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The Crystal Structure of Cesium Hexasulfide*

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Cesium hexasulfide forms triclinic crystals, space group $P\bar{1}$, with two molecules in the unit cell of dimensions $a = 11{\cdot}53$, $b = 9{\cdot}18$, $c = 4{\cdot}67$ Å, $\alpha = 89°\ 13'$, $\beta = 95°\ 12'$, and $\gamma = 95°\ 8'$. The crystal structure has been completely determined, the positional parameters being refined by double Fourier series based on 382 terms derived from visual intensity measurements. The cesium atoms are completely ionized, and the resulting hexasulfide ion is shown to be nonbranched and nonplanar. The average S–S–S angle is 108·8°. Two kinds of S–S bond exist, of length 2·02 and 2·11 Å, alternately arranged along the hexasulfide chain. The dependence of the S–S bond distance upon the amount of double-bond character is similar to the C–C relationship. The crystal is characterized by the van der Waals contacts of 3·39 Å between the ends of neighboring hexasulfide ions which form infinite helices of sulfur atoms.

As part of a larger research program in this Laboratory of investigating the properties of the VI_b group of the periodic table, attention has been turned to a study of the polysulfides. Much of the earlier work on the molecular structure of the polysulfides, in which the possibilities of side-chain formation are discussed, has been reviewed by Dawson, Mathieson & Robertson (1948) and by Koch (1949). Recent dipole-moment measurements on *n*-hexadecyl polysulfides (Woodrow, Carmack & Miller, 1951) have indicated that a nonbranched structure is the more probable. Measurements of bond lengths and angles in sulfur chains have shown rather wide variations. The S–S bond distance has been reported as 2·12 Å in orthorhombic sulfur (Warren & Burwell, 1935), 2·15 Å in barium trisulfide (Miller & King, 1936), 2·07 Å in S_8 vapor (Lu & Donohue, 1944), 2·15 Å in *p*, *p*′-dibromodiphenyl disulfide (Toussaint, 1945), 2·04 Å in dimethyl trisulfide (Donohue & Schomaker, 1948), 2·07 Å in bisphenylsulfonyl sulfide (Mathieson & Robertson, 1949), and 2·05 Å in 2,2′-diiododiethyl trisulfide (Donohue, 1950). The S–S–S angle has been given various values in the range 103° to 113°. Pauling (1949) has developed a theoretical discussion of the dihedral angle in the sulfur chain, and has concluded that the most likely angle is *c.* 100°.

Stability in long-chain alkali polysulfides is reported (Biltz & Wilke-Dörfurt, 1905) to increase with the size of the cation, and, since it was desirable to consider a polysulfide of maximum length, cesium hexasulfide was chosen for this study.

Crystal data

Cesium hexasulfide Cs_2S_6; mol.wt. 458·18; m.p. 185° C. (Abrahams, Grison & Kalnajs, 1952); $D_{\text{obs.}} = 3{\cdot}076$ g.cm.$^{-3}$ (measured by pyknometer and by flotation); $D_{\text{calc.}} = 3{\cdot}109$ g.cm.$^{-3}$; triclinic with

$$a = 11{\cdot}53 \pm 0{\cdot}02,\quad b = 9{\cdot}18 \pm 0{\cdot}02,\quad c = 4{\cdot}67 \pm 0{\cdot}02\ \text{Å},$$
$$\alpha = 89°\ 13' \pm 10',\quad \beta = 95°\ 12' \pm 10',\ \text{and}$$
$$\gamma = 95°\ 8' \pm 10';$$

no reflection systematically absent; space group $P\bar{1}$ or $P1$. Piezoelectric tests gave a negative result. Application of the Wilson (1949) ratio for the detection of centers of symmetry, $\varrho = \langle|F_o|\rangle^2/\langle F_o^2\rangle$, gave an average value of 0·655, taking 250 ($hk0$) reflections split into two groups in the range $(\sin\theta/\lambda)^2$ from 0·025 to 0·420. This may be compared with the predicted value of 0·637 for centrosymmetric crystals and 0·785 for noncentrosymmetric crystals. The space group was chosen as $P\bar{1}$. Two molecules per cell; no molecular symmetry required; absorption coefficient for X-rays ($\lambda = 0{\cdot}7107$ Å), $\mu = 85{\cdot}6$ cm.$^{-1}$. Volume of the unit cell is 489·4 Å^3. Total number of electrons per unit cell $= F(000) = 412$.

Analysis of the structure

The presence of the cesium atoms naturally suggested use of the Patterson method for an initial determination of the heavy-atom position. An F^2_{hk0} synthesis is shown in Fig. 1, viewed along the short *c* axis. This could be interpreted by placing the two cesium

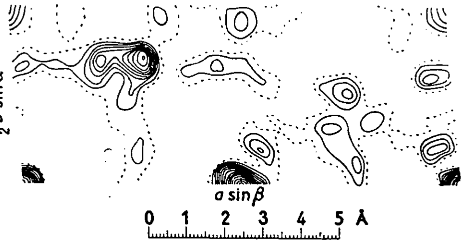

Fig. 1. Patterson projection of half a unit cell along the *c* axis, the contours being at equal but arbitrary intervals except at the origin peak, where the intervals are doubled.

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atoms in the asymmetric unit at (0·142, 0·357) and (0·376, 0·653). The phases given by these coordinates were then introduced into an (*hk*0) Fourier series and summed on the X-ray Analog Computer by kind permission of Prof. R. Pepinsky. Various phase permutations were used in attempts to minimize the background, and the best resulting Fourier series gave the cesium atoms the coordinates (0·131, 0·347) and (0·369, 0·653), indicating a center of symmetry between them, but did not reveal the position of the sulfur chain.

The method of Wilson (1942) and Harker (1948) was used to place the intensities on an absolute scale. The scale factor thus derived was finally found to be only 10·4 % too high. The temperature factor B in the expression $\exp\,[-B\,(\sin\theta/\lambda)^2]$ was found to have a value of 1·64 Å^2, which remained unaltered throughout the investigation. The parameters of the sulfur atoms were now obtained by a consideration of the terms $F_o - F_{\mathrm{Cs}}$ since the difference was approximately on the absolute scale and was associated with a known phase. The set of sulfur coordinates thus derived, together with the cesium positions from XRAC, had a value of $R_1 = \Sigma||F_o|-|F_c||\div\Sigma|F_o| = 0{\cdot}47$. This value, although large, is quoted here in view of the current discussions on the meaning of R_1 at its upper limits. The usual iterative process of refinement of the positional parameters by double Fourier series was then undertaken. After twelve such series all phases were completely determined, and the final projection, giving excellent resolution of all the atoms, is shown in Fig. 2. The explanatory diagram of this electron-density map is given in Fig. 3.

