Acta Cryst. (1961). **14**, 1008

The lattice and molecular constants in orthorhombic sulfur.

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(*Received* 17 *April* 1961)

The lattice constants of orthorhombic sulfur have recently been reported by Swanson, Cook, Isaacs & Evans (1960). They treated the higher order lines in the powder pattern measured with a Geiger counter diffractometer by the method of least-squares to get the results in Table 1, first entry. A fuller re-examination of this data by Caron & Donohue (1961), who also used a least-squares treatment, led to the second entry in Table 1 with the given standard errors in the new lattice constants. The lattice constants measured by one of the present authors from precession photographs, given as the third entry in Table 1, appear systematically too small by 0·2–0·5%.

Table 1. *Lattice constants of orthorhombic sulfur*

a (Å)	*b* (Å)	*c* (Å)	Reference
10·468	12·870	24·49	Swanson *et al.* (1960)
10·467 ± 1*	12·870 ± 1	24·493 ± 3	Caron & Donohue (1961)
10·437 ± 10	12·845 ± 10	24·369 ± 10	Abrahams (1955)
10·4646 ± 1	12·8660 ± 1	24·4860 ± 3	Present work

* Standard errors are given in terms of the last significant digits of the value of the lattice constant.

There has been sufficient interest in the bond lengths and other molecular constants in orthorhombic sulfur (e.g., Dawson (1960), Abrahams (1961), Caron & Donohue (1961)) to render desirable the remeasurement of the lattice constants of this crystal. Accordingly, single crystals were grown* from solution of high purity sulfur† in toluene. The new measurements were made by Bond's (1960) precision single crystal technique using Cu $K\alpha_1$ ($\lambda = 1{\cdot}53739$ kX.) and Co $K\alpha_1$ ($\lambda = 1{\cdot}78529$ kX.) radiation. The corresponding lattice constants at 24·8 ± 0·1 °C. are listed as the final entry in Table 1, using the conversion 1 kX. = 1·00202 Å. As a cross check on these constants, the (777) spacing was measured and found to be 1·10083 ± 3 Å, which compares exactly with that calculated from the values of *a*, *b* and *c* in Table 1 of 1·10083 Å. A full account of this lattice constant determination will be given elsewhere (Cooper, 1961). It may be seen from Table 1 that Caron & Donohue's lattice constants are all slightly larger than those now presented, and that the departure from the new *b*-value is significant.

The new lattice constants do not significantly change the bond lengths and angles calculated by Caron & Donohue (1961) on the basis of the 1960 *C* set of atomic position coordinates (Abrahams, 1961). However, the values of the molecular constants based on the present lattice constants and these atomic coordinates are given in Table 2 for completeness.

Table 2. *Molecular constants in orthorhombic sulfur*

Bond lengths		Bond angles		Dihedral angles	
S_1–S_3	2·045 Å	S_1'–S_1–S_3	108° 14′	$S_1S_3S_2/S_3S_2S_4$	101° 5′
S_2–S_3	2·051	S_3–S_2–S_4	108° 00′	$S_1'S_1S_3/S_1S_3S_2$	99° 6′
S_2–S_4	2·048	S_1–S_3–S_2	107° 10′	$S_3S_2S_4/S_2S_4S_4'$	98° 3′
S_1–S_1'	2·043	S_4'–S_4–S_2	108° 57′	$S_3S_1S_1'/S_1S_1'S_3'$	97° 23′
S_4–S_4'	2·050			$S_2S_4S_4'/S_4S_4'S_2'$	95° 1′
Mean	2·048 ± 2		107° 55′ ± 8′		98° 39′ ± 28′

The mean S–S bond distance of 2·048 ± 2 Å is identical with that obtained from Caron & Donohue's (1961) lattice constants, and as pointed out by these authors, is 0·007 Å larger than obtained using Abrahams' (1955) lattice constants. The 2·048 Å value must hence be regarded as the best S–S bond length in orthorhombic sulfur.

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* We are indebted to J. Kalnajs of M.I.T. for these crystals.

† Originally presented by R. Fanelli, Texas Gulf Sulfur Company, New York for optical absorption studies by Bass (1953).