

337. *The Structure of the Dinitrosulphite and Sulphamate Ions.*

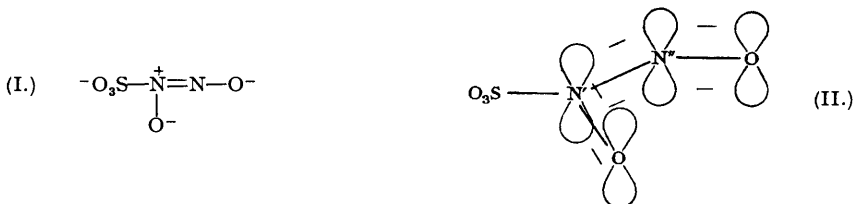
By G. A. JEFFREY and H. P. STADLER.

The earlier work on potassium "dinitrosulphite" $K_2SO_3 \cdot N_2O_2$ (Cox, Jeffrey, and Stadler, *J.*, 1949, 1783) has been extended by the X-ray analysis of the isomorphous ammonium compound $(NH_4)_2SO_3 \cdot N_2O_2$ with a technique leading to greater precision in the measurement of the bond lengths. These are S-O 1.44, S-N 1.79, N-N 1.33, N-O 1.28₅ Å. Comparison with values reported for other molecules indicates that S-N is a single bond, and that N-N and N-O are multiple bonds of order 1.5 or greater. The structure of the ion is in good general agreement with the molecular-orbital calculations by Evans and Gergely, although the N-O π -bonding may have been underestimated.

The structure of some related molecules is discussed.

The structure analysis of potassium sulphamate $KSO_3 \cdot NH_2$ by Brown and Cox (*J.*, 1940, 1) has also been extended by the inclusion of "termination-of-series" corrections. The bond lengths S-N 1.60 and S-O 1.44 Å., are not significantly different from the earlier values. The sulphamate ion is well represented by $H_2N^+SO_3^{-2}$. The significant difference between the S-N bond lengths in the two ions is ascribed to different degrees of π -bonding, and appears to be related to the ease of hydrolysis in acid solution. In the sulphamate group of both ions the S-O lengths all correspond to double bonds.

THE X-ray structure analysis of Pelouze's salt, $K_2SO_5N_2$ (Cox, Jeffrey, and Stadler, *Nature*, 1948, 162, 770; *J.*, 1949, 1783), showed that the anion had a configuration and structure which, in terms of a conventional bond diagram, is best represented by (I). Of particular interest was



the planarity of the N_2O_2 group and the character of the N-N and N-O bonds, the length of the former corresponding to a double bond and of the latter to bond orders of about 1.2. A description of the electronic structure of the ion was given by Evans and Gergely (*Nature*, 1948, 162, 771)

on the basis of the assumption of a molecular orbital system of π -bonding throughout the N_2O_2 group as pictorially represented in (II). Evans and Gergely's estimates of the bond orders agreed quite well with the observed bond lengths, but owing to the large experimental errors associated with the structure analysis, the agreement could only provide confirmation of the general qualitative description of the electronic structure. It seemed desirable therefore to measure the molecular dimensions as accurately as possible in order to test the theoretical treatment more critically, and if necessary to indicate the directions in which the theory might be improved to achieve a more exact description of the electron distribution in the ion.

The object of the original X-ray analysis was to establish the then unknown configuration of the potassium salt, and the refinements of experimental and computational techniques necessary to achieve a higher degree of accuracy in the atomic co-ordinates were not attempted. The errors associated with the original bond lengths were estimated at about ± 0.06 A. and for some bonds it appears that this was an underestimate.

