	-19	26			
			814	-30	33	254	60	53	1,12,1	-16	14
764	-32	38	816	-27	36	256	28	29	1,12,5	25	21
						258	-18	19	1,12,9	-15	19
271	-28	25	121	-22	20	2,5,10	-53	43	3,12,1	-19	18
273	-48	41	123	-42	36	2,5,12	25	26	3,12,3	12	12
277	54	49	129	46	51	2,5,14	19	23	3,12,5	30	23
2,7,11	-19	18	1,2,13	16	18	2,5,16	13	13	3,12,7	14	12
2,7,13	-40	35	1,2,15	-19	20						
2,7,17	24	21	1,2,19	-6	7	454	27	24	2,13,0	11	15

oxygen. The scaling factor obtained from $\Sigma|F_c|/\Sigma|F_0|$ was 0.956 showing that the approximation to absolute values of F^2 had been good. Although the mean value of the

FIG. 3. Projection along [100] with the positive direction of the a -axis away from the reader. Fractional x co-ordinates to two decimal places are marked for one asymmetric unit. Atoms at $x \sim 0$ are shown by thin and those at $x \sim \frac{1}{2}$ by thick circles.

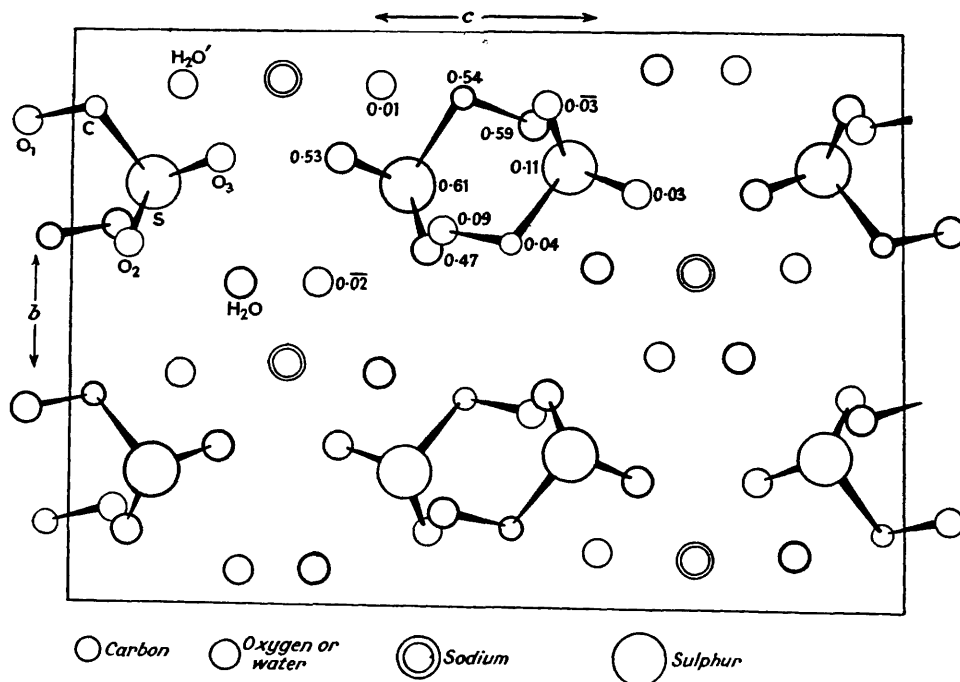


TABLE 2.

Atom	x/a	y/b	z/c	X (Å)	$\sigma(x)$ (10^4 Å)	Y (Å)
S	0.1066	0.2743	0.1012	0.722	8	2.972
Na	0.2740	0.0926	0.2557	1.858	14	1.003
C	0.0414	0.1422	0.0343	0.248	44	1.541
O ₁	0.0931	0.1686	-0.0492	0.558	29	1.827
O ₂	-0.0272	0.3725	0.0679	-0.163	31	4.035
O ₃	0.0262	0.2299	0.1842	0.157	23	2.491
H ₂ O	0.4768	0.4347	0.2084	2.861	33	4.710
H ₂ O'	-0.0124	-0.3976	0.1379	-0.074	38	4.308

Atom	$\sigma(y)$ (10^4 Å)	Z (Å)	$\sigma(z)$ (10^4 Å)	ρ_0/ρ_c	$e/\text{Å}^3$	$\partial^2\rho/\partial x_i^2$ Obs./calc.
S	29	1.617	13	0.99	41.7	1.01
Na	58	4.083	22	0.97	25.1	1.00
C	125	0.548	65	1.00	9.9	1.02
O ₁	107	-0.786	40	0.99	14.1	1.03
O ₂	109	1.084	44	0.93	13.5	0.96
O ₃	87	2.941	53	0.96	14.7	1.06
H ₂ O	102	3.329	48	0.93	13.3	0.97
H ₂ O'	105	2.203	48	0.99	13.5	1.04

curvature is given, there is actually a slight tendency to anisotropic thermal vibration, the motion being larger in the b -axis direction; the mean values for all atoms are:

observed/calculated $\partial^2\rho/\partial x^2 = 1.01 : 1$; $\partial^2\rho/\partial y^2 = 0.98 : 1$; $\partial^2\rho/\partial z^2 = 1.04 : 1$; $\rho = 0.968 : 1$.

