LETTERS TO THE EDITORS

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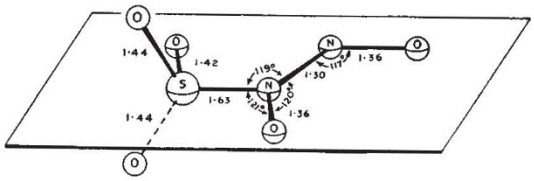
Structure of the Dinitrososulphite Ion

SINCE the observation by Davy[1] that nitric oxide is absorbed by alkaline potassium sulphite to form a crystalline compound (shown later by Pelouze[2] to have the composition $K_2SO_5N_2$), several conflicting formulæ have been suggested to account for its chemistry[3–6].

We have found that the corresponding thallium and ammonium salts are isomorphous with the potassium salt, and this has enabled us, by direct X-ray crystal analysis, to determine the structure of the dinitrososulphite ion independently of any preconceived formulation. The results of Fourier syntheses show the configuration of the ion to be as in the accompanying figure.



An interesting feature of the structure is that the S atom and the N_2O_2 group lie in one plane and that the bond-angles approximate closely to 120°. This, together with the short N—N distance of 1·30 A., implies, as suggested by Evans and Gergely (see following communication), a double-bond between the nitrogen atoms with trigonal [sp^2] hybridization. It invites comparison with the structure of dimethyl nitramine[7]. Both the N—O distances of 1·36 A. correspond to a bond-order of about 1·2 if compared with the most recently suggested covalent radii[8,9].

As was to be expected (cf. the structure of the sulphamate ion[10]), the SO_3 and the adjoining nitrogen atom form an approximately tetrahedral group, with S—O = 1·44 A. and S—N = 1·63 A.

Although three-dimensional methods were used in the structure analysis, we cannot at this stage exclude the possibility of the bond-lengths being subject to errors up to ± 0·06 A., owing to the large absorption errors unavoidable in intensity measurements with the potassium salt. The isomorphous ammonium salt will be used to obtain more exact values for the atomic parameters.

We wish to thank Mr. F. J. Garrick and Mr. A. White for the preparation and chemical analysis of the thallium salt.

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[6] Weitz, E., and Achterberg, F., *Ber.*, **66**, 1718 (1933).
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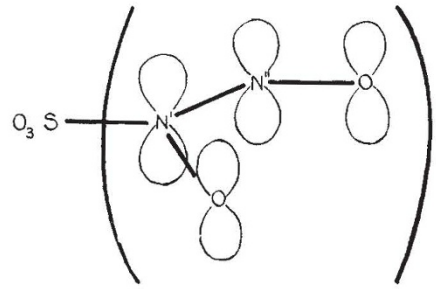
[10] Brown, C. J., and Cox, E. G., *J. Chem. Soc.*, 1 (1940).

THE trigonal planar symmetry of the three bonds formed by the nitrogen atom attached to the sulphur atom in the structure described in the preceding communication suggests that the orbitals of this nitrogen atom correspond in bond formation to a hybridization of the type $(1s)^2(2p)^2(2s2p^2)^3$ rather than to $(1s)^2(2s)^2 2p_x 2p_y 2p_z$. In the former electronic configuration, the three sp^2 orbitals will possess trigonal symmetry, and there will be one doubly occupied π-orbital orthogonal to the plane of the sp^2-orbitals. This type of hybridization has been postulated by us[1] in a discussion of the properties of the >N—H O=C< structure in proteins.



We have based molecular orbital calculations on the structure shown in the accompanying illustration, in which the π-orbitals are occupied by six electrons, the whole group within the brackets having a full negative charge. Since the SO_3 group has a tetrahedral structure, it appears reasonable to neglect conjugation of this group with the π-electrons of the nitrogen and oxygen atoms; we have therefore dealt with the four atomic centres in the structure within the brackets.

The secular equation for this array of centres is:

$$\begin{vmatrix} q_O - E & \beta_{ON'} & O & O \\ \beta_{ON'} & q_{N'} - E & \beta_{N'N''} & O \\ O & \beta_{N'N''} & q_{N''} - E & \beta_{N''O} \\ O & O & \beta_{N''O} & q_O - E \end{vmatrix} = 0$$

where the β's stand for exchange integrals and the q's for Coulombic integrals.

The ionization potential[2] and thus the Coulombic integral of the trigonal nitrogen N′ is lower than that of the pyramidal nitrogen N″. Since all the β's are very nearly the same, a difference between $q_{N'}$ and $q_{N''}$ of the order of the difference in the ionization potentials would lead to a structure with unequal NO bond-distances. The inductive effect of the sulphur atom of the SO_3 group on the N′ to which it is attached, must, however, be taken into account, and because of the symmetry of the structure we have assumed that this effect offsets the difference in the q's.

We find the following values for the charge densities and the bond-orders:

Atom	O	N′	N″	O
Charge	− 0·724	+ 0·724	− 0·276	− 0·724
Bond-order	1·45	1·72	1·45	

when $q_{N'} = q_{N''} = q_O$

Atom	O	N′	N″	O
Charge	− 0·84	+ 0·84	− 0·16	− 0·84
Bond-order	1·40	1·76	1·40	

when $q_{N'} = q_{N''}$, and $q_O - q_N = 0·5$.

It is interesting to compare these results with the experimental values reported above. For this purpose we have used the covalent radii given by Gordy[3] to

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