The (*h*0*l*) series was used for the evaluation of the z coordinates. The F^2_{h0l} series (Fig. 4) was not readily interpretable because of considerable overlap among the interatomic vectors. Since the x coordinates of all eight atoms in the asymmetric unit were known, and because of the simple nature of the structure factor, it was not difficult to postulate z coordinates for the cesium atoms which gave an acceptable fit for the (*h*0*l*) structure factors. The phases from the cesium atoms at (0·095, 0·660) and (0·385, 0·740) were again

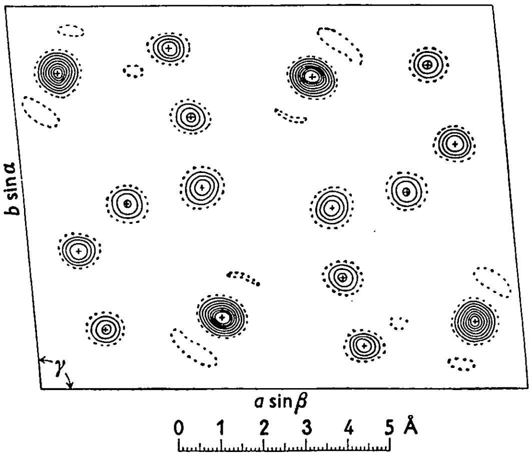

Fig. 2. Projection of the unit cell along the c axis. Each contour for the sulfur atoms represents a density increment of 8 e.Å^{-2}, and for the cesium atoms is 16 e.Å^{-2}, the 8-electron line being broken. The origin is at the midpoint of the b axis.

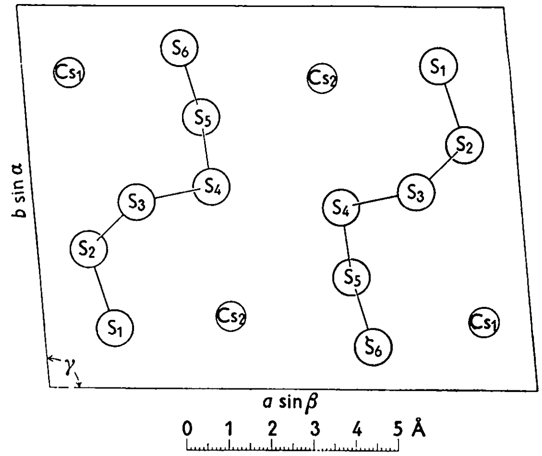

Fig. 3. Arrangement of the ions in the c-axis projection.

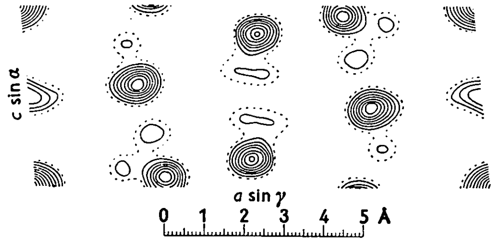

Fig. 4. Patterson projection of half a unit cell along the b axis, the contours being at equal but arbitrary intervals except at the origin peak, where the intervals are doubled.

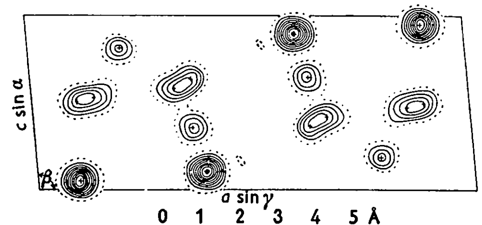

Fig. 5. Normal projection of the unit cell along the b axis. Contour scale as in Fig. 2.

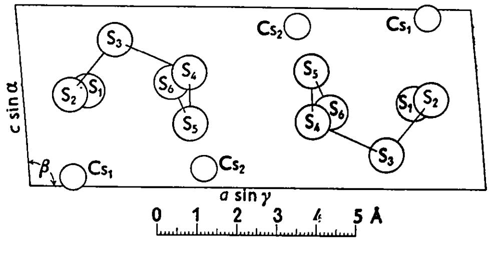

Fig. 6. Arrangement of the ions in the b-axis projection.

Table 1. *Coordinates referred to the crystal axes and a set of orthogonal axes. Origin at the center of symmetry*

	x/a	x' (Å)	y/b	y' (Å)	z/c	z' (Å)
Cs_1	0·0959	0·819	0·3237	2·961	0·0500	0·233
Cs_2	0·3849	4·650	−0·3103	−2·834	0·1018	0·473
S_1	0·1456	1·737	−0·3432	−3·124	0·5312	2·468
S_2	0·1024	1·082	−0·1379	−1·248	0·5022	2·333
S_3	0·2137	2·135	−0·0146	−0·112	0·8085	3·756
S_4	0·3689	3·962	0·0272	0·266	0·6355	2·953
S_5	0·3601	3·832	0·2086	1·916	0·3518	1·634
S_6	0·3295	3·238	0·3872	3·555	0·5752	2·672

Table 2. *Dimensions in the hexasulfide ion*

S_1–S_2 = 1·99 Å
S_2–S_3 = 2·10
S_3–S_4 = 2·03
S_4–S_5 = 2·12
S_5–S_6 = 2·03

$\angle\ S_1S_2S_3 = 110^\circ\ 00'$
$\angle\ S_2S_3S_4 = 106^\circ\ 24'$
$\angle\ S_3S_4S_5 = 109^\circ\ 40'$
$\angle\ S_4S_5S_6 = 109^\circ\ 10'$

*$S_1S_2S_3/S_2S_3S_4 = 101^\circ\ 14'$
$S_2S_3S_4/S_3S_4S_5 = 98^\circ\ 4'$
$S_3S_4S_5/S_4S_5S_6 = 118^\circ\ 36'$

* Dihedral angle.

used in computing Fourier series on XRAC. These phases immediately produced a recognizable polysulfide chain, and hence, by normal double Fourier series refinement, the electron-density map of Fig. 5 was produced. The line diagram of Fig. 6 shows the arrangement of atoms observed along the b axis. Owing to the length of the a axis and consequent atomic overlap, the $(0kl)$ projection is not given.