Attempted Location of Hydrogen Atoms.—Although this structure is not a promising one for the location of hydrogen atoms, the $(0kl)$ difference projection was computed, with the result shown in Fig. 2. There are peaks large enough to be hydrogen atoms but while some

are within reasonable distance of oxygen atoms others are so far away that they are obviously spurious.

It is interesting that, although the same parameters were used for calculating this projection and for a three-dimensional difference synthesis, some of the shifts indicated here are the same as those found three-dimensionally, while others differ in both magnitude and direction. This indicates that the limits of true refinement by two-dimensional methods had been reached.

Discussion of the Structure.—The structure as a whole can be visualised in terms of anions and water molecules lying at approximately $x = 0$ and $x = \frac{1}{2}$ with the Na^+ ions at $x = \frac{1}{4}$ and $x = \frac{3}{4}$ (see Fig. 1), so that projected along [100] it appears as in Fig. 3. Thin and thick circles represent atoms at approximately $x = 0$ and $x = \frac{1}{2}$ respectively; the x co-ordinates of some of the atoms are marked. Strong hydrogen bonds (2.63 Å) between $\text{O}_{(1)}$ and $\text{O}_{(2)}$ connect the anions in a spiral parallel to the a -axis, in which direction the $\text{O}_{(3)}-\text{Na}^+$ electrostatic attraction also forms a continuous link. Each $\text{O}_{(3)}$ has two Na^+ neighbours at 2.52 and 2.46 Å (the longer distance being from O at $x \sim 0$ to Na at $x \sim \frac{1}{4}$), and each Na^+ has two $\text{O}_{(3)}$ neighbours. In the c -direction the structure is held by the same $\text{Na}^+-\text{O}_{(3)}$ bonds, but in the b -direction there are only weak bonds between the ions in the two halves of the unit cell divided by the line $y = \frac{1}{2}$. These bonds are a weak hydrogen bond (2.87 Å) from $\text{O}_{(1)}$ to a water molecule with similar x -co-ordinates, and the attraction between this water molecule and the Na^+ ion. The weaker bonding along b is consistent with the somewhat greater thermal vibration indicated by the values of $\partial^2\rho/\partial y^2$.

In spite of the fact that there are so many water molecules and oxygen atoms present, the only hydrogen bonds in the structure are the two to the CH_2OH oxygen. The bonds to $\text{O}_{(1)}$ are $\text{C}-\text{O}_{(1)} = 1.409$ Å, $\text{O}_{(1)}-\text{O}_{(2)} = 2.63$ Å, and $\text{O}_{(1)}-\text{H}_2\text{O} = 2.87$ Å, with the angles $\text{C}-\text{O}_{(1)}-\text{O}_2$ $108^\circ 42'$, $\text{C}-\text{O}_{(1)}-\text{H}_2\text{O}$ 134° , $\text{H}_2\text{O}-\text{O}_{(1)}-\text{O}_{(2)}$ 96° , indicating a pyramidal arrangement. The sodium ion is surrounded by four water molecules and two $\text{O}_{(3)}$ atoms of the anion in a distorted octahedron. The interatomic distances are shown in Table 3; the letter L refers to atoms with $z = 0$ to $\frac{1}{4}$ and M to those with $z = \frac{1}{4}$ to $\frac{1}{2}$.

TABLE 3. Bond lengths (Å) and angles (standard deviations in parentheses).

<i>The salt.</i>							
$\text{Na}-\text{H}_2\text{O}'$	L 2.48	$\text{Na}-\text{O}_{(2)}$	M 2.46	$\text{O}_{(3)}-\text{L}-\text{O}_{(3)}$	M 3.99	$\text{O}_{(3)}-\text{L}-\text{H}_2\text{O}$	L 3.22
$\text{Na}-\text{H}_2\text{O}'$	M 2.46	$\text{Na}-\text{H}_2\text{O}$	L 2.53	$\text{O}_{(3)}-\text{L}-\text{H}_2\text{O}'$	L 3.63	$\text{O}_{(3)}-\text{L}-\text{H}_2\text{O}'$	M 3.30
$\text{Na}-\text{O}_{(3)}$	L 2.52	$\text{Na}-\text{H}_2\text{O}$	M 2.47	$\text{H}_2\text{O}'-\text{L}-\text{H}_2\text{O}$	L 3.82	$\text{H}_2\text{O}-\text{L}-\text{H}_2\text{O}'$	M 3.05
<i>Hydroxymethanesulphinat ion.</i>							
S-C	1.838 (0.0107)	S- $\text{O}_{(3)}$	1.511 (0.0057)	$\text{O}_{(3)}-\text{S}-\text{O}_{(3)}$	108.5°	$\text{O}_{(3)}-\text{S}-\text{C}$	100.0°
S- $\text{O}_{(2)}$	1.495 (0.0084)	C- $\text{O}_{(1)}$	1.409 (0.0081)	$\text{O}_{(3)}-\text{S}-\text{C}$	101.5°	$\text{O}_{(1)}-\text{C}-\text{S}$	110.0°

