Acta Cryst. (1956). **9**, 579

The Structure of Sodium Dithionite and the Nature of the Dithionite Ion

By J. D. Dunitz*

National Institutes of Health, Bethesda 14, Maryland, U.S.A.

(*Received* 7 *December* 1955)

The structure of sodium dithionite has been determined by X-ray analysis. The crystals are monoclinic, $a = 6{\cdot}404 \pm 0{\cdot}0045$, $b = 6{\cdot}559 \pm 0{\cdot}0028$, $c = 6{\cdot}586 \pm 0{\cdot}0056$ Å, $\beta = 119^\circ\,31' \pm 0^\circ\,02'$, space group $P2/c$, with two molecules of $Na_2S_2O_4$ in the unit cell. The structure was refined by successive difference Fourier projections on (001), (010) and (100). The anion consists of two SO_2^- units, joined by a very long S–S bond (2·39 Å), in an eclipsed configuration with the planes of opposite SO_2^- groups only 30° from parallel. It has approximate C_{2v} symmetry. The sodium coordination is of an unusual type. The electronic structures of SO_2, SO_2^-, and $^-O_2S\text{–}SO_2^-$ are discussed.

Introduction

Sodium dithionite (hydrosulphite, hyposulphite), $Na_2S_2O_4$, has been in common laboratory use as a reducing agent for many years but its structure has remained controversial (Sidgwick, 1950) with very little evidence available. Klemm (1937) has shown that the salt is diamagnetic and hence cannot contain the paramagnetic free radical anion SO_2^-, and Simon & Küchler (1949) have examined the Raman spectrum of dithionite solutions. They associate the presence of a Raman line at 465 cm.$^{-1}$ with an S–S single bond and, on the basis of selection rules, suggest that the anion is planar or nearly so, with probable symmetry D_{2h}. The structure of the salt now been determined by X-ray analysis.

Experimental

A sample of anhydrous sodium dithionite, crystallized by salting out with sodium chloride from aqueous solution, was obtained from the Virginia Smelting Company, West Norfolk, Virginia. This preparation consisted mostly of agglomerates of very small crystallites but some larger crystals, generally with smaller ones adhering, could be isolated. Many of these were found to have re-entrant angles, indicating twinning. Only a small proportion of the apparently single crystals examined with X-rays proved satisfactory in that they were untwinned and the fragments of adhering crystals were so small as not to interfere seriously with the indexing of reflexions.

The crystals are monoclinic, point group $C_{2h}(2/m)$ and occur in a variety of habits, mostly as rather thick platelets bounded by {100}, {001}, {10$\bar{1}$}, and {10$\bar{2}$} with {010} as the basal plane across which cleavage is pronounced.

Unit-cell dimensions were determined from ($hk0$) and ($h0l$) zero-layer Weissenberg photographs on which sodium chloride powder lines had been superimposed to provide a set of standard θ values based on $a_0(\text{NaCl}) = 5{\cdot}62869$ X. (van Bergen, 1941) $= 5{\cdot}64006$ Å (Cu $K\alpha_1 = 1{\cdot}54050$ Å $= 1{\cdot}537395$ X.). The θ values of several high-order reflexions were estimated simply by interpolation between the NaCl powder lines, using a travelling microscope for the measurements; no determination of camera radius or of film shrinkage is required. The cell constants and their standard deviations were then calculated by least-squares analysis of the derived $\sin\theta$ values; they are

$$a = 6{\cdot}404 \pm 0{\cdot}0045,\quad b = 6{\cdot}559 \pm 0{\cdot}0028,$$
$$c = 6{\cdot}586 \pm 0{\cdot}0056\ \text{Å},\quad \beta = 119^\circ\,31' \pm 0^\circ\,02'\,.$$

The only systematic absence is ($h0l$) when l is odd, so that the space group is either Pc or $P2/c$, the latter being indicated by the crystal morphology and confirmed by the subsequent course of the analysis. The density calculated for 4 formula units of $NaSO_2$ is 2·40 g.cm.$^{-3}$ (found, 2·37 g.cm.$^{-3}$).

Visual intensity measurements were made on zero-layer, multiple film, Weissenberg photographs of the three axial zones with the aid of a calibrated intensity scale. Out of 55 possible ($hk0$) reflexions within the range $\sin\theta < 0{\cdot}990$ (Cu $K\alpha$ radiation) 53 were recorded with measurable intensity, the corresponding figures for ($h0l$) being 47 out of 48, and for ($0kl$) 51 out of 53. Absorption corrections were not applied and the intensities were converted directly to relative F^2 values by multiplication by the usual Lorentz and polarization factors. Rough values for scale and temperature factors were obtained by Wilson's (1942) method.

Space-group considerations

Further support for the space group being $P2/c$, rather than Pc, was provided by statistical tests (Howells, Phillips & Rogers, 1950) of the intensity distribution of the ($hk0$) and ($0kl$) reflexions and, later, by the distribution of peaks in the corresponding

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* Visiting Scientist, 1954–5, National Institute of Mental Health, National Institutes of Health, Public Health Service, Department of Health, Education, and Welfare, Bethesda 14, Maryland, U.S.A. Present address: The Royal Institution, 21 Albemarle Street, London W. 1, England.