The final values of R_1 for the three principal zones are 0·170 for the $(hk0)$, 0·205 for the $(h0l)$ and 0·206 for the $(0kl)$ structure factors, with an over-all average of 0·188 for the 535 possible zonal planes within a reciprocal sphere of radius $\sin\theta = 0{\cdot}495$ for Mo $K\alpha$ radiation. The calculated structure factors were based upon the Hartree atomic scattering curve for sulfur and the Thomas–Fermi curve for cesium, the temperature factor 1·64 Å^2 previously determined being used.

Atomic coordinates

The atomic positions, taken as coincidental with the centers of electron mass in Figs. 2 and 5, are collected in Table 1. All three coordinates for each atom are clearly resolvable, except for the z coordinates of S_1, S_2, S_4, and S_6, which could be obtained with fair accuracy since the overlapping peaks are quite symmetrical. The coordinates referred to the triclinic crystal axes are denoted by x, y, z, while x', y', and z' denote orthogonal coordinates referred to the a, b' and c' axes, where b' is chosen normal to a in the ab plane and c' is mutually normal to a and b'. These orthogonal coordinates are useful in calculating interatomic distances and are derived by the relations

$$\begin{aligned} x' &= x+y\cos\gamma+z\cos\beta, \\ y' &= y\sin\gamma+z(\cos\alpha-\cos\beta\cos\gamma)/\sin\gamma, \\ z' &= z(1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma \\ &\qquad +2\cos\alpha\cos\beta\cos\gamma)^{\frac{1}{2}}/\sin\gamma \end{aligned}$$

(Dresden, 1930, p. 117).

Dimensions in the hexasulfide ion

These coordinates result in the dimensions for the hexasulfide ion shown in Table 2.

Errors in the coordinates

In any crystal-structure determination, a knowledge of the errors in the observed coordinates, and hence in the bond distances and angles, is of considerable importance. A principal source of error often lies in the termination of the Fourier series at finite values of h, k, l. This error was evaluated in the usual way by summing a Fourier series using the calculated structure factors as the coefficients. The errors in the atomic coordinates in the $(hk0)$ projection as given by $\Delta x_j = |x_{j,\text{obs.}} - x_{j,\text{calc.}}|$ and $\Delta y_j = |y_{j,\text{obs.}} - y_{j,\text{calc.}}|$ are listed in Table 3.

Table 3. *Errors caused by finite-series termination*

	Δx (Å)	Δy (Å)
Cs_1	0·006	0·000
Cs_2	0·001	0·003
S_1	0·019	0·009
S_2	0·012	0·009
S_3	0·022	0·006
S_4	0·010	0·011
S_5	0·002	0·006
S_6	0·016	0·015

An $(h0l)$ projection using the calculated F_{h0l} terms was not evaluated, since there is no reason for the average value of Δz to be appreciably different from Δx or Δy. It may be noted that this cause of error was unlikely to be high, since all measurable reflections occurred within the Cu $K\alpha$ range. No further data were obtained on using Mo $K\alpha$ radiation.

Various other methods are available of estimating the error in the observed coordinates. Booth (1945, 1946, 1947) has extensively investigated the relations between observed and calculated structure factors and the corresponding errors in atomic coordinates, and these are used here because of their ease in application.

Table 4. *Estimated errors in the coordinates*

	Method	Estimated error (Å)
Δ_{xyz}	Finite termination of series	0·010
$\bar{\delta}_n$	Booth (1945) in (*hk*0) zone where $R_2 = 0{\cdot}030$	0·002
$\bar{\delta}_n$	Booth (1945) in (*h*0*l*) zone where $R_2 = 0{\cdot}036$	0·018
$\varepsilon_{\mathrm{Cs}}$	Booth (1946)	$< 0{\cdot}006$
ε_{S}	Booth (1946)	$< 0{\cdot}020$
$\varepsilon_{\mathrm{Cs}}$	Booth (1947)	$< 0{\cdot}007$
ε_{S}	Booth (1947)	$< 0{\cdot}023$
$\sigma(r)_{\mathrm{Cs}}$	Cruickshank (1949)	0·002
$\sigma(r)_{\mathrm{S}}$	Cruickshank (1949)	0·011

However, there are many simplifications in these relations, and probably the errors indicated by them are only an approximate measure of the real error. Booth (1945) has shown that the expression $R_2 = \Sigma(|F_o|-|F_c|)^2 \div \Sigma|F_o|^2$ is related to $\bar{\delta}_n$, the r.m.s. error in all the coordinates in the structure.

Another measure of the coordinate error (Booth, 1946) is given by $\varepsilon_j < 90{\cdot}8\ \Delta\varepsilon \div N_j(\lambda p_j)^{\frac{3}{2}}\sqrt{V}$, where $\Delta\varepsilon$ is the probable error in $F(hkl)$, N_j is the atomic number of the jth atom, λ is the wavelength, p_j is defined as $D(r) = A \exp(-p_j r^2)$ in which $D(r)$ is the density distribution of the jth atom, A is unity, r is the radial distance from the atomic center and V is the volume of the unit cell. From the (*hk*0) projection it is found that $p_{\mathrm{Cs}} = 7{\cdot}5$ and $p_{\mathrm{S}} = 6{\cdot}3$. Booth (1947) shows also that $\varepsilon \leqq 0{\cdot}66\ \Delta\varepsilon \div N\sqrt{v}$, where the symbols have the same meaning as in the previous expression, v being the projection area. In both (*hk*0) and (*h*0*l*) zones, the errors in the structure factors used in the Fourier series have a normal frequency distribution, with a probable error $\Delta\varepsilon = \pm 5{\cdot}9$.

