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The Experimental Charge Distribution in Sulfur Containing Molecules. Analysis of Cyclic Octasulfur at 300 and 100 K

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Abstract: X-ray and neutron diffraction measurements on cyclooctasulfur have been analyzed as part of a series of charge density analyses of sulfur containing molecules. The x-ray data (at 300 and 100 K) and the combination of x-ray and neutron data indicate a contraction of the atomic density at about 0.6 Å from the nucleus compared with the isolated spherical sulfur atom. Difference density at the midpoint of the S–S bond is about 0.05 e Å^{-3}, which is considerably lower than observed in diffraction studies of bonds between carbon and nitrogen atoms. Evidence is obtained for the directional character of the sulfur lone pair orbitals. An orbital exponent refinement of both room and low temperature x-ray data gives a best experimental single ζ value of 1.99 a_0^{-1} for the M shell orbitals assuming unperturbed K and L shells. Observed bond lengths and angles are in agreement with earlier, less precise, measurements.

Until recently charge density studies by diffraction methods have been concerned largely with development of methods. However, many computational procedures have now been developed and experimental errors have been reduced and are better understood. As a result experimental information on the charge distribution in crystals is becoming available and it is now feasible to study a number of related systems and thus concentrate on the chemical significance of the results.[2]

This report represents the first of a series of charge density studies of small sulfur containing molecules. Orthorhombic elemental sulfur was selected as a logical first choice, because knowledge of the charge distribution in monatomic sulfur may facilitate subsequent studies of more complex sulfur containing compounds.

Many organic and inorganic sulfur compounds are quite suitable for charge density analysis. Though the sulfur atom has more core electrons than carbon, nitrogen, and oxygen atoms, it is not so heavy that it is beyond the reach of x-ray charge density measurements.[3] There are a number of outstanding issues of chemical significance. It is usually assumed that sp hybridization is less important in sulfur than in first-row elements, a view supported by calculations of overlap integrals.[4] The question of participation of d orbitals is more controversial. The general lowering of theoretical energies when d functions are included has been attributed to limitations in the basis-set composition,[5] yet a consistent explanation[6] of the bonding in the "cage" compound S_4N_4 invokes the use of d orbitals to explain the short "across the ring" S···S distances of 2.58 and 2.69 Å found by Sharma and Donohue.[7] The most striking feature of the sulfur–sulfur interaction is the wide range of S–S distances from 1.99 Å in 4-phenyl-1,2-dithiolium cyanate[8] to 2.36–2.6 Å in thiathiaphtenes,[9] 2.58 and 2.69 Å in S_4N_4,[7] 2.98 Å in $S_4(NH)_4$,[10] to 3.33 Å in the across the ring "bond" in the present study of cyclooctasulfur. Also noteworthy are the 2.79 Å S . . . S *intra*chain and 3.48 Å *inter*chain interactions[11] in the polymeric low temperature superconductor $(SN)_x$. Short distances are also found in the triangular arrangement of the disulfide group and chloride ion in substituted dithiolium chlorides.[8]

Of further interest is the bonding between sulfur and nitrogen. The planarity of the S(NH)S group in $S_4(NH)_4$ and similar compounds[10] implies a partial double bond character, that must be absent in the "saturated" S–N system in the NH_3SO_3 zwitterion sulfamic acid.[12] ESCA measurements indicate that the SN bond in sulfur nitrogen ions[5b] is very polar, and a theoretical analysis of S_4N_4 suggests that the SN bonds[14] are bent much like the bent bonds in organic small ring compounds that have been observed in experimental charge density studies.[15]

The crystal structure of cyclooctasulfur at room temperature was studied by x-ray film techniques by Abrahams and collaborators.[16] The detailed analysis of the data during the period 1956–1965 has been reviewed by Donohue.[17] For the present study, room temperature x-ray and neutron, and low temperature (100 K) x-ray diffractometer data are used. Among further studies are an x-ray and neutron low temperature in-

Table I. Crystallographic Data for Orthorhombic Cyclooctasulfur (S_8) (M = 256.