Scale factors, form factors and bond lengths in orthorhombic sulfur. By S. C. ABRAHAMS, *Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey, U.S.A.*

Dawson (1960a) has recently found the scale factor for the empirical form factor of sulfur (Abrahams, 1955), in the range $0\cdot3 \leq \sin\theta/\lambda \leq 0\cdot6$ Å^{-1}, to be about 25% too high in comparison with a new (Dawson, 1960b) form factor. Doubt was cast, in the 1960a paper, on the reliability of the 1955 atomic coordinates and hence on the final S–S bond distance.

The 1046 measured orthorhombic sulfur structure factors (Table 9 in the 1955 paper) have now been used in two sets of complete least-squares refinements, using the Dawson (1960b) form factor. In these refinement sets, the three position and six thermal-vibration parameters for each atom, as well as the single scale factor, were the variables. The Busing–Levy (1959) program written for the IBM 704 computer was used. Two of the four sets of weights examined in 1955 were assigned, corresponding to (*a*) and (*c*) in paragraph 7 of that paper. In the first set, hereafter referred to as 1960A, all standard deviations in F_{meas}. were taken as unity, except for the unobserved structure factors (one-half of its maximum value given in the 1955 Table 9 was used in each such case) for which the standard deviations were arbitrarily taken as 10. In the second set, hereafter 1960C, for $|F_{\mathrm{meas}}.| \geq 100$, $\sigma F_{\mathrm{meas}}. = 0\cdot1|F_{\mathrm{meas}}.|$; for $|F_{\mathrm{meas}}.| < 100$, $\sigma F_{\mathrm{meas}}. = 10$, and for unobserved terms, $\sigma F_{\mathrm{meas}}. = 20$ (as in case 1960A, one-half maximum value was used for each unobserved term).

The results of three refinement cycles in each of the 1960A and C sets (in which complete convergence was obtained) are presented in Table 1 with the corresponding 1955 values.

Two important conclusions can be drawn from Table 1. First, it is evident that the scale factor has a high degree of dependence upon the weighting scheme; second, the bond lengths have a low dependence upon the scale factor. The correlation between bond lengths and weights is subtle and is difficult to compute, although it is demonstrable both from Table 1 of this paper and from Table 5 of the 1955 paper.

The complete least-squares analysis also allows the computation of the r.m.s. components of thermal displacement along the principal axes of the vibrational ellipsoid. These values are given in Table 2 for the two sets of weights used.

Table 2. *R.m.s. thermal displacements along the principal axes* (Å)

	1960A			1960C		
	1	2	3	1	2	3
S_1	0·247	0·194	0·153	0·176	0·222	0·257
S_2	0·161	0·215	0·243	0·189	0·228	0·250
S_3	0·242	0·195	0·174	0·253	0·214	0·190
S_4	0·244	0·189	0·151	0·264	0·207	0·170

The standard deviation in the 1960A set is 0·005–0·006 Å, and in the 1960C set it is 0·004 Å. The maximum difference between these two sets occurs for the amplitude of displacement of atom S_1 along its third principal axis. Comparison with its standard deviation indicates this difference to be very highly significant. A similar, and compensating, difference is obtained between the 1960A and 1960C scale factors (Table 1). The apparent correlation between scale factor, weights, and thermal displacements (e.g., correlation coefficient* for scale and $\beta_{33}(S_1)$ is 0·39), together with other possible correlations not revealed because of the limited number of variables in this analysis, indicates some indeterminacy in these quantities.

The principal reason for this communication is to re-establish the value for the mean S–S distance in orthorhombic sulfur. This distance is $2\cdot041 \pm 0\cdot003$ Å from the 1960C set, considered here to be based on the best set of weights. There is no significant difference between this value and the 1955 value of $2\cdot037 \pm 0\cdot005$ Å, based on a combined least-squares and Fourier series determination, nor with the 1960A value of $2\cdot043 \pm 0\cdot003$ Å.

References

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* A discussion of the relations between parameter interactions and the correlation matrix has recently been given by Geller (1960).

Table 1. 1955 *and* 1960 S_8 *scale factors and bond lengths*

	1960A	1955a	1960C	1955c
Scale factor	$0\cdot850 \pm 0\cdot008$	1·000	$0\cdot762 \pm 0\cdot015$	1·000
S_1–S_3	$2\cdot047 \pm 0\cdot006$ Å	$2\cdot044 \pm 0\cdot007$ Å	$2\cdot038 \pm 0\cdot005$ Å	$2\cdot038 \pm 0\cdot007$ Å
S_2–S_3	$2\cdot047 \pm 0\cdot006$	$2\cdot047 \pm 0\cdot007$	$2\cdot041 \pm 0\cdot004$	$2\cdot044 \pm 0\cdot007$
S_2–S_4	$2\cdot037 \pm 0\cdot006$	$2\cdot029 \pm 0\cdot007$	$2\cdot041 \pm 0\cdot005$	$2\cdot036 \pm 0\cdot007$
S_1–S_1'	$2\cdot027 \pm 0\cdot008$	$2\cdot027 \pm 0\cdot010$	$2\cdot041 \pm 0\cdot007$	$2\cdot037 \pm 0\cdot010$
S_4–S_4'	$2\cdot058 \pm 0\cdot008$	$2\cdot056 \pm 0\cdot010$	$2\cdot046 \pm 0\cdot007$	$2\cdot036 \pm 0\cdot010$
Mean S–S	$2\cdot043 \pm 0\cdot003$	$2\cdot040 \pm 0\cdot004$	$2\cdot041 \pm 0\cdot003$	$2\cdot038 \pm 0\cdot004$