Cruickshank (1949) more recently has derived a relationship between expressions of the form

$$\sigma(R_h) = \frac{2\pi}{av}\{\sum_2 h^2 \Delta F^2\}^{\frac{1}{2}} ,$$

the curvature of the peaks in the electron-density function $\partial^2\varrho/\partial r^2 = -2pN(p/\pi)^{\frac{3}{2}}$, and the standard deviations in the peak positions, retaining the symbolism already defined. The structure factors in Table 7 then correspond to

$$\sigma(R_h) = 2{\cdot}35;\ \sigma(R_k) = 3{\cdot}06;\ \sigma(R_l) = 4{\cdot}45\ \mathrm{e.\AA^{-3}}\,.$$

$$\partial^2\varrho/\partial r^2 = -3004 \text{ for cesium and } -566 \text{ for sulfur.}$$

The standard deviation $\sigma(r)$ is taken as $[\sigma(x)^2+\sigma(y)^2+\sigma(z)^2]^{\frac{1}{2}}$.

The estimated values for the errors in the coordinates based on these methods are collected in Table 4. Hence this set of estimated errors, together with the agreement among the lengths of bonds chemically identical but crystallographically independent, make it appear likely that no bond length is in error by more than ±0·03 Å, and therefore no angle by more than ±2·0°.

Interionic distances

The closest approach distances among the cesium and hexasulfide ions are collected in Table 5, using the

Table 5. *Interionic distances less than* 4·0 Å.

$\mathrm{S}'_{1F} \ldots \mathrm{S}_{6F} = 3{\cdot}39$ Å
$\mathrm{S}_{5F} \ldots \mathrm{S}_{3C} = 3{\cdot}50$
$\mathrm{S}_{2F} \ldots \mathrm{S}_{2E} = 3{\cdot}61$
$\mathrm{S}_{2F} \ldots \mathrm{S}_{3C} = 3{\cdot}72$
$\mathrm{S}_{4C} \ldots \mathrm{S}_{5F} = 3{\cdot}77$
$\mathrm{S}_{4C} \ldots \mathrm{S}_{5B} = 3{\cdot}95$

$\mathrm{Cs}_{1F} \ldots \mathrm{S}_{5F} = 3{\cdot}48$
$\mathrm{Cs}_{1F} \ldots \mathrm{S}_{6F} = 3{\cdot}49$
$\mathrm{Cs}_{2F} \ldots \mathrm{S}_{1F} = 3{\cdot}54$
$\mathrm{Cs}_{1F} \ldots \mathrm{S}_{2E} = 3{\cdot}55$
$\mathrm{Cs}_{1F} \ldots \mathrm{S}_{1E} = 3{\cdot}56$
$\mathrm{Cs}'_{2F} \ldots \mathrm{S}_{6F} = 3{\cdot}59$

$\mathrm{Cs}_{1F} \ldots \mathrm{S}_{2D} = 3{\cdot}62$ Å
$\mathrm{Cs}_{2F} \ldots \mathrm{S}_{6A} = 3{\cdot}62$
$\mathrm{Cs}_{1F} \ldots \mathrm{S}_{6C} = 3{\cdot}64$
$\mathrm{Cs}_{2F} \ldots \mathrm{S}_{1C} = 3{\cdot}65$
$\mathrm{Cs}_{2F} \ldots \mathrm{S}_{3C} = 3{\cdot}68$
$\mathrm{Cs}_{1F} \ldots \mathrm{S}_{1D} = 3{\cdot}72$
$\mathrm{Cs}'_{2F} \ldots \mathrm{S}_{6D} = 3{\cdot}72$
$\mathrm{Cs}_{1F} \ldots \mathrm{S}_{3C} = 3{\cdot}73$
$\mathrm{Cs}_{2F} \ldots \mathrm{S}_{5A} = 3{\cdot}77$
$\mathrm{Cs}_{2F} \ldots \mathrm{S}_{4C} = 3{\cdot}77$
$\mathrm{Cs}_{1F} \ldots \mathrm{S}'_{1F} = 3{\cdot}79$
$\mathrm{Cs}_{2F} \ldots \mathrm{S}_{5B} = 3{\cdot}82$
$\mathrm{Cs}_{1F} \ldots \mathrm{S}'_{1C} = 3{\cdot}91$

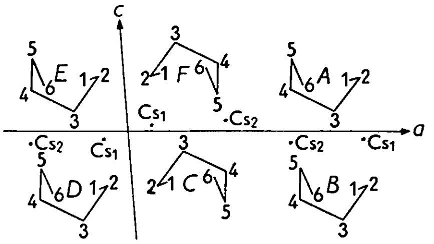

Fig. 7. Naming of six asymmetric units, viewed along the *b* axis.

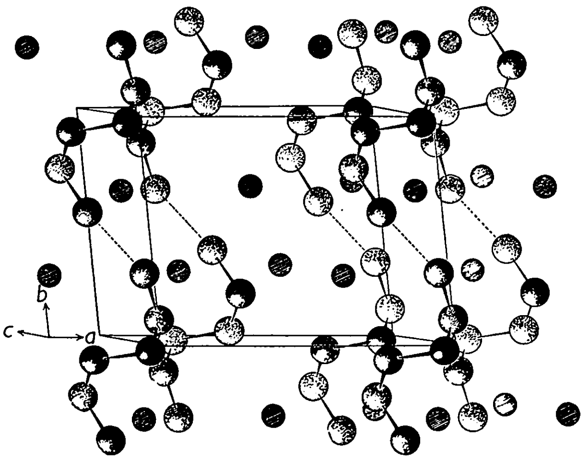

Fig. 8. A clinometric view of the structure, showing the outlines of one unit cell. The hatched circles represent cesium atoms, the shaded circles sulfur atoms.

same numbering system as previously, and naming six adjoining asymmetric units as in Fig. 7. The primed atoms are one translation up the *b* axis. It may be seen that there are no really short interionic distances. A clinometric view of the structure in Fig. 8 shows the helices formed by the hexasulfide ions.