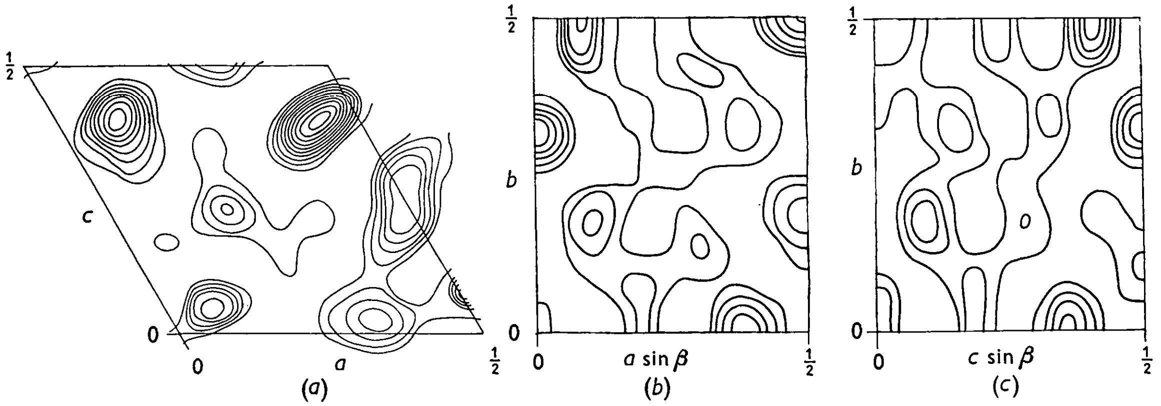
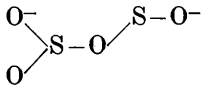
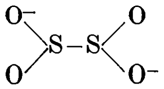


Fig. 1. Patterson projections, sharpened, with origin peak removed. Positive contours only are shown.

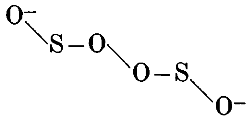
Patterson projections. Statistical treatment of the ($h0l$) reflexions led to an inconclusive result, but the distribution of Patterson peaks again indicated the centrosymmetric structure. Thus the initial assumption of $P2/c$ as the space group was repeatedly confirmed and there is no doubt that it is correct. For two molecules of $Na_2S_2O_4$ in the unit cell, each molecule is required to possess either a centre of symmetry or a twofold axis of rotation parallel to b. Asymmetric structures such as the 'mixed anhydride' of sulphurous and sulphoxylic acids (I) are immediately excluded. The only reasonable structure allowed is (II), since the peroxide structure (III) is incompatible with the chemical evidence.



(I)



(II)



(III)

Structure analysis

The derivation of an approximately correct trial structure proved to be unexpectedly difficult, considering that there are only 4 atoms in the asymmetric unit of structure, and was ultimately achieved only by devious combinations of several methods. Here the details can be given only in brief outline.

Attention was first directed to analysis of the ($h0l$) reflexions. The (010) Patterson projection was computed, first unsharpened and then sharpened by dividing all coefficients by Σf_i^2 (Fig. 1(a)). The most prominent features could be accounted for on the basis of a centrosymmetric arrangement of the heavier atoms. With $x_S = 0{\cdot}167$, $z_S = 0{\cdot}010$, $x_{Na} = 0{\cdot}267$, $z_{Na} = 0{\cdot}389$, the calculated F values gave the promising agreement factor $R = 0{\cdot}23$ for all reflexions out to $\sin\theta = 0{\cdot}87$ ($R = \Sigma||F_o|-|F_c||\div\Sigma|F_o|$). A Fourier series based on the signs associated with this arrangement showed no indication whatsoever of the presence of the lighter oxygen atoms, and when insertion of these atoms at various positions which seemed reasonable on stereochemical grounds led to no improvement, but rather to a deterioration of the structure-factor agreement, the structure was abandoned as incorrect. Application of inequality relationships, following the procedures outlined by Grison (1951), led to the ostensible derivation of a large proportion of signs but the resulting Fourier projection was of no help in deducing a trial structure; many of the sign determinations proved later to have been incorrect.

Sharpened Patterson projections on (001) and (100) (Fig. 1(b) and (c)) were then calculated but, although partial interpretations were obvious, no convincing trial structure could be derived from them. Likewise, inequality methods again led to Fourier projections which defied any reasonable interpretation. The inequality relations led to a positive sign for $F(020)$ and to Fourier projections characterized by marked accumulations of electron density at $y = 0$ and $y = \frac{1}{2}$. Now $F(010)$ is close to zero and it is not possible to account for this if the sulphur and sodium atoms are placed at $y = 0$ and $y = \frac{1}{2}$ respectively; for if the

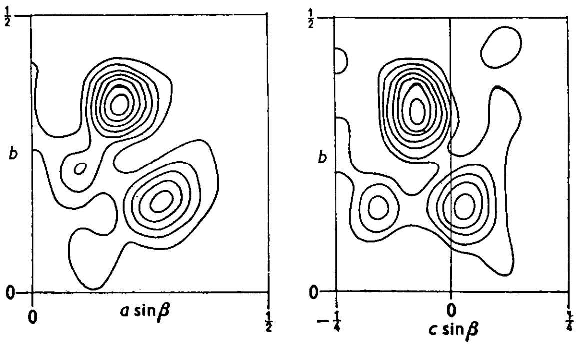


Fig. 2. Fourier projections based on signs determined from inequalities, but with $F(020)$ assumed to be negative.

oxygen atoms are bonded to the sulphur their contributions to $F(010)$ cannot have opposite phase to the sulphur contribution. The sign of $F(020)$ was therefore *assumed* to be negative and the signs of all other reflexions which were derived from relationships involving the sign of $F(020)$ were reversed. The new electron-density projections (Fig. 2) led to a much more reasonable interpretation, which could also be reconciled with the appearance of the Patterson projections. Preliminary structure-factor calculations for this rough structure gave R values of 0·26, 0·17 and 0·24 for the $(hk0)$, $(h0l)$ and $(0kl)$ data respectively, the agreement improving rapidly on subsequent refinement.

