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DIRECT DETERMINATION OF THE CONFIGURATION OF A BENZENEDIAZOTATE: THE CRYSTAL STRUCTURE OF *SYN*-SODIUM BENZENEDIAZOTATE-4-SULPHONATE

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Summary The crystal structure of *syn*-sodium benzenediazotate-4-sulphonate shows this to be the *cis*- and not the *trans*-isomer

Arenediazonium cations react in aqueous solution at pH > 8 according to the following scheme:

$$\mathrm{ArN_2^+} + 2\mathrm{OH^-} \rightleftharpoons \underset{\text{diazohydroxide}}{\mathrm{ArN_2OH}} + \mathrm{OH^-} \rightleftharpoons \underset{\text{diazotate}}{\textit{syn}\text{-}\mathrm{ArN_2O^-}} + \mathrm{H_2O}$$

$$\textit{syn}\text{-}\mathrm{ArN_2O^-} \rightleftharpoons \textit{anti}\text{-}\mathrm{ArN_2O^-}$$

The structures of the resulting diazotates have been controversial since Schraube and Schmidt[1] identified the two isomers. It has long been accepted that they are geometrical isomers[2] and by analogy with similar compounds, it has been assumed that the *syn*-form is cisoid and the *anti*-form transoid. However, Sterba *et al.*,[3] from studies of the reactions of six diazotates bearing 2-substituents, suggested in 1973 that the *syn*-form should be regarded as *trans* and the anti-form as *cis*.

The sole crystal structure that has been determined for a diazotate is that for potassium *syn*-methyldiazotate[4] which has a *cis* configuration. As this does not provide direct evidence concerning the suggestion of Sterba *et al.*,[3] we have examined aromatic diazotates for which no crystal structures have been reported. Of several salts with different substituents and cations, only the title compound gave crystals at all suitable for X-ray study.

Syn-sodium benzenediazotate-4-sulphonate was prepared as described,[5] except that a more dilute solution was used which yielded ultimately extremely small colourless needles. These could not be recrystallised, but the u.v. spectra of their solutions agreed with the literature.[5] Microanalysis indicated a formulation: $C_6H_4N_2SO_4 2Na.3H_2O$.

Data were collected on a Syntex-$P2_1$ four-circle diffractometer. The crystal was maintained at 150 K to minimise decomposition during X-ray analysis (which was extensive at ambient temperature). A total of 838 reflections were observed.

The structure is shown in Fig. 1. The *syn*-diazotate is confirmed to have a *cis* configuration. The C(4)-N(1)-N(2)-O(4) group is planar, making an angle of 69.06 with the ring plane. The C(4)-N(1) bond is out of the plane of the ring by 5.6° ($\pm 0.2^{\circ}$), probably due to lattice forces. The aromatic ring is slightly distorted, but less so than in simple arenediazonium salts[6] or those bearing 4-amino substituents.[7]

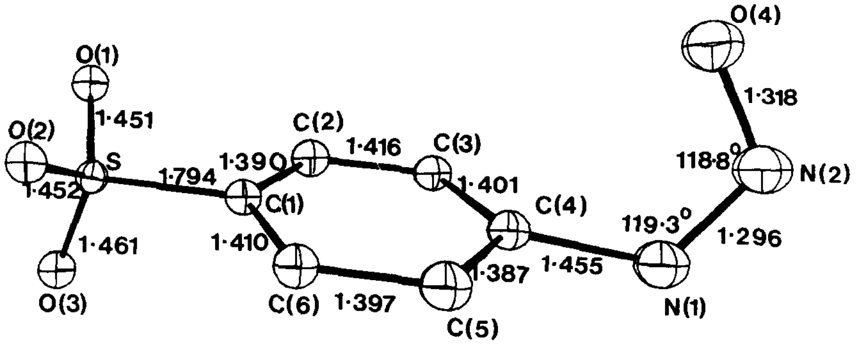
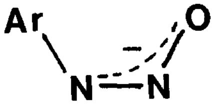


FIG. 1 Crystal structure of *syn*-benzenediazotate-4-sulphonate ion. Standard deviations in bond lengths vary in the range 0.012 Å (N-N) to 0.015 Å (C-C).

Comparison with potassium *syn*-methyldiazotate shows significant differences:-

(i) N(1)-N(2) and N(2)-O(4) in the title compound are fairly similar, *i.e.* 1.296 and 1.318 Å, whereas in the aliphatic diazotate, they are substantially different, *i.e.* 1.246 and 1.306 Å respectively. This indicates a delocalised structure for the title compound, viz:



(ii) The angle C_4-N_1-N_2 (119.3°) of the aromatic compound is closer to pure sp^2 than in the aliphatic diazotate (116.2°).

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