Discussion

This investigation of the crystal structure of cesium hexasulfide has unambiguously demonstrated the polysulfide chain to be nonbranched and nonplanar. The crystal is characterized by the presence of van der Waals approaches of 3·39 Å between the ends of neighboring hexasulfide ions, which result in the formation of infinite helices of sulfur atoms. The cesium ions occur approximately in layers which are alternately separated by hexasulfide ions, and by the van der Waals connections between these ions (Fig. 8). The helical axis is very nearly normal to these cesium ion layers. This sulfur helix with an S–S–S angle of about 108·8° may be compared with the helices found in metallic selenium and tellurium (Grison, 1951) in which the corresponding angles are 105° and 102°, respectively. It is of some interest that if the trigonally symmetrical selenium and tellurium helix is compressed to about 80% of its length, the resulting helix, now with no symmetry, is very nearly identical with the polysulfide helix.

The alternating variations in bond length along the hexasulfide chain are probably the most important aspect of this structure. Two kinds of bond appear to be present, of length 2·02 Å and 2·11 Å, the difference between them being well outside the experimental error of $\pm 0{\cdot}03$ Å. It may be seen from Table 4 that each cesium atom is approximately surrounded by nine or ten sulfur atoms, all at about the same distance, which hence makes covalent bond formation unlikely. The cesium atoms may therefore be regarded, to a good approximation, as completely ionized. In this case, the hexasulfide ion will possess a negative charge of two, the two electrons being distributed throughout the ion. No investigator has reported an S–S single covalent-bond distance of more than 2·11 Å (within the limits of error quoted), which value may now be regarded as the true S–S single-bond length, assuming no S–S bond contains less than one electron pair.* With this postulate, the extra two electrons may be regarded as localized in the three bonds of length 2·02 Å, i.e. each of these bonds containing two-thirds of an electron in excess of a single bond will possess a one-third double-bond character. The length of a pure S–S double bond has not been reported, but if it is assumed to be close to the $^3\Sigma_g^-$ state in S_2, the spectroscopic value of 1·89 Å may be taken (Herzberg, 1950, vol. 1, p. 566). A value of 1·92 Å has also been measured in S_2 at 800° C. by electron diffraction (Maxwell, Mosley & Hendricks, 1936), and probably the true value lies between these distances. A plot of S–S distance versus the double-bond character thus deduced from these three bonds of 2·11, 2·02, and 1·89 Å results in the curve given in Fig. 9. The corresponding curve for carbon is given in the same diagram for comparison.

Fig. 9 may now be used in interpreting some of the variation, between 2·11 and 2·04 Å, in the S–S bond lengths previously reported as due to the amount of double-bond character present. This double-bond character of up to *c.* 25% may well be caused by the inductive and tautomeric effects of the groups adjacent to the S–S bond. The curve in Fig. 9 will be better established after the bond lengths in the penta- and tetrasulfide ions have been measured; this work is now in progress.

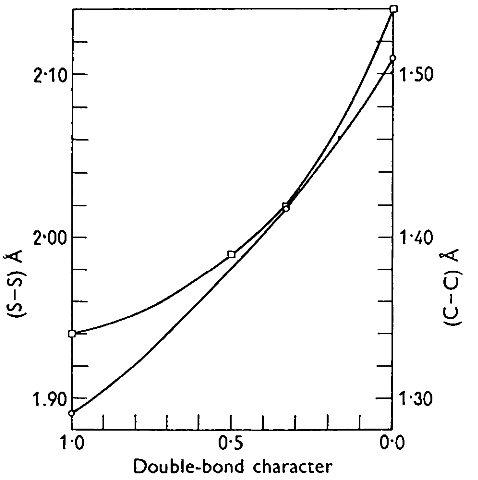

Fig. 9. The relation between interatomic distance and amount of double-bond character in the S–S and C–C bond. The circles represent the sulfur data, and the squares are for carbon.

Alternations in the bond lengths of a polysulfide will be produced only if there are $2n+1$ perturbed S–S bonds, where $n \geq 1$; otherwise all the bonds will be equal. It may be noted that similar alternations in bond lengths along an aliphatic chain have been observed in the case of adipic and sebacic acids (Morrison & Robertson, 1949*a*, *b*) and hexamethylene diamine (Binnie & Robertson, 1950). A full explanation of this effect has not been offered, although it has

Table 6. *Dipole moments of some alkyl polysulfides*

n-Hexadecyl monosulfide	1·47 D.	Woodrow, Carmack & Miller (1951)
n-Hexadecyl disulfide	2·00	
n-Hexadecyl trisulfide	1·63	
n-Hexadecyl tetrasulfide	2·16	
Ethyl disulfide	1·99	Westlake, Laquer & Smyth (1950)
Ethyl trisulfide	1·64	
Methyl disulfide	1·95	Kushner, Gorin & Smyth (1950)
Methyl trisulfide	1·66	

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* A re-examination of the crystal structure of orthorhombic sulfur will be undertaken to obtain a more accurate value for this bond length.