The principal corrections necessary for high accuracy are (i) crystal adsorption corrections; these are important because of the high absorption coefficient of the potassium ions, but in application would involve very laborious calculations; and (ii) the "termination-of-series" corrections in the Fourier syntheses. Other recent investigations on sulphur-containing

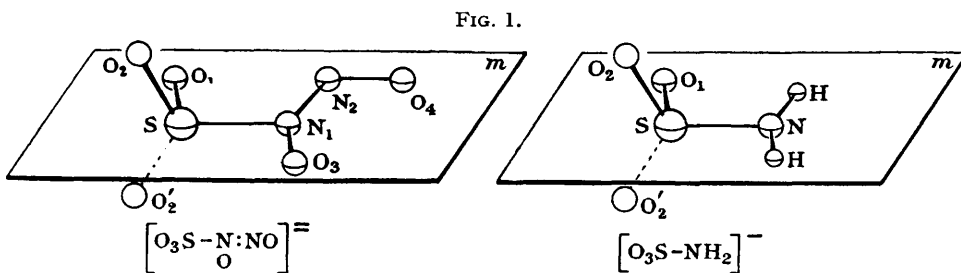
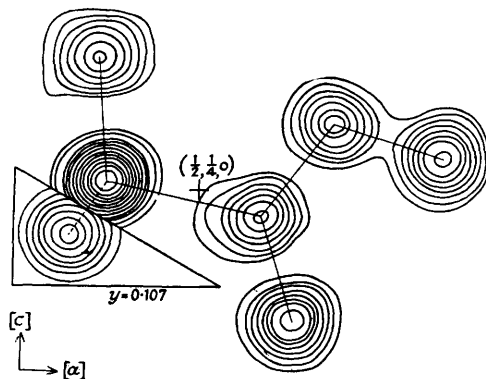


FIG. 2.



structures [*e.g.*, thiophthen (Cox, Gillot, and Jeffrey, *Acta Cryst.*, 1949, **2**, 356) and isoprene sulphone (Jeffrey, *ibid.*, 1951, **4**, 58)] showed that these corrections could lead to amendment of bond lengths by as much as 0.06 A. in certain cases.

To overcome the absorption errors, a new series of careful experimental measurements were made on the isomorphous ammonium salt, $(NH_4)_2SO_3 \cdot N_2O_2$, with the object of obtaining as accurate and complete a set of X-ray intensities as possible. The known structure of the potassium salt was then used as a starting point for the more refined analysis of the ammonium salt.

The "termination-of-series" effects were corrected for by the now standard technique first suggested by Booth (*Proc. Roy. Soc.*, 1946, *A*, **188**, 77) of examining the Fourier synthesis with the calculated structure factors as coefficients; this method had already been successfully applied in the thiophthen, isoprene sulphone, and several other structure analyses.

The marked difference of the S-N bond-lengths in potassium dinitrosulphite and potassium

sulphamate $\text{KSO}_3 \cdot \text{NH}_2$ (Brown and Cox, *J.*, 1940, 1; Ketelaar and Heilmann, *Z. Krist.*, 1941, 103, 41) which has already been remarked upon (Cox, Jeffrey, and Stadler, *loc. cit.*) was thought worthy of further study, and a refinement of the analysis of the sulphamate ion has therefore been made. No new experimental measurements have been made on this compound because the original data were recorded with Mo- K_α radiation for which the crystal absorption errors could be neglected. The termination-of-series errors, however, were likely to be as important as for the dinitrosulphite salt, and the necessary calculations to correct for these effects were carried out on Brown and Cox's original data.

The space-groups for the dinitrosulphite and sulphamate salts are *Pmna* and *Pbma*, respectively, and in both crystal structures the anions are oriented with their mirror planes of symmetry (see Fig. 1) at $y = \frac{1}{2}$. The atomic co-ordinates were therefore obtained from (i) sectional Fourier syntheses at $y = \frac{1}{2}$ with the observed and calculated structure factors as coefficients; and (ii) section and line syntheses through the oxygens symmetrically above and below the mirror planes, which were also computed for the observed and calculated structure factors. The greater part of these calculations were carried out on Hollerith computing equipment, by using methods described elsewhere (*e.g.*, Greenhalgh and Jeffrey, *Acta Cryst.*, 1950, 3, 311; Greenhalgh, *Proc. Leeds Phil. Lit. Soc.*, 1950, in the press).

