

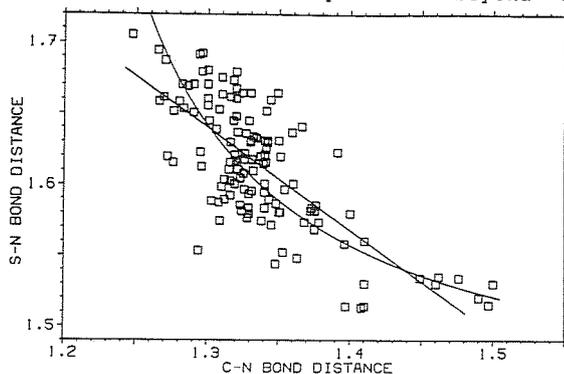
if half of the potassium positions are replaced by sodium, the rest will be looked at as voids  $\square$ . From this viewpoint  $\text{Na}\square\text{NbCl}_6$  and the isotopic  $\text{Na}\square\text{TaCl}_6$  represent low-symmetry variants of the  $\text{K}_2\text{PtCl}_6$  structure. Among other features it is important to note that the sodium ions and voids occupy alternate layers aligned parallel to (001).

Despite similar unit-cell dimensions the structure of  $\text{Na}\square\text{SbCl}_6$  differs in two respects. Sodium atoms and voids  $\square$  are found on separate rods which extend both in *c*-direction (Wyckoff positions 2e and 2f); the formation of separate layers  $\parallel(001)$  is not observed. Another obstacle is the different orientation of the  $\text{SbCl}_6^-$  ions. A related arrangement is however shown by rutile where chains of interconnected  $\text{TiO}_6$  units form a three-dimensional network. In the hexachloroantimonate two thirds of these 'octahedra' remain vacant to comply with stoichiometry, schematically  $\square\square\text{SbCl}_6$ . As in the case of rutile one obtains a threefold superstructure (space group  $P4_2/mnm$ ,  $c' = 3c$ ) with  $P4_2/m$  being an immediate subgroup.

04.1-9 ON THE GEOMETRY AND THE BONDING RELATIONSHIPS AT THE TWOFOLD COORDINATED NITROGEN IN C-N-S AND S-N-S FRAGMENTS.  
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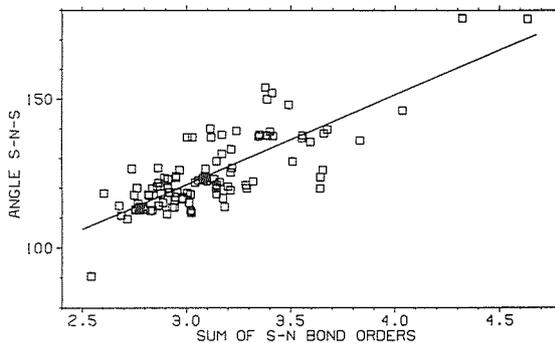
For molecular fragments C-N-S or S-N-S containing a twofold coordinated nitrogen, correlations can be found between the two bond distances and the enclosed bond angle derived from X-ray data. For both systems all coordination numbers of nitrogen bound atoms were permitted in these considerations.

The relationship between the two bond distances (SN vs. CN) in the C-N-S fragment is shown in Fig. 1. Due to the small variations of the bond angles, the latter may be in a first approximation neglected. The regression line is well defined by the 128 data points ( $k = -0.75$ ) but is unsuitable for an extrapolation beyond the



given range of distances. For extrapolation a better description is provided by a hyperbolic function  $d(\text{SN}) - d_1 = a / (d(\text{CN}) - d_2)$  ( $k = 0.80$ ) which for very large values of the SN or CN distances leads to the known CN or SN triple bond lengths, respectively. Assuming that the sum in bond order of the two bonds to the nitrogen equals 3, the following relationships between bond order and bond distances can be deduced:  $d(\text{SN}) - 1.3 = 0.45 / \text{BO}(\text{SN})$ ;  $d(\text{CN}) - 1.0 = 0.48 / \text{BO}(\text{CN})$ .

With respect to the S-N-S system, the correlation between the sum of bond orders (derived from the respective bond distances by the formula given above) and the enclosed bond angles is shown in Fig. 2. The least squares line shown has the form  $\angle \text{SNS} / 30 = \text{BO}(\text{SN}) + \text{BO}(\text{SN}) + 1$  ( $k = 0.80$ ). A comparable correlation between bond distances and angles has been previously proposed by Banister and Durrant (J. Chem. Res. (S) 1978, 150), who considered compounds with selected coordination numbers at the sulphur atoms.

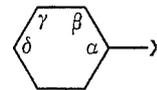


04.1-10 ANGULAR RING DISTORTIONS IN BENZENE DERIVATIVES: THE EFFECT OF THE  $\text{NO}_2$  AND  $\text{COOH}$  SUBSTITUENTS

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Angular distortions in polysubstituted benzene rings may be described, at least as a first approximation, by superimposing separate contributions from each substituent. The effect of a substituent may then be expressed by a set of four 'angular substituent parameters',  $\Delta\alpha = \alpha - 120^\circ$ ,  $\Delta\beta = \beta - 120^\circ$ ,  $\Delta\gamma = \gamma - 120^\circ$ ,  $\Delta\delta = \delta - 120^\circ$ .



Angular parameters for several substituents, including  $\text{NO}_2$  and  $\text{COOH}$ , have been derived by regression from large samples of polysubstituted benzene rings [Domenicano & Murray-Rust, Tetrahedron Lett. 2283 (1979); Norrestam & Schepper, Acta Chem. Scand. A35, 91 (1981)]. We have recently shown, however, that deviations from additivity occur when a  $\pi$ -donor is para to a  $\pi$ -acceptor, due to cooperative interactions between substituents [Colapietro et al., Z. Naturforsch. 37b, 1309 (1982)]. There are also indications that deviations from additivity occur with some ortho-disubstituted derivatives. Accurate angular parameters must be derived, therefore, either by direct measurement on monosubstituted derivatives, or by regression from polysubstituted derivatives with appropriate patterns of substitution.

The following benzene derivatives, containing only  $\text{NO}_2$