Table 7. *Measured and calculated values of the structure factors*

hkl	F_m	F_c	*hkl*	F_m	F_c	*hkl*	F_m	F_c	*hkl*	F_m	F_c
100	< 8	+3	$2\bar{6}0$	75	−82	6,10,0	18	+13	$9\bar{4}0$	77	−75
200	9	+4	$2\bar{7}0$	68	+82	690	79	−67	$9\bar{5}0$	53	+73
300	67	+48	$2\bar{8}0$	52	−51	680	55	+40	$9\bar{6}0$	20	+28
400	210	−221	$2\bar{9}0$	60	−66	670	30	+18	$9\bar{7}0$	23	−32
500	16	−7	$2,\overline{10},0$	31	+29	660	103	−97	$9\bar{8}0$	51	+51
600	74	−63	$2,\overline{11},0$	38	−26	650	52	+48	$9\bar{9}0$	22	+24
700	82	−88	3,11,0	13	−4	640	86	+85	10,7,0	43	+27
800	81	+80	3,10,0	24	+8	630	81	−81	10,6,0	74	+63
900	11	+9	390	46	−23	620	27	−31	10,5,0	50	−38
10,0,0	66	+61	380	13	+4	610	64	+68	10,4,0	41	−24
11,0,0	47	+47	370	25	−22	$6\bar{1}0$	43	−44	10,3,0	65	+59
12,0,0	11	−15	360	70	−56	$6\bar{2}0$	123	+127	10,2,0	13	+2
13,0,0	32	+33	350	9	−1	$6\bar{3}0$	30	−26	10,1,0	20	−30
14,0,0	31	−23	340	12	+2	$6\bar{4}0$	74	−77	$10,\bar{1},0$	< 11	+5
15,0,0	18	−21	330	11	+5	$6\bar{5}0$	95	+100	$10,\bar{2},0$	63	−65
010	25	−39	320	7	−9	$6\bar{6}0$	< 11	−4	$10,\bar{3},0$	40	+44
020	93	−111	310	15	−11	$6\bar{7}0$	61	−72	$10,\bar{4},0$	11	+5
030	223	+205	$3\bar{1}0$	16	−13	$6\bar{8}0$	42	+39	$10,\bar{5},0$	58	−70
040	29	−25	$3\bar{2}0$	54	−42	$6\bar{9}0$	10	+13	$10,\bar{6},0$	13	+20
050	64	−65	$3\bar{3}0$	18	+16	$6,\overline{10},0$	13	−24	$10,\bar{7},0$	10	+24
060	123	+128	$3\bar{4}0$	25	+28	$6,\overline{11},0$	24	+24	$10,\bar{8},0$	28	−26
070	23	+21	$3\bar{5}0$	16	+16	790	7	−7	$10,\bar{9},0$	6	−3
080	65	−61	$3\bar{6}0$	37	+31	780	30	−8	11,7,0	4	+8
090	60	+56	$3\bar{7}0$	29	+30	770	< 11	+3	11,6,0	7	+8
0,10,0	34	+33	$3\bar{8}0$	43	−40	760	13	−8	11,5,0	33	−27
0,11,0	58	−58	$3\bar{9}0$	< 11	−8	750	< 11	+3	11,4,0	18	+16
001	87	+74	$3,\overline{10},0$	57	+51	740	24	−16	11,3,0	< 11	+11
002	135	+113	$3,\overline{11},0$	29	−21	730	44	−45	11,2,0	41	−38
003	< 17	−2	4,10,0	40	−43	720	10	+10	11,1,0	30	+32
004	19	−27	490	32	−18	710	32	−37	$11,\bar{1},0$	18	−31
005	19	−28	480	84	+72	$7\bar{1}0$	< 9	+4	$11,\bar{2},0$	13	−18
006	12	−13	470	54	−49	$7\bar{2}0$	25	+15	$11,\bar{3},0$	20	+25
1,11,0	7	−6	460	85	−88	$7\bar{3}0$	49	−45	$11,\bar{4},0$	< 11	−14
1,10,0	37	−29	450	88	+101	$7\bar{4}0$	38	−31	$11,\bar{5},0$	11	−21
190	34	+26	440	37	−35	$7\bar{5}0$	10	−6	$11,\bar{6},0$	36	+49
180	46	+21	430	86	−111	$7\bar{6}0$	60	−60	$11,\bar{7},0$	< 8	−8
170	11	+2	420	184	+193	$7\bar{7}0$	39	−36	$11,\bar{8},0$	26	−45
160	34	−14	410	57	−41	$7\bar{8}0$	47	+48	12,5,0	28	+17
150	32	−31	$4\bar{1}0$	135	+144	$7\bar{9}0$	37	−28	12,4,0	87	−75
140	19	−15	$4\bar{2}0$	27	+25	$7,\overline{10},0$	43	−38	12,3,0	15	+10
130	13	−6	$4\bar{3}0$	136	−129	890	22	−16	12,2,0	68	+42
120	12	+4	$4\bar{4}0$	96	+97	880	76	−61	12,1,0	64	−75
110	< 4	−6	$4\bar{5}0$	45	+48	870	66	+57	$12,\bar{1},0$	33	+34
$1\bar{1}0$	8	−16	$4\bar{6}0$	63	−79	860	45	+29	$12,\bar{2},0$	40	−50
$1\bar{2}0$	< 11	−9	$4\bar{7}0$	33	+39	850	86	−74	$12,\bar{3},0$	23	−33
$1\bar{3}0$	16	+17	$4\bar{8}0$	42	+52	840	79	+75	$12,\bar{4},0$	19	+25
$1\bar{4}0$	74	−79	$4\bar{9}0$	41	−58	830	24	+21	$12,\bar{5},0$	11	−16
$1\bar{5}0$	< 8	−11	$4,\overline{10},0$	< 10	+6	820	103	−127	$12,\bar{6},0$	< 8	−15
$1\bar{6}0$	77	+77	$4,\overline{11},0$	60	+60	810	77	+86	13,4,0	26	−27
$1\bar{7}0$	28	−23	5,10,0	42	+18	$8\bar{1}0$	93	−93	13,3,0	36	+36
$1\bar{8}0$	11	−5	590	15	+6	$8\bar{2}0$	57	+48	13,2,0	22	+25
$1\bar{9}0$	46	+26	580	< 11	+8	$8\bar{3}0$	70	+69	13,1,0	37	−36
$1,\overline{10},0$	58	−35	570	< 11	−2	$8\bar{4}0$	70	−61	$13,\bar{1},0$	< 9	+10
$1,\overline{11},0$	< 7	−5	560	53	+38	$8\bar{5}0$	11	−2	$13,\bar{2},0$	42	−65
2,11,0	10	−8	550	50	+47	$8\bar{6}0$	46	+49	$13,\bar{3},0$	24	+42
2,10,0	39	−35	540	29	+14	$8\bar{7}0$	48	−42	$13,\bar{4},0$	22	+37
290	85	+83	530	42	+33	$8\bar{8}0$	10	−6	$13,\bar{5},0$	28	−51
280	< 11	−4	520	47	+63	$8\bar{9}0$	48	+59	$13,\bar{6},0$	6	+16
270	74	−76	510	13	+8	$8,\overline{10},0$	8	−15	14,2,0	28	+25
260	116	+110	$5\bar{1}0$	74	+66	980	26	+5	14,1,0	14	+20
250	< 9	−2	$5\bar{2}0$	36	−28	970	9	+14	$14,\bar{1},0$	25	+25
240	134	−156	$5\bar{3}0$	8	−6	960	35	−21	$14,\bar{2},0$	25	+25
230	72	+81	$5\bar{4}0$	115	+123	950	< 11	−9	$14,\bar{3},0$	18	−20
220	68	+86	$5\bar{5}0$	29	−27	940	13	+24	$14,\bar{4},0$	18	+26
210	99	−114	$5\bar{6}0$	48	−58	930	24	−19	15,0,1	16	−2
$2\bar{1}0$	70	+64	$5\bar{7}0$	45	+49	920	34	−41	14,0,1	45	−43
$2\bar{2}0$	183	−184	$5\bar{8}0$	39	−26	910	33	+45	13,0,1	< 20	+11
$2\bar{3}0$	78	−72	$5\bar{9}0$	37	−29	$9\bar{1}0$	37	−36	12,0,1	< 20	−8
$2\bar{4}0$	102	+126	$5,\overline{10},0$	45	+37	$9\bar{2}0$	86	+89	11,0,1	< 19	+11
$2\bar{5}0$	89	−100	$5,\overline{11},0$	20	−7	$9\bar{3}0$	< 11	−5	10,0,1	84	+102