One characteristic of the structure is that it leads to overlapping of the atoms in all three projections, and especially in the (010) projection where the sulphur and sodium atoms overlap. It is this feature which is responsible for most of the difficulties encountered. The scale and temperature factors estimated by Wilson's (1942) method were incorrect since the average value of F^2 for the $(h0l)$ reflexions is given not by Σf_i^2 but more nearly by $(f_S+f_{Na})^2+2f_O^2$. In the final correlations between observed and calculated structure factors the initial scale factor for $F(h0l)$ had to be multiplied by 20%, and the temperature factor reduced from $\exp(-0{\cdot}635 \sin^2\theta)$ to $\exp(-0{\cdot}335 \sin^2\theta)$. These errors in scale and temperature factors have a profound influence on the application of inequality methods and practically all of the erroneous sign determinations can be attributed to them. In the (010) sharpened Patterson projection the Na–S peak stands out very clearly near the origin but unfortunately it was not recognized as such for a long time.

There is no doubt that the use of full three-dimensional intensity data would have led in a fairly straightforward manner to the correct structure. But the accumulation of the data would have been much more tedious and the calculations required outside the scope of the available computing facilities. All of the Fourier-series calculations in this work were carried out with the aid of a desk machine and Beevers–Lipson strips. The series were summed at intervals of $\frac{1}{30}$th of the cell edges.

Refinement of parameters

The procedure adopted was to refine each of the three projections independently by repeated difference syn-

Table 1. *Coordinates used for final structure-factor calculations*

	(hk0)		(h0l)		(0kl)	
	x	y	x	z	y	z
S	0·187	0·344	0·189	−0·074	0·345	−0·075
Na	0·267	−0·148	0·263	−0·025	−0·150	−0·023
O_1	0·314	0·201	0·314	−0·145	0·193	−0·147
O_2	0·117	0·236	0·115	0·086	0·239	0·083

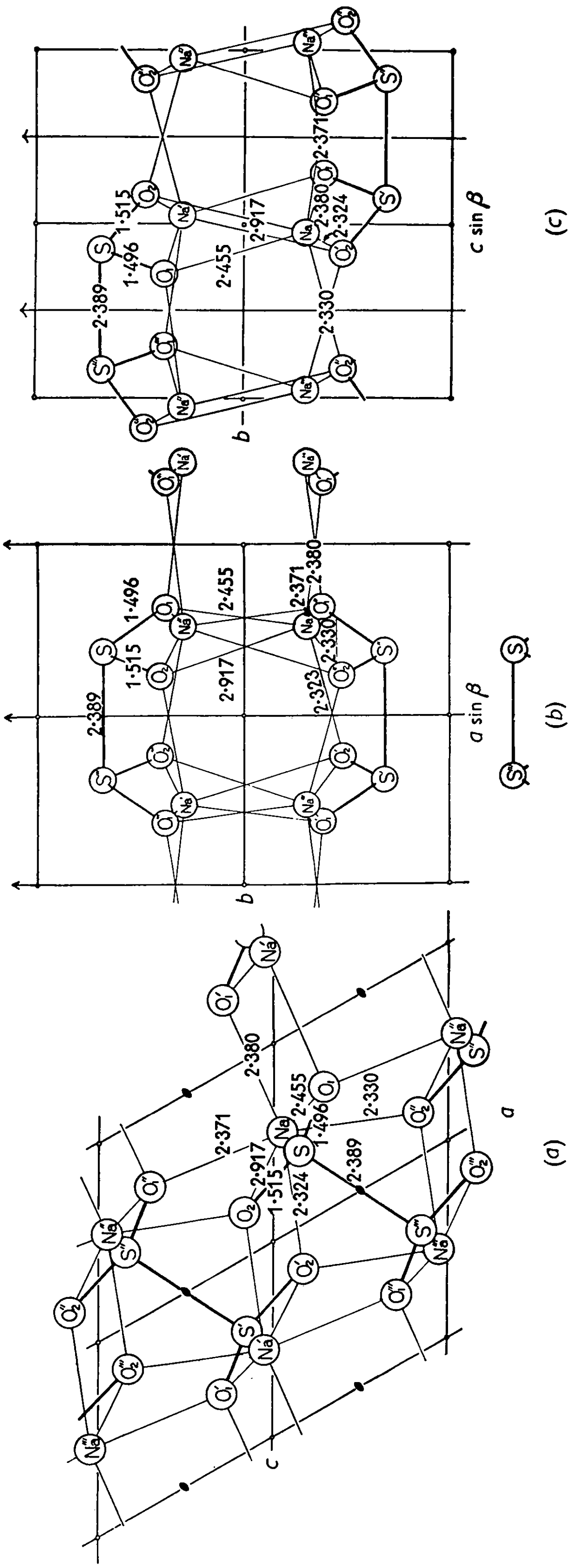


Fig. 3. Projections of structure.