The structure analysis of the ammonium dinitrosulphite was refined directly from the co-ordinates of the potassium salt, and required three successive Fourier syntheses and sets of structure factor calculations. The final agreement index $\Sigma(|F_{\text{obs.}}| - |F_{\text{calc.}}|) / \Sigma |F_{\text{obs.}}|$ was 0.19. The electron-density contour map is shown in Fig. 2. The results of the calculations are given in Table I which refers to the numbering of the atoms given in Fig. 1.

TABLE I.

Ammonium Dinitrosulphite.—Space-group, *Pmna*, $Z = 4$; cell dimensions: $a = 7.445 \pm 0.003$, $b = 8.154 \pm 0.004$, $c = 10.261 \pm 0.010$ A.; $V = 622.9$ A.³; $M = 176.16$.

Atomic co-ordinates (A.) from the cell origin.

Column A gives the co-ordinates from $F_{\text{obs.}}$ syntheses.

Column Δ gives the "termination-of-series" correction.

Column C gives the co-ordinates corrected for termination-of-series errors.

Atom.	X.			Y.			Z.		
	A.	Δ .	C.	A.	Δ .	C.	A.	Δ .	C.
S	2.653	+ 0.001	2.654	2.038	0.000	2.038	0.085	- 0.001	0.084
N ₁	4.433	- 0.022	4.411	2.038	0.000	2.038	- 0.310	+ 0.018	- 0.292
N ₂	5.249	- 0.010	5.239	2.038	0.000	2.038	0.749	- 0.004	0.745
O ₁	2.561	0.000	2.561	2.038	0.000	2.038	1.513	+ 0.032	1.545
O ₂	2.237	- 0.027	2.210	0.871	- 0.049	0.822	- 0.517	- 0.017	- 0.534
O ₃	4.760	+ 0.012	4.772	2.038	0.000	2.038	- 1.524	- 0.002	- 1.526
O ₄	6.473	- 0.003	6.470	2.038	0.000	2.038	0.365	+ 0.017	0.382
NH ₄	0.357	—	—	- 0.057	—	—	2.001	—	—

Atomic co-ordinates in fractions of cell dimensions.

	<i>x.</i>	<i>y.</i>	<i>z.</i>		<i>x.</i>	<i>y.</i>	<i>z.</i>		<i>x.</i>	<i>y.</i>	<i>z.</i>
S	0.3565	0.2500	0.0082	O ₁	0.3440	0.2500	0.1506	O ₃	0.6409	0.2500	0.8513
N ₁ ...	0.5925	"	0.9715	O ₂	0.2968	0.1008	0.9480	O ₄	0.8692	"	0.0373
N ₂ ...	0.7037	"	0.0726	O ₂ '	0.2968	0.3992	0.9480	NH ₄ ...	0.048	0.993	0.195

Bond lengths (A.) and valency angles.

S-N ₁	1.791	N ₁ -N ₂	1.327	O ₁ -S-O ₂	114.2°	S-N ₁ -N ₂	116.5°
S-O ₁	1.464	N ₁ -O ₃	1.286	O ₂ -S-O ₂ '	116.0	S-N ₁ -O ₃	118.4
S-O ₂	} 1.434	N ₂ -O ₄	1.284	O ₁ -S-N ₁	105.7	O ₃ -N ₁ -N ₂	125.1
S-O ₂ '					O ₂ -S-N ₁	102.2	N ₁ -N ₂ -O ₄

For the potassium sulphamate, all Brown and Cox's experimental data were included in the calculations with the exception of the terms for three reflections, (061), (171), (544), for which the agreement between the observed and calculated structure factors was exceptionally poor. The termination-of-series corrections were therefore somewhat larger than if these terms had been included in the calculated syntheses. The results for the sulphamate structure analysis are given in Table II.

TABLE II.

Potassium Sulphamate.—Space-group, *Pbma*, $Z = 4$; cell dimensions: $a = 8.333$, $b = 8.302$, $c = 5.907$ Å.; $V = 408.6$ Å.³; $M = 135.18$.

Atomic co-ordinates (A) from cell origin.

Column references as in Table I.