Table 7 (*cont.*)

hkl	F_m	F_c	*hkl*	F_m	F_c	*hkl*	F_m	F_c	*hkl*	F_m	F_c
901	18	−18	303	78	−55	406	10	−7	063	13	−8
801	17	+15	203	27	+19	306	15	−26	053	20	+27
701	25	+14	103	60	−43	206	36	−43	043	16	+24
601	158	−111	$10\bar{3}$	71	+58	106	< 16	+9	033	< 13	+8
501	17	+25	$20\bar{3}$	12	+17	$10\bar{6}$	12	+12	023	< 13	−18
401	66	−66	$30\bar{3}$	138	+104	$20\bar{6}$	38	+36	013	< 13	+2
301	121	−80	$40\bar{3}$	17	−11	$30\bar{6}$	< 16	−2	$01\bar{3}$	< 13	−15
201	126	+82	$50\bar{3}$	28	−28	$40\bar{6}$	38	+36	$02\bar{3}$	< 13	−7
101	< 10	−4	$60\bar{3}$	28	+26	$50\bar{6}$	< 15	−3	$03\bar{3}$	< 13	−2
$10\bar{1}$	39	+35	$70\bar{3}$	116	−104	$60\bar{6}$	14	−24	$04\bar{3}$	< 13	+5
$20\bar{1}$	29	+13	$80\bar{3}$	19	−21	$70\bar{6}$	< 13	+1	$05\bar{3}$	< 14	−12
$30\bar{1}$	120	+84	$90\bar{3}$	14	−6	$80\bar{6}$	12	−24	$06\bar{3}$	< 13	+6
$40\bar{1}$	38	−37	$10,0,\bar{3}$	31	−24	0,12,1	< 13	+8	$07\bar{3}$	18	−18
$50\bar{1}$	< 10	−8	$11,0,\bar{3}$	76	+80	0,11,1	< 14	−23	$08\bar{3}$	40	−54
$60\bar{1}$	102	−84	$12,0,\bar{3}$	10	+25	0,10,1	< 14	+24	$09\bar{3}$	< 13	+16
$70\bar{1}$	109	−92	$13,0,\bar{3}$	10	+14	091	< 14	+26	$0,10,\bar{3}$	< 12	+10
$80\bar{1}$	45	+33	$14,0,\bar{3}$	18	+31	081	43	−57	$0,11,\bar{3}$	34	−33
$90\bar{1}$	12	−14	$15,0,\bar{3}$	24	−22	071	20	+26	094	< 12	+12
$10,0,\bar{1}$	58	+49	12,0,4	7	+16	061	46	+43	084	30	+36
$11,0,\bar{1}$	60	+68	11,0,4	11	−18	051	128	+110	074	< 13	−5
$12,0,\bar{1}$	< 20	−2	10,0,4	< 18	+10	041	63	+52	064	< 13	−8
$13,0,\bar{1}$	44	+49	904	42	+46	031	170	+135	054	13	+21
$14,0,\bar{1}$	< 20	−5	804	< 19	+6	021	142	−119	044	13	−24
$15,0,\bar{1}$	18	−24	704	53	+58	011	62	−48	034	13	−25
14,0,2	47	−50	604	14	−16	$01\bar{1}$	103	−77	024	40	+33
13,0,2	19	−14	504	43	−38	$02\bar{1}$	87	−61	014	< 13	−18
12,0,2	31	+29	404	< 19	+8	$03\bar{1}$	146	+113	$01\bar{4}$	14	+21
11,0,2	14	−9	304	112	−108	$04\bar{1}$	12	−12	$02\bar{4}$	< 14	−7
10,0,2	68	+69	204	< 19	−11	$05\bar{1}$	92	−110	$03\bar{4}$	< 14	−23
902	19	+20	104	< 19	−2	$06\bar{1}$	83	+90	$04\bar{4}$	18	−28
802	13	+17	$10\bar{4}$	161	+140	$07\bar{1}$	< 14	+18	$05\bar{4}$	< 13	−16
702	68	+63	$20\bar{4}$	26	+22	$08\bar{1}$	108	−103	$06\bar{4}$	< 13	+5
602	70	−61	$30\bar{4}$	< 19	+2	$09\bar{1}$	35	+46	$07\bar{4}$	< 13	−6
502	26	−27	$40\bar{4}$	60	+52	$0,10,\bar{1}$	25	+32	$08\bar{4}$	< 13	+4
402	140	−114	$50\bar{4}$	74	−78	$0,11,\bar{1}$	< 14	−40	$09\bar{4}$	< 12	−5
302	155	−120	$60\bar{4}$	< 19	−4	$0,12,\bar{1}$	24	+33	$0,10,\bar{4}$	20	−19
202	81	+74	$70\bar{4}$	19	−17	0,12,2	< 10	−4	085	18	+31
102	39	−25	$80\bar{4}$	62	−62	0,11,2	20	−24	075	28	−44
$10\bar{2}$	197	+142	$90\bar{4}$	14	+24	0,10,2	< 14	−6	065	< 13	−3
$20\bar{2}$	10	−9	$10,0,\bar{4}$	14	−2	092	14	−14	055	68	+64
$30\bar{2}$	133	+104	$11,0,\bar{4}$	13	+9	082	32	−42	045	31	−32
$40\bar{2}$	81	−69	$12,0,\bar{4}$	36	+30	072	< 12	+10	035	< 14	−13
$50\bar{2}$	124	−116	$13,0,\bar{4}$	< 15	−6	062	< 12	+15	025	63	+67
$60\bar{2}$	16	−19	905	39	+44	052	80	−71	015	< 13	−11
$70\bar{2}$	83	−78	805	< 11	−2	042	60	−53	$01\bar{5}$	37	+44
$80\bar{2}$	17	+23	705	< 12	+22	032	12	+15	$02\bar{5}$	< 13	+8
$90\bar{2}$	9	+12	605	< 18	+22	022	84	−76	$03\bar{5}$	< 14	−15
$10,0,\bar{2}$	9	−2	505	18	−26	012	23	−22	$04\bar{5}$	45	+57
$11,0,\bar{2}$	68	+71	405	13	+21	$01\bar{2}$	116	−98	$05\bar{5}$	20	+20
$12,0,\bar{2}$	< 20	+22	305	30	−32	$02\bar{2}$	80	−65	$06\bar{5}$	16	−32
$13,0,\bar{2}$	44	+35	205	52	−47	$03\bar{2}$	142	+121	$07\bar{5}$	< 14	+22
$14,0,\bar{2}$	< 19	+12	105	< 19	+4	$04\bar{2}$	80	−67	$08\bar{5}$	10	+14
$15,0,\bar{2}$	37	−31	$10\bar{5}$	19	+20	$05\bar{2}$	66	−56	056	30	+34
14,0,3	14	−24	$20\bar{5}$	19	+17	$06\bar{2}$	96	+88	046	< 10	−21
13,0,3	15	−22	$30\bar{5}$	23	+19	$07\bar{2}$	< 13	−11	036	< 11	−12
12,0,3	18	+7	$40\bar{5}$	67	+58	$08\bar{2}$	< 13	−16	026	31	+42
11,0,3	< 14	−11	$50\bar{5}$	< 19	+3	$09\bar{2}$	50	+58	016	11	−11
10,0,3	19	+31	$60\bar{5}$	19	+12	$0,10,\bar{2}$	< 13	−2	$01\bar{6}$	51	+59
903	31	+29	$70\bar{5}$	30	−36	$0,11,\bar{2}$	30	−36	$02\bar{6}$	11	−8
803	14	+15	$80\bar{5}$	58	−57	$0,12,\bar{2}$	< 10	+26	$03\bar{6}$	36	−40
703	60	+53	$90\bar{5}$	< 18	+16	0,10,3	< 14	−4	$04\bar{6}$	10	+30
603	51	−40	$10,0,\bar{5}$	16	−23	093	< 14	−1	$05\bar{6}$	7	+6
503	29	−33	$11,0,\bar{5}$	< 13	+12	083	< 14	+14	$06\bar{6}$	6	−20
403	13	−17	$12,0,\bar{5}$	10	+18	073	17	−26			