Table 2. *Observed and calculated structure factors* (*half-absolute scale*), *from coordinates of Table* 1

Values are listed separately for (*hk*0), (*h*0*l*) and (0*kl*) in order of increasing sin θ. The disagreement factor *R*, over all measurable reflexions except (200), (020) and (002) is 0·098 for (*hk*0), 0·063 for (*h*0*l*) and 0·106 for (0*kl*). (N.B.—The signs of reflexions with *l* odd are reversed in this table.)

*hk*0	sin θ	F_o	F_c
010	0·117	1·6	+ 1·4
100	0·138	13·6	+13·9
110	0·181	7·4	− 7·7
020	0·235	30·0	−36·4
120	0·273	6·8	− 7·3
200	0·276	32·3	−38·1
210	0·300	3·2	− 3·0
030	0·352	4·8	− 5·2
220	0·363	12·4	+13·5
130	0·378	10·0	+ 9·7
300	0·415	9·6	− 9·5
310	0·431	12·3	+13·3
230	0·448	3·7	+ 3·8
040	0·470	14·5	−13·1
320	0·477	3·7	+ 3·4
140	0·490	1·0	+ 0·5
330	0·544	19·4	−20·3
240	0·545	14·8	+15·4
400	0·553	4·7	+ 3·4
410	0·565	5·5	+ 5·3
050	0·587	3·1	+ 4·4
420	0·601	2·6	+ 2·8
150	0·603	2·2	− 1·2
340	0·627	6·0	+ 5·4
250	0·649	< 1·2	− 0·7
430	0·656	5·8	− 6·2
500	0·691	2·2	− 0·1
510	0·701	11·2	−10·4
060	0·705	15·9	+15·1
160	0·718	2·0	+ 0·9
350	0·719	5·0	+ 4·8
440	0·726	9·0	− 9·5
520	0·730	2·2	+ 3·0
260	0·757	12·0	−13·5
530	0·776	15·1	+16·7
450	0·807	1·5	− 1·1
360	0·818	5·4	− 4·9
070	0·822	6·8	− 7·1
600	0·829	3·4	+ 3·9
170	0·834	3·3	− 4·3
540	0·836	7·7	− 7·6
610	0·838	7·2	− 6·3
620	0·862	2·4	− 2·3
270	0·867	3·3	+ 2·0
460	0·896	4·9	+ 5·3
630	0·901	8·2	+ 8·9
550	0·907	4·2	− 4·4
370	0·921	7·3	+ 7·5
080	0·939	1·0	+ 1·8
180	0·950	1·5	+ 1·6
640	0·953	1·7	− 1·7
700	0·968	0·8	+ 0·9
710	0·975	3·7	+ 3·5
280	0·979	< 0·6	− 0·4
560	0·987	5·0	+ 6·3

*h*0*l*	sin θ	F_o	F_c
100	0·138	13·6	+14·1
$10\bar{2}$	0·234	17·6	−17·2
002	0·269	28·0	+31·7
$20\bar{2}$	0·275	13·9	−15·7
200	0·276	32·3	−38·4
102	0·358	26·6	+29·0
$30\bar{2}$	0·367	7·3	+ 8·7
300	0·415	9·6	− 9·9
$20\bar{4}$	0·468	9·0	− 9·1
202	0·471	20·3	−19·6
$40\bar{2}$	0·481	14·2	+14·7
$10\bar{4}$	0·485	17·2	−17·5
$30\bar{4}$	0·491	19·0	+19·7
004	0·538	3·8	− 4·2
$40\bar{4}$	0·549	28·3	+27·7
400	0·553	4·7	+ 4·6
302	0·595	23·0	−21·6
$50\bar{2}$	0·606	5·2	+ 4·4
104	0·618	12·3	+10·3
$50\bar{4}$	0·633	4·1	− 3·8
500	0·691	2·2	+ 1·0
$30\bar{6}$	0·702	23·0	+23·8
$20\bar{6}$	0·712	3·1	− 3·3
204	0·716	3·8	+ 3·7
$40\bar{6}$	0·719	11·7	+12·6
402	0·724	< 0·9	− 0·5
$60\bar{4}$	0·733	20·6	−20·2
$60\bar{2}$	0·735	10·7	− 9·8
$10\bar{6}$	0·748	16·8	−15·8
$50\bar{6}$	0·761	14·4	−15·7
006	0·806	7·7	− 7·3
$60\bar{6}$	0·824	8·1	− 8·6
304	0·825	7·2	− 6·7
600	0·829	3·4	+ 2·8
$70\bar{4}$	0·844	4·4	− 4·5
502	0·856	1·4	+ 1·7
$70\bar{2}$	0·867	10·4	−10·0
106	0·883	1·0	− 0·5
$70\bar{6}$	0·904	6·8	+ 7·5
$40\bar{8}$	0·936	6·9	− 6·6
404	0·942	4·5	− 4·5
$30\bar{8}$	0·943	10·8	+ 9·8
$50\bar{8}$	0·950	11·1	−11·1
$80\bar{4}$	0·962	4·4	+ 4·1
700	0·968	0·8	− 0·4
$20\bar{8}$	0·970	5·6	+ 6·4
206	0·973	5·2	+ 4·9
$60\bar{8}$	0·982	3·6	+ 3·2