Atom.	X.			Y.			Z.		
	A.	Δ.	C.	A.	Δ.	C.	A.	Δ.	C.
S	1.136	+ 0.020	1.156	2.075	0.000	2.075	1.063	- 0.010	1.053
N	2.577	+ 0.044	2.621	2.075	0.000	2.075	1.671	+ 0.016	1.687
O ₁	1.319	- 0.019	1.300	2.075	0.000	2.075	- 0.374	+ 0.004	- 0.370
O ₂	0.520	- 0.019	0.501	0.816	+ 0.070	0.885	1.520	0.000	1.520
O ₂ '	0.520	- 0.019	0.501	3.336	- 0.070	3.266	1.520	0.000	1.520
K	2.083	—	—	0.00	—	—	3.916	—	—

Atomic co-ordinates in fractions of cell dimensions.

	$x.$	$y.$	$z.$		$x.$	$y.$	$z.$		$x.$	$y.$	$z.$
S	0.139	0.250	0.178	O ₁	0.156	0.250	0.938	O ₂ '	0.060	0.394	0.260
N	0.315	0.250	0.286	O ₂	0.060	0.106	0.260	K	0.250	0.000	0.663*

* Original value from Brown and Cox (*loc. cit.*).

Interatomic distances (A.) and valency angles.

S-N	1.60	S-O ₂	1.45	O ₁ -S-N	108°	O ₂ -S-O ₂ '	111°
S-O ₁	1.42			O ₂ -S-N	107	O ₁ -S-O ₂	112

The Accuracy of the Results.—The standard deviations of the atomic co-ordinates were calculated from the differences between the observed and calculated structure factors, and the curvature of the atomic electron-density peaks by the formulæ derived by Cox and Cruickshank (*Acta Cryst.*, 1948, 1, 92). For the ammonium dinitrososulphite, the standard deviations of the individual atomic co-ordinates in the x and z directions are given in Table III. The values for

TABLE III.

Standard deviations of atomic co-ordinates (A.) for (NH₄)₂SO₃·N₂O₂.

	$x.$	$z.$		$x.$	$z.$		$x.$	$z.$
S	0.0035	0.0030	O ₃	0.0112	0.0085	N ₁	0.0129	0.0099
O ₁	0.0141	0.0121	O ₄	0.0137	0.0101	N ₂	0.0132	0.0108
O ₂	0.0141	0.0111						

the oxygen and nitrogen atoms are not significantly different; the z co-ordinates appear to be slightly more reliable than the x co-ordinates. From the root-mean-square values, the standard deviations, σ , for the bonds are

$$\sigma \text{ for S-N and S-O, } 0.0124 \text{ Å.}; \sigma \text{ for N-N and N-O, } 0.0168 \text{ Å.}$$

For the potassium sulphamate structure the agreement between the observed and calculated structure factors was less good. The mean standard deviation for the sulphur atom was 0.0085 Å., and for the nitrogen and oxygen atoms 0.025 Å. For the bond lengths the standard deviation was 0.028 Å. This lower standard of accuracy, as compared with the dinitrososulphite analysis, probably reflects the greater difficulty of obtaining accurate eye-estimated intensity measurements from photographs taken with molybdenum radiation.

Using the significance test $P = 1 - \text{erf}(\Delta/\sqrt{2}\sigma)$, where P is the probability that a difference Δ is due to random errors, we used these standard deviations to compare the various experimental and theoretical bond lengths, with the following conclusions: (a) The difference of 0.19 Å. between the S-N bonds for the dinitrososulphite and the sulphamate ions corresponds to a P value of $< 1 \times 10^{-9}$ and is highly significant. (b) The difference of 0.03 between S-O₁ and S-O₂ of ammonium dinitrososulphite corresponds to $P = 0.09$ and is probably not significant, particularly in view of the large termination-of-series corrections to the O₂ position (without which the S-O₂ distance would be 1.38 Å.). (c) The comparison with the two sets of theoretical bond lengths (A.) obtained by Evans and Gergely (*loc. cit.*) is tabulated below:

	Calc.	Exptl.	$P.$		Calc.	Exptl.	$P.$
N-N	1.30	1.327	0.11, not significant	N-O	1.32	1.285	0.036, possibly significant
	1.29	—	0.027, possibly significant		1.33	—	0.007, significant

DISCUSSION.