been described as a form of hyperconjugation. It is hoped to develop a more exact mechanism which will account for this tendency towards conjugation in perturbed, saturated, chain-like structures.

Further evidence for this conjugation effect in the S–S bond character in polysulfides is afforded by recent dipole-moment measurements on some alkyl polysulfides which have shown an interesting alternation in the dipole moments of even- and odd-membered chains (Table 6). The consistently high lue for theva dipole moment of the polysulfides with an odd number of S–S bonds may thus be correlated with a tendency to form linkages of enhanced partial double-bond nature.

Experimental

The crystals were prepared as described by Abrahams, Grison & Kalnajs (1952). They were rapidly oxidized in air to $Cs_2S_2O_3$ and rhombic sulfur, and hence were enclosed within thin-walled Pyrex capillary tubing (wall thickness 0·005–0·01 mm.). An exact chemical analysis of the crystals used was not possible since it appeared that crystals large enough for analysis had a variable sulfur content, although the four crystals used in this investigation (largest $0{\cdot}50 \times 0{\cdot}50 \times 1{\cdot}00$ mm. and smallest $0{\cdot}10 \times 0{\cdot}15 \times 0{\cdot}50$ mm.) gave identical photographic records with respect to intensity and spacing.

Weissenberg and precession cameras were employed in this investigation, using both Cu $K\alpha$ ($\lambda = 1{\cdot}5418$ Å) and Mo $K\alpha$ ($\lambda = 0{\cdot}7107$ Å) radiations. It was observed that the reflections had no appreciable intensity beyond the range of the Cu $K\alpha$ sphere on the Weissenberg camera on substituting Mo $K\alpha$ radiation. Hence the use of the shorter wavelength with the precession camera, keeping a precession angle of 30°, effectively covered all measurable reflections. The intensities were measured visually, using a multiple-film technique for correlating the weak and strong reflections with Cu $K\alpha$ radiation and a multiple-exposure method with the Mo $K\alpha$ radiation. Absorption corrections were not made since the crystals were small. The ratio of the strongest intensity to the weakest in the several zones was about 1000 to 1 for ($hk0$), 1000 to 1 for ($h0l$) and 2000 to 1 for ($0kl$).

Hönl's (1933 *a*, *b*) theory for the anomalous dispersion of the K electrons as tabulated by James (1948, p. 608) predicts a value for δf, in the cesium atomic scattering curve, of about $-1{\cdot}3$ for Mo $K\alpha$ and $-1{\cdot}1$ for Cu $K\alpha$ radiation. The correction for the dispersion of the L electrons it not well known, but probably is not large. The resulting change in the f-curve of about 2–3 %, together with the close agreement between structure factors measured with both radiations, did not appear to warrant modifying the atomic scattering curve of cesium.

The values for the measured structure factors were derived from the intensities in the usual way, Waser's (1951) Lorenz and polarization correction being used for the intensities measured on the precession camera. The calculated structure factors were based on the atomic coordinates in Table 1, and both sets of structure factors are collected in Table 7.

The structure factors have been calculated by a punched-card method accurate to four figures. The Fourier series have been summed by a variety of methods: with Beevers & Lipson strips; by a punched-card method; and by a method just developed for use with Whirlwind, the high-speed electronic digital computer at the Massachusetts Institute of Technology. The electron densities were sampled at 12° intervals along each axis. The positions of the contour lines were obtained from the summation totals by careful graphical interpolation on a scale of 5 cm. to 1 Å in directions parallel with each axis.

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