0*kl*	sin θ	F_o	F_c
010	0·117	1·6	+ 1·7
011	0·187	11·8	−10·8
020	0·235	30·0	−35·5
002	0·269	28·0	+31·6
021	0·271	6·6	+ 6·1
012	0·293	1·8	+ 1·7
030	0·352	4·8	− 5·7
022	0·357	12·6	−11·4
031	0·377	3·3	− 2·3
013	0·420	6·3	− 4·6
032	0·443	< 1·0	− 0·6
023	0·467	18·9	+20·0
040	0·470	14·5	−14·3
041	0·489	2·0	− 1·5
033	0·535	7·5	− 6·8
004	0·538	3·8	− 3·7
042	0·541	13·6	−12·4
014	0·550	6·9	+ 5·9
050	0·587	3·1	+ 4·7
024	0·587	6·3	+ 5·2
051	0·602	9·1	+ 8·5
043	0·619	11·1	−11·2
034	0·643	7·3	− 7·1
052	0·646	2·7	− 1·7
015	0·682	2·6	+ 3·2
060	0·705	15·9	+16·3
053	0·712	13·0	+12·8
025	0·712	17·6	+16·1
044	0·714	4·6	− 4·9
061	0·717	4·8	− 4·7
062	0·754	9·1	+ 9·6
035	0·759	3·3	− 3·8
054	0·796	2·1	− 2·9
006	0·806	7·7	− 6·9
063	0·812	6·2	− 5·7
016	0·815	9·8	+ 8·6
045	0·820	10·7	−10·9
070	0·822	6·8	+ 6·3
071	0·833	4·6	+ 5·4
026	0·840	4·7	+ 3·9
072	0·865	2·0	− 0·1
036	0·880	12·7	−13·2
064	0·886	< 1·3	+ 0·8
055	0·892	4·3	+ 4·1
073	0·916	5·5	− 6·7
046	0·933	2·3	+ 2·0
080	0·939	1·0	+ 1·7
017	0·948	2·4	+ 2·7
081	0·949	4·0	+ 4·3
027	0·970	3·0	+ 1·5
065	0·974	2·1	− 2·1
082	0·977	1·8	+ 2·8
074	0·982	5·5	+ 6·5

Table 3. *Atomic coordinates* (*and their standard deviations*) *from final difference syntheses*

The cell edges are approximately equal and the atoms spherically symmetric so that $\sigma_{hk0} = \sigma(x) = \sigma(y)$, etc. Atoms with bracketed coordinates overlap and their σ's may be underestimated

	(*hk*0)			(*h*0*l*)			(0*kl*)		
	x	*y*	σ	*x*	*z*	σ	*y*	*z*	σ
S	0·1870	0·3438	0·0013	(0·1890	−0·0735)	0·0005	0·3447	−0·0745	0·0012
Na	(0·2666	−0·1474)	0·0017	(0·2619	−0·0250)	0·0007	(−0·1498	−0·0232)	0·0016
O_1	(0·3140	0·2017)	0·0025	0·3155	−0·1447	0·0010	0·1913	−0·1463	0·0023
O_2	0·1170	0·2360	0·0025	0·1150	0·0860	0·0010	(0·2404	0·0835)	0·0023

theses (Cochran, 1951*a*, *b*). About five iterations were required for each. Calculated structure factors were based on James & Brindley atomic scattering factors (Landolt-Börnstein, 1950) multiplied by a spherically symmetric temperature factor taken as $\exp(-0.335 \sin^2\theta)$ in the latter stages. For the oxygen atoms a scattering curve midway between those for O and O^- was assumed. The final structure factors, calculated from the coordinates of Table 1, are listed in Table 2 together with the observed values. The disagreement factor R is quite low for this type of work, 0·098, 0·063 and 0·106 for the ($hk0$), ($h0l$) and ($0kl$) reflexions respectively, omitting a few strong low-order terms (200), (020) and (002), which probably suffer from extinction.

The resulting (F_o-F_c) values were used as coefficients for a final set of difference syntheses which led to the adjusted coordinates of Table 3 with standard deviations estimated from the root-mean-square gradient of the difference maps (Cochran, 1951*a*):

$$\sigma(X_i) = \frac{\sigma(\varrho_o-\varrho_c)}{\partial^2\varrho_o(X_i)/\partial X^2}\ .$$

Accuracy considerations

Significant differences between the two independent measurements of each of the 12 position parameters (Table 3) occur for x_{Na}, y_{O_1} and y_{O_2}. The sodium atom is poorly resolved in all projections. For the oxygens, one measurement is obtained for a well resolved atom, the other for the lighter of a pair of overlapping atoms. The usual simplified formulae for the standard deviation do not apply in the case of overlapping (Cruickshank & Robertson, 1953) and the values given may be underestimates here. The agreement is quite satisfactory for the other nine coordinates and their standard deviations appear to be quite realistic.

Interatomic distances and angles

Interatomic distances and angles have been calculated from the coordinates of Table 4, obtained by taking weighted averages of the results of Table 3. The standard deviations of these coordinates, based on the earlier results and uncorrected for the effect of overlapping, correspond to radial standard deviations in the atomic positions of about 0·008 Å for sulphur, 0·011 Å for sodium, and 0·015 Å for oxygen, with the y components rather less precise than x or z.