The Dinitrososulphite Ion.—Although the refinement of the analysis has changed the bond lengths appreciably from the values previously reported, the general description of the structure is still that approximately represented by the bond diagram (I). The S-N length of 1.79 Å. must correspond very closely to that of a pure single σ -bond. There are no recorded measurements of other S-N single bonds, except in the structure of N_4S_4 , for which values of 1.74 Å. (Hassell and Viervoll, *Tidsskr. Kemi Berg.*, 1943, **3**, 7) and 1.62 Å. (Lu and Donohue, *J. Amer. Chem. Soc.*, 1944, **66**, 818) have been reported from electron-diffraction studies; this however appears to be a cyclic molecule of unusual configuration with a non-bonded S-S distance of 2.69 Å. The sum of Pauling's covalent radii ("Nature of the Chemical Bond," 1945) gives 1.74 Å. for a single N-S bond, and the same value is obtained from the radii revised by Stevenson and Schomaker (*J. Amer. Chem. Soc.*, 1941, **63**, 47) using an electronegativity correction. On the other hand, analogy with the well-established C-N = 1.48 Å., C-S = 1.81 Å. (cf. Cox and Jeffrey, *Proc. Roy. Soc.*, in the press), and N-N = 1.48 Å. suggests a value close to 1.81 Å. for N-S.

The N-N bond length of 1.33 Å. corresponds to a considerable amount of π -bonding, being much closer to the double-bond value of 1.26 Å. than to the single-bond value of 1.48 Å. A similar multiple N-N bonding has been found in dimethylnitramine (III), with N-N = 1.26 Å.



by Costain and Cox (*Nature*, 1947, **160**, 826) and 1.30 Å. by Bastiansen using electron diffraction (cf. *Acta Cryst.*, 1950, **3**, 53), and in ethylenedinitramine (IV), with N-N = 1.33 Å. by Llewellyn and Whitmore (*J.*, 1948, 1316).

The two N-O bonds in the dinitrososulphite ion are identical in length, within the limits of the experimental errors, at 1.28₅ Å. This is considerably shorter than reported in the preliminary work, but longer than the N-O bond lengths found for the nitro-group and the nitrate and nitrite ions, for which the more recent experimental measurements (in Å.) are given below :

(CH ₃) ₂ N·NO ₂	1.25	Costain and Cox (<i>loc. cit.</i>).
NO ₂ ·C ₆ H ₄ ·NO ₂	1.21	Llewellyn (<i>J.</i> , 1947, 884).
CH ₃ ·NO ₂	1.22	Rogowski (<i>Ber.</i> , 1942, 75 , 244).
NH ₄ ·NO ₃ ·2HNO ₃	1.20	Duke and Llewellyn (<i>Acta Cryst.</i> , 1950, 3 , 305).
	1.22	
	1.33	
NO ₃ in NO ₂ +NO ₃ ⁻	1.24	Grisson, Eriks, and Vries (<i>ibid.</i> , p. 190).

It corresponds to a π -bond order of 0.5, or greater if we take the N-O single-bond length to be near the value of 1.45 Å. in hydroxylammonium chloride and bromide (Jerslev, *Acta Cryst.*, 1948, **1**, 21).

The N₁ bond formation is based on the trigonal hybridisation [sp^2]¹, [sp^2]¹, [sp^2]¹, p^3 of the valency electrons with the idealised valency angles of 120°. The observed angles of S-N₁-N₂ = 117°, S-N₁-O₃ = 118°, and O₃-N₁-N₂ = 125° show a deviation from the trigonal symmetry which is accounted for by the strong repulsion to be expected between the negatively charged O₃ and O₄, at an equilibrium distance in the ion of 2.55 Å. Similarly, the N₁-N₂-O₄ angle of 112° is greater than the ideal 90° for a pyramidal nitrogen, and corresponds to a hybridisation intermediate between s^3 , p^1 , p^1 , p^1 and [sp^2]¹, [sp^2]¹, [sp^2]², p^1 . Despite this difference in the two nitrogen atoms, the structure analysis shows no difference between the two N-O bond lengths. This fully justifies the assumption to that effect made in the calculations of Evans and Gergely (*loc. cit.*), whose theoretical results agree well with the more accurate bond lengths for the dinitroso-group. The comparison given above suggests that possibly the calculated N-N bond order is too great, and, of more significance, the N-O π -bonding has been underestimated. This comparison of bond lengths, however, is dependent upon the N-N and N-O bond order-length relationship, for which the direct experimental data are at present somewhat inadequate. Until this limitation has been removed, the theoretical discussion by Evans and Gergely appears to give as good a description of the electronic distribution in the dinitroso-group as can be expected.