The C-O bond length is shorter than 1.437 Å, the mean value of a number of X-ray and electron-diffraction determinations (Cox and Jeffrey, *Proc. Roy. Soc.*, 1951, *A*, 207, 110) and therefore suggests that there may be about 12% of double-bond character in the bond. However, very few accurate measurements of C-O single bond distances have been made and it is by no means certain what precision can be assigned to the "standard" value of 1.437 Å, so that the present value may not be significantly different from it. On the other hand, the C-S bond is longer than 1.81 Å, the mean value of many determinations, and the difference is just significant with $\Delta/\sigma = 2.6$ if there is no error in the value 1.81 Å. The curve of bond order against bond length curve for C-S given by Cox and Jeffrey (*loc. cit.*) yields on extrapolation an order 0.84 for the observed value 1.838 Å, so that the sum of the orders of the two carbon bonds is about 1.96. Although the order determined in this way is only approximate, it suggests that there may be some tendency toward dissociation into separate CH_2O molecules only loosely associated with the SO_2^- ion, thus confirming the postulate made on p. 3065.

The case of the S-O bonds is interesting. First, they are equal in spite of having very different environments; only $\text{O}_{(3)}$ is in contact with a cation and a configuration without resonance might have been expected. Secondly, the S-O bond length of 1.50 ± 0.01 Å is unusual, being significantly longer than the 1.44 Å normally found in sulphur acid anions, sulphones, etc., and shorter than the 1.6 Å found for S-O-X bonds in, for example,

potassium ethyl sulphate (Jarvis, *Acta Cryst.*, 1953, 6, 327). The only accurate similar value reported is 1.493 Å in SO, but it is uncertain whether this refers to the ground state (Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York, 1950, p. 573). Discussion of the significance of the present result is deferred for a later paper dealing with sulphur-oxygen compounds more generally.

EXPERIMENTAL

Crystals of sodium formaldehyde sulphonylate dihydrate were grown from aqueous solution. Analysis showed them to contain 96.9% of $\text{NaHSO}_2 \cdot \text{H} \cdot \text{CHO} \cdot 2\text{H}_2\text{O}$.

The dimensions of the orthorhombic unit cell, measured by the method of Straumanis, are $a = 6.78$, $b = 10.835$, $c = 15.97$ Å, all ± 0.01 Å, whence $U = 1173.5 \text{ Å}^3$. The axial ratios determined goniometrically (Osann, *Ber.*, 1905, 38, 2290) were 0.8421 : 1 : 0.6783 compared with $2a : b : c = 0.8487 : 1 : 0.6784$ from the unit cell dimensions. The density calculated by assuming eight formula units (8×154) per unit cell is 1.73 g./c.c., in satisfactory agreement with 1.75 g./c.c. measured by the flotation method.

The space group $Pbca-D_{2h}^{15}$ was uniquely determined from the systematic absences ($0kl$) when $k = 2n + 1$, ($h0l$) when $l = 2n + 1$, and (hkl) when $h = 2n + 1$. No molecular symmetry is required.

Sets of equi-inclination Weissenberg photographs were taken about the three principal axes using Ni-filtered Cu-K_α radiation. Intensity determination was carried out by the multiple-film technique, and the densities were compared visually with those on a calibration strip, made by exposing the film to the reflections from one plane for various lengths of time. Cochran's chart (*J. Sci. Instr.*, 1948, 25, 253) was used for the application of the usual Lorentz and polarisation corrections. Approximate absolute values of F^2 for ($0kl$) reflections were obtained from the relative intensities by Wilson's statistical method (*Acta Cryst.*, 1949, 2, 318). Values of F^2 for all (hkl) reflections were obtained by correlation, those for ($0kl$) being used as standard.

No absorption correction was made ($\mu = 52.1 \text{ cm.}^{-1}$); the crystals used were approximately cylindrical about the axis of rotation and 0.2 mm. in radius.

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DEPARTMENT OF INORGANIC AND STRUCTURAL CHEMISTRY,
THE UNIVERSITY OF LEEDS.

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