Table 4. *Coordinates used to calculate interatomic distances and angles*

	x	y	z
S	0·1887	0·3443	−0·0736
Na	0·2626	−0·1487	−0·0247
O_1	0·3153	0·1930	−0·1450
O_2	0·1153	0·2375	0·0856

Important distances and angles are listed in Table 5 and shown in Fig. 3. The standard molecule at (x, y, z) is unprimed, that at ($\bar{x}$, $\bar{y}$, $\bar{z}$) is primed, that at (x, $\bar{y}$, $\frac{1}{2}+z$) is double primed, and that at ($\bar{x}$, y, $\frac{1}{2}-z$) is triple primed.

Table 5. *Interatomic distances and angles*

Intramolecular		Intermolecular	
S–O_1	1·496 Å	S–S′	3·642 Å
S–O_2	1·515		
		Na–O_1	2·455
S—S‴	2·389	Na–O_2	2·917
		Na–O_1''	2·371
O_1–O_2	2·439	Na–O_1'	2·380
O_1–O_2'''	2·868	Na–O_2'	2·324
		Na–O_2''	2·330
O_1–S–O_2	108° 11′		
O_1–S–S‴	98 01	O_1–O_2''	3·244
O_2–S–S‴	99 23	O_1''–O_1'	3·276
		O_1–O_1'	3·347
		O_2–O_2'	3·394
		O_2'–O_2''	3·166
		O_1'–O_2''	3·704

Angle between S—S and plane of SO_2^-, 105° 18′.

Discussion

The principal interest of this work lies in the first determination of the structure of the dithionite anion, which consists of two SO_2^- units related by a twofold rotation axis, with a S–S separation of 2·389 Å. The two independent S–O distances in the half-anion, 1·498 and 1·515, are not significantly different and neither are the two independent S–S–O angles, 98° 01′ and 99° 23′. If we regard the two oxygen atoms as equivalent then the symmetry of the anion is increased from C_2 to C_{2v}. Although exact C_{2v} symmetry is quite compatible with the space-group requirements it is not demanded by them, and it may well be that small departures from ideal C_{2v} symmetry are real and occur in the crystal as a result of the asymmetry of the oxygen environment with respect to the sodium ions.

The S–S distance is appreciably longer than those previously reported for disulphides and polysulphide chains. Abrahams & Grison (1953) have summarized the available evidence for such compounds in which S–S distances range from 2·04 to 2·15 Å. They concluded that the most likely distance for the S–S single bond was about 2·11 Å, but in a later paper Abrahams (1954) suggested a slightly smaller value, 2·08 Å. In dimethanesulphonyl disulphide, $(CH_3SO_2)_2S_2$, distances of 2·06 and 2·10 Å are reported (Sörum, 1953) and Foss, Furberg & Zachariasen (1954) have found distances of 2·10, 2·02 and 2·13 Å in the tetrasulphide chain of barium tetrathionate dihydrate.

The value found here is 2·389 Å with an estimated standard deviation of about 0·01 Å (note that the uncertainty in the y coordinate does not contribute to the standard deviation of this interatomic distance) and the very large difference between this and the S–S distances previously reported is an indication that the central bond of the dithionite anion differs considerably from a typical disulphide link. If we assume the S–S single-bond distance to be 2·08 Å then application of Pauling's (1947) relationship between bond number and bond length, $-\Delta R(n) = 0{\cdot}353 \log n$, yields 0·36 for the bond number n. We must conclude that the central S–S bond is very weak compared with a normal disulphide bond. This result is consistent with some recent chemical evidence on the ready cleavage of the central bond of dithionite. According to van der Heijde (1953) almost instantaneous exchange of S^{35} occurs between dithionite and sulphur dioxide in neutral or acid solution. No exchange occurs, however, between SO_2 and trithionate, with presumably normal S–S bonds.

A tabulation (Jeffrey & Stadler, 1951) of the more reliable S–O distances in oxides, oxy-acids and oxy-acid salts of sulphur shows that this bond length tends to be remarkably constant and close to 1·43 Å, the distance found in sulphur dioxide (Dailey, Golden & Wilson, 1947; Post, Schwartz & Fankuchen, 1952). The distances found in this analysis, 1·496 and 1·515 Å with estimated standard deviations of less than 0·02 Å, appear to be slightly, although significantly, longer.

The O–S–O angle is close to tetrahedral, but the two S–S–O angles, both close to 99°, deviate markedly. The angle between the S–S bond and the normal to the plane of the SO_2^- group is only about 15° (for tetrahedral bonding it would be 36°), and the distance between the oxygen atoms O_1 and O_2''' at opposite ends of the molecule is only 2·87 Å. Since the negative charge of the anion must be concentrated to a large extent on the oxygen atoms, with consequent electrostatic repulsion between them, one might have expected a structure in which opposite pairs of charged oxygen atoms were as far from one another as possible. The eclipsed configuration with planes of opposite SO_2^- groups only 30° from parallel is quite the contrary.

The sodium coordination is also rather unusual. Four nearest neighbour oxygen atoms, all attached to different SO_2^- units, occur in a distorted square arrangement on one side of the sodium ion (Na $\cdots$ O, 2·33–2·38 Å). On the other side are two oxygen atoms of a single SO_2^- unit, at distances 2·46 and 2·92 Å. In the (010) projection (Fig. 3(*a*)) the sulphur and sodium atoms overlap but they are separated by almost exactly $\frac{1}{2}y$ or 3·3 Å.

It is clear from Fig. 3(*b*) and (*c*) that the structure consists of layers perpendicular to the *b* axis, held together by strong Na–O interactions. Double layers are formed by the weaker interactions, 2·46 and 2·92 Å, between any sodium and the SO_2^- unit almost vertically above or below it. Between one double layer and the next there are no interatomic distances less than 3·3 Å, which provides the explanation of the cleavage across the (010) plane.