In qualitative terms, the six π -electrons of the $N_2O_2^-$ occupy three molecular orbitals; two of these are bonding in character and extend over all four atoms, while the third is largely non-bonding, with concentrations of electron density on the oxygen atoms.

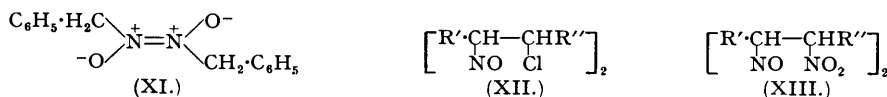
In terms of the valence-bond diagram, the structure of the ion can be described as a hybrid of (I) with (V) and (VI), (I) being the most important. The parent acid is unknown and probably unstable under all conditions. It could be formulated as (VII) or (VIII).



Although we have hitherto used the long-established name "dinitrosulphite," it is not at all appropriate. By analogy of (VIII) with the amine- and hydroxylamine-sulphonic acids, the salts should be called nitrosylhydroxylaminesulphonates. A structurally related compound is nitrosophenylhydroxylamine, (IX) or (X), which is a true monobasic acid forming an



ammonium salt. A similar type of N_2O_2 group has been found in the dimer of *p*-bromonitrosobenzene (Darwin and Crowfoot Hodgkin, *Nature*, 1950, 166, 827) and may be expected to occur in other bisnitroso-compounds, such as bis- α -nitrosobenzyl (XI) (cf. Hammick, Illingworth,



Edwards, and Ewbank, *J.*, 1931, 3105), and the "nitrosochloride" (XII) and "nitrosite" (XIII) compounds.

The Sulphamate Ion.—Although there are some differences between the new atomic co-ordinates and those derived by Brown and Cox (*loc. cit.*), the tendency has been for the ion to shift as a whole and the new molecular dimensions are not significantly different from those previously reported. There are no other experimental measurements of S-N distances, but comparison with the dinitrosulphite value and the covalent radii sum of 1.54 Å. indicates that the bond length in the sulphamate ion is close to that which may be associated with a double bond. As suggested in the earlier paper (Cox, Jeffrey, and Stadler, *loc. cit.*), the ion is better represented by (XIV) than by (XV). The nitrogen valency directions will therefore be trigonal and planar, and the hydrogen atoms will lie in the mirror plane of symmetry of the molecule (as in Fig. 1).



On the basis of N-O distances of 3.05 and 3.16 Å. between adjacent sulphamate ions, Ketelaar and Heilmann (*loc. cit.*) postulate hydrogen bonding in the crystal structure. The corresponding new intermolecular distances are N...O₁ 3.04 Å., N...O₂ and N...O₂' 3.49 Å.; the former is in the plane of the molecules concerned and the latter make an angle of 15° to the plane at the nitrogen end. Brown and Cox, who obtained similar interatomic distances, did not consider them short enough to imply hydrogen bridges of any appreciable strength. This view is supported by the N₂...O₁ distance of 3.03 Å. between adjacent ions in the dinitrosulphite structure, where there are no hydrogen atoms attached to the nitrogen. In the sulphamate structure, this distance of 3.04 Å., which is admittedly somewhat shorter than is generally associated with molecular packing in crystal structures, must correspond to the effect of the electrostatic attraction between the N⁺ and O⁻. The existence of the similar distance in the dinitrosulphite structure suggests that the N₂ might also carry a positive charge, although the quantum-mechanical calculations and the valence-bond concept suggest a small negative charge.

The S-N Bonds.—The S-N bonds of the dinitrosulphite and sulphamate ions differ by 0.19 Å., and comparison with the covalent radii tables shows that these bonds are close in character to the extremes of a single and a double bond, respectively. This implies that the bonding between sulphur and nitrogen always tends to have a multiple character, to a degree depending upon the nature of the adjoining atoms or groups in the molecule. In the dinitroso-

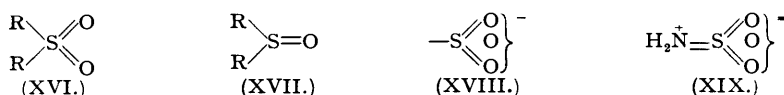
sulphite ion, however, the extensive π -bonding and electron attraction of the dinitroso-group restricts the S-N linkage almost entirely to the two σ -electrons. This may well account for the remarkable chemical properties of the dinitrososulphite ion and for the apparent incompatibility of an S-N bond with the ease of decomposition to sulphate and nitrous oxide in the presence of acids which led to the long controversy over the configuration of the salt. Potassium sulphamate does not hydrolyse readily at room temperature and requires heating in a sealed tube with hydrochloric acid at 140° to give NH_4^+ and SO_4^{2-} ; the free acid is also stable and can be crystallised from acid solutions of its salts, in very marked contrast to the behaviour of dinitrososulphites in the presence of acids.

In the series of amine-sulphonates, $\text{NH}_2\cdot\text{SO}_3^-$, $\text{NH}(\text{SO}_3)_2^-$, and $\text{N}(\text{SO}_3)^=$, the rate of hydrolysis increases with the number of sulphonate groups, and further structural investigations are in progress to discover whether this can be correlated with changes in bond character. A similar progression in stability to acid hydrolysis is found in the hydroxylaminesulphonates, of which $[\text{HO}\cdot\text{NH}\cdot\text{SO}_3]^-$ is the most stable, although less so than the sulphamate ion.

The Sulphonate Group, $-\text{SO}_3^-$.—In the dinitrososulphite and sulphamate ions the bond lengths in the SO_3 group are, respectively, 1.46, 1.43, 1.43 Å., and 1.42, 1.45, 1.45 Å. An estimate of the probable errors in the analyses shows that no measurement is significantly different from the mean of 1.44 Å. This value is consistent with other measurements of S-O bonds (in Å.) given below:

Length.	Substance.	Method.	Author.
1.43	SO_3	Elect. diffn.	Palmer (<i>J. Amer. Chem. Soc.</i> , 1938, 60 , 2360).
1.45	SOCl_2	"	<i>Idem (ibid.)</i> .
1.433	SO_2	Spect.	Dailey, Golden, and Wilson (<i>Physical Rev.</i> , 1947, 72 , 871).
1.47	$(\text{CH}_3)_2\text{SO}$	Elect. diffn.	Bastiansen and Viervoll (<i>Acta Chem. Scand.</i> , 1948, 2 , 702).
1.43	$(\text{CH}_3)_2\text{SO}_2$	"	Rundle (see <i>Acta Cryst.</i> , 1950, 3 , 53).
1.44	$\text{C}_5\text{H}_8\cdot\text{SO}_2$ (β -isoprene sulphone)	X-Ray	Jeffrey (<i>ibid.</i> , 1951, 4 , 58).
1.52	$\text{Na}_2\text{SO}_4\text{-III}$	X-Ray	Frevel (<i>J. Chem. Physics</i> , 1940, 8 , 290).