There are thus several unusual features associated with this structure: (i) The S–S bond distance is more than 0·2 Å longer than distances found in typical disulphide or polysulphide molecules. (ii) The dithionite anion adopts an eclipsed configuration with the planes of opposite SO_2^- groups only 30° from parallel. (iii) The sodium coordination is of a type not previously encountered.

Consideration of the electronic structure of the half-anion SO_2^- allows us to derive a qualitative explanation of the first two features. First it should be noted that SO_2^- is isoelectronic with chlorine dioxide, a paramagnetic molecule (Taylor, 1926) which exists predominantly as the free radical, at least in the vapour phase, although it has been tentatively proposed that a small amount of dimer or higher polymer may exist (Nielsen & Woltz, 1952). The analogy with ClO_2 might therefore lead us to expect that the central bond of the dimer $^-O_2S\text{–}SO_2^-$ might not be very stable, but it would not, of course, afford any explanation of the eclipsed structure. A more detailed examination of the electronic structure is required, and we begin by considering the distribution of the 18 valency electrons of the neutral sulphur dioxide molecule in non-localized orbitals. This is, neglecting *d* orbitals:

	Electrons
(*a*) 2 unshared pair orbitals on each oxygen atom	= 8
(*b*) 1 unshared pair orbital on sulphur	= 2
(*c*) 2 σ bonding orbitals	= 4
(*d*) 1 π bonding orbital	= 2
(*e*) 1 π non-bonding orbital	= 2
	18

The extra electron required for the formation of SO_2^- must be accommodated in the next most stable orbital, the anti-bonding π orbital, $b_1''-\bar{\pi}_u$ in Walsh's (1953) notation, localized mainly on the sulphur atom. This orbital is unlikely, however, to be purely p_π in character. Moffitt (1950) and Pauling (1952) have emphasized the importance of *dp* hybridization in the more stable π orbitals of sulphur dioxide and it is likely to be of even greater importance here. The combination of p_π and d_π character leads to an orbital of the form shown in Fig. 4(*a*). Since this orbital is anti-bonding the π-bond order is reduced on going from SO_2 to SO_2^- with consequent increase in the S–O bond distance, as observed.

Two SO_2^- units, each with its odd electron in this hybrid $b_1''-\bar{\pi}_u$ orbital, are now imagined to dimerize to a dithionite anion. The bonding energy will depend on the degree to which these orbitals overlap, and this in turn will depend on the mutual orientation of the two SO_2^- units. We see from Fig. 4(*b*) that the coplanar anion is excluded because of repulsions between the two unshared pairs on each sulphur atom. In non-planar arrangements the repulsion between the unshared pairs is reduced but good overlap of the hybrid *dp* orbitals can still be obtained, both for centrosymmetric and eclipsed structures. To distinguish

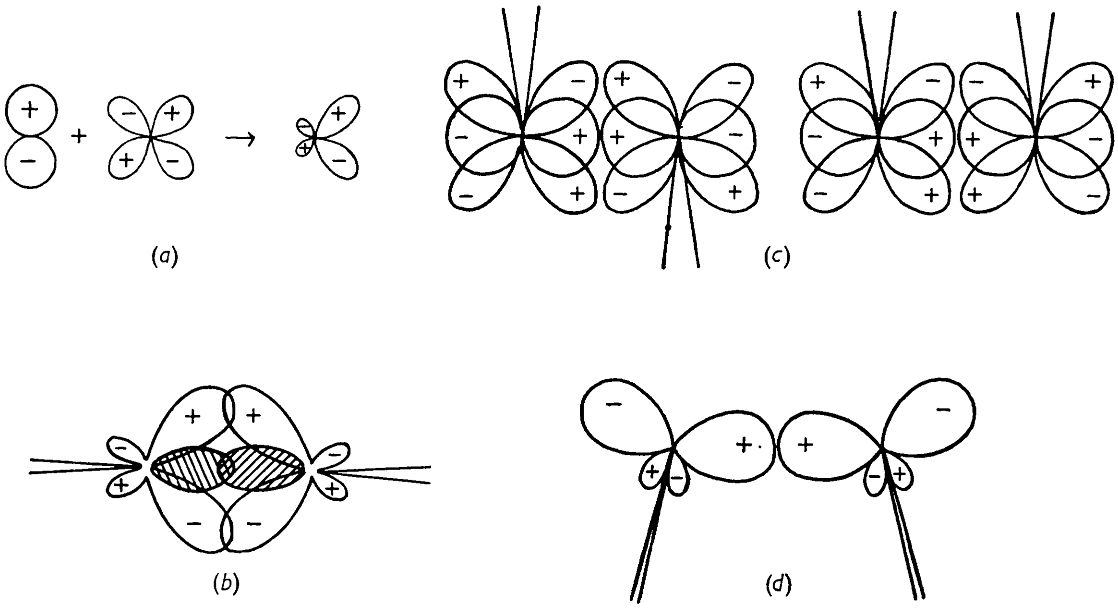


Fig. 4. (*a*) Demonstrating formation of a *dp* hybrid orbital. (*b*) Dimerization of two SO_2^- units to form a coplanar anion. The unshared pairs on the sulphur atoms repel one another since their orbitals (shaded) overlap strongly. (*c*) Dimerization of two SO_2^- units to form centrosymmetric or eclipsed anions. In the centrosymmetric form the p_σ–p_σ overlap is diminished by the *d* contribution; in the eclipsed form it is augmented. (*d*) Overlap of *dp* hybrid orbitals in eclipsed anion with opposite SO_2^- groups inclined at 30° to one another.

between these we must consider the contributions of the separate component overlaps. The major $p_\sigma-p_\sigma$ component has maximum overlap when the planes of the SO_2^- groups are perpendicular to the S–S bond. The effect of adding *d* character is shown in Fig. 4(*c*), where the signs of the lobes are determined by the condition that the *dp* hybrid orbitals be directed away from the S–O bonds. In the centrosymmetric structure the overlap is diminished by addition of *d* character, but in the eclipsed the overlap is augmented with resulting stabilization. The approximate form of the resultant overlap for the structure found in the crystal is shown in Fig. 4(*d*).

The S–S bond will differ from a typical disulphide bond in that the bonding orbital, instead of being almost pure p_σ, is one with a much lower electron affinity and a considerable amount of *d* character. According to Craig, Maccoll, Nyholm, Orgel & Sutton (1954), d_π–d_π bonding wherein both *d* orbitals are from the same quantum shell of the two atoms is quite weak, and hence the total binding energy of the S–S bond in dithionite should be smaller than in a pure $p_\sigma-p_\sigma$ disulphide bond. The effect of *d* character is thus quite different here from that in the S–O bonds of neutral SO_2 where the *d* character of the sulphur atomic orbitals increases the S–O bonding energy by altering the charge distribution and allowing extra π bonding (Moffitt, 1950; Pauling, 1952). Here the *d* character occurs in the primary bond and has the effect of weakening it.

It is not a necessary consequence of this theory that the negative charge of the SO_2^- unit or of the dimer be concentrated entirely on the sulphur atoms. In the neutral SO_2 molecule the polar nature of the S–O bonds leads to an accumulation of negative charge on the oxygen atoms and to a positive charge on the sulphur atom. The net charge distribution has been estimated as $S^{+0\cdot48}O_2^{-0\cdot24}$ by Moffitt (1950) and as $S^{+0\cdot46}O_2^{-0\cdot22}$ by Pauling (1952), in good agreement with the observed dipole moment, 1·61 D. The presence of an extra electron in the antibonding orbital concentrated largely on the sulphur atom will tend to decrease still further the electron affinity of the other sulphur orbitals and so increase the polarity of the S–O bonds. The sulphur atom may have a net negative charge but it is unlikely to be very large, and most of the charge is still expected to be associated with the oxygen atoms.

The reducing action of dithionite probably proceeds simply by loss of an electron to any suitable electron acceptor with formation of sulphur dioxide.

The author wishes to acknowledge his thanks to Dr L. E. Orgel for valuable discussion and to Dr Alexander Rich for assistance in some of the preliminary stages of this work.

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The Crystal and Molecular Structure of 4,5-Diamino-2-Chloropyrimidine

By (Miss) Noel E. White and C. J. B. Clews

Department of Physics, The University of Western Australia, Nedlands, Western Australia

(*Received* 20 *February* 1956)

The crystal and molecular structure of 4,5-diamino-2-chloropyrimidine has been determined by two-dimensional Fourier methods. The monoclinic unit cell has dimensions $a = 3{\cdot}73$, $b = 12{\cdot}637$, $c = 12{\cdot}437$ Å, $\beta = 98° 6'$, and the space group is $P2_1/c$. The crystal structure has been solved by the 'heavy atom' technique, the position of the chlorine atom being found from a 'modified' Patterson projection. A difference synthesis projected on the (100) plane clearly indicates the positions of the hydrogen atoms, showing that the molecule is in the amino form and that the molecules are held together by a system of hydrogen atoms between the nitrogen atoms of the amino groups and the ring nitrogens of neighbouring atoms.

1. Introduction

Certain of the pyrimidines—cytosine, thymine, uracil—, together with purines and sugars, constitute building units of the nucleic acids and nucleoproteins. Hence a detailed knowledge of their molecular structure and bonding in the crystalline state is of great interest and importance, and some years ago one of us initiated a programme of research into the crystal structures of pyrimidines and purines (Clews & Cochran, 1948, 1949; Broomhead, 1948, 1951; Cochran, 1951) in connexion with the chemical investigations of Todd and his co-workers on the nucleic acids which he has summarized in a recent lecture (Todd, 1955). The 4,5-diamino pyrimidines are intermediates in the synthesis of another important group of biological substances, the pteridines; thus 4,5-diamino-2-chloropyrimidine condenses with polyglyoxal to form 2-chloropteridine (Albert, Brown & Cheeseman, 1951). This pyrimidine also presented an opportunity of obtaining further data on the formation of hydrogen bonds of the type $N\text{–}H \cdots N$, which have been discussed in an earlier paper (Clews & Cochran, 1949).

2. Experimental

A sample of 4,5-diamino-2-chloropyrimidine, kindly provided by Prof. A. Albert of the Department of Medical Chemistry of the Australian National University, was crystallized from water in the form of fine needles. As attempts to grow larger crystals were unsuccessful, all photographs were taken using one crystal with an approximately uniform cross-sectional diameter of 0·1 mm. and extension in the direction of the *a* axis of 1 mm. Owing to the crystal dimensions