The S-O distance is remarkably constant in a variety of molecules and ions; the only exception to this is the result from the modification III of anhydrous sodium sulphate, which was reported very briefly and without sufficient detail for the accuracy to be assessed. The earlier X-ray analyses on crystal structures containing SO_4^{2-} , SO_3^- , $\text{S}_2\text{O}_5^{2-}$, $\text{S}_3\text{O}_8^{2-}$, and $\text{S}_2\text{O}_8^{2-}$ report values varying from 1.39 to 1.50 Å., which are conveniently tabulated by Phillips, Hunter, and Sutton (*J.*, 1945, 149), who point out that the more reliable S-O distances are very short, about 0.05 Å. shorter than the Pauling covalent radii sum, and would appear to correspond to sulphur-oxygen double bonds. From a theoretical molecular-orbital treatment of S-O bonds in sulphones and sulfoxides, Moffitt (*Proc. Roy. Soc.*, 1950, *A*, **200**, 409) concludes that



the 3d orbitals of the sulphur are utilised in bond hybridisation and that these molecules are best represented by (XVI) and (XVII). The calculated π -bond orders for the sulphur-oxygen bonds are about 0.9 and the atoms have formal charges in the direction $\overset{+}{\text{S}}-\overset{-}{\text{O}}$. Our results for the bond lengths in the sulphonate group suggest the analogous representation (XVIII) with bonds of similar character. The electronic distribution for the sulphamate ion is then described by (XIX), with S-O π -bond orders of about 0.9 as in the sulphones; in view of the difference of 0.16 Å. between $\text{S}=\overset{-}{\text{O}}$ and $\text{S}=\overset{+}{\text{N}}$, the S-N π -bond order is probably rather less than 0.9. There will be an accumulation of negative charge towards the oxygens and away from the nitrogen in the ion, as supported by the following cation-anion interatomic distances in the crystal structure:

Cation-anion interatomic distances (in Å.)

$\text{NH}_2\cdot\text{SO}_3\text{K}$.		$(\text{NH}_4)_2\text{SO}_3\cdot\text{N}_2\text{O}_2$.	
K O_1	2.75	NH_4 O_1	3.08, 3.04
K O_2	2.84, 3.00	NH_4 O_2	2.94, 3.05
K O_3	1.84, 3.00	NH_4 O_3	2.91, 3.08
K N	3.08	NH_4 O_4	2.96, 3.16
		NH_4 N_1	3.62, 3.74, 4.03
		NH_4 N_2	3.38, 3.54, 3.86

EXPERIMENTAL.

Ammonium Dinitrosulphite.—The salt was prepared by a method analogous to that of Weitz and Achterberg (*Ber.*, 1933, **66**, 1718) for the potassium salt. To avoid decomposition, the crystal had to be cooled during the exposure to X-rays. It was enclosed in a Cellophane tube through which passed a stream of cold dry air supplied by evaporation of liquid air in a Dewar syphon.

The unit cell dimensions were measured from photographs taken by Straumanis's method and calculated for Cu-K_α 1.5411 Å.

To minimise absorption errors in the intensity measurements, small, evenly developed crystals of 0.2 mm. diameter were used. Weissenberg equi-inclination photographs were taken for the layer lines 0 to 3 about [010], and 0 to 4 about [100] and [001]. In order to estimate by eye the full range of intensities, the multiple-film technique with four films interleaved with 0.001'' aluminium foil was used. The comparatively large uncertainties in the high-intensity reflections were reduced by correlating them amongst themselves on photographs taken by the "double-slit Weissenberg method" (Stadler, *Acta Cryst.*, 1950, **3**, 262). After application of the usual geometrical correction factors, the correlation factors between the layer lines of the [010] and [100] which gave the best self-consistency were applied to bring all the estimated intensities on to the same relative scale. The intensities on the layer lines of the [001] were then corrected to that scale. Of the 764 possible reflexions which could be recorded with Cu-K_α radiation, 588 intensities were measured. No corrections were applied for extinction.

The authors express their gratitude to Professor E. G. Cox, for his interest and criticism, and to the University of Leeds for a senior Ellison Fellowship awarded to one of them (H. P. S.). They are also pleased to acknowledge the computational assistance given by Miss Barbara Long and Mr. D. Greenhalgh, and Mr. Grudemo during his visit from the Cement och Betong Institut, Stockholm. Much of the experimental and computational work was done with equipment provided by the Royal Society, D.S.I.R., and Imperial Chemical Industries Limited.

THE UNIVERSITY OF LEEDS.

[Present address]: KING'S COLLEGE, NEWCASTLE-ON-TYNE.

[Received, November 27th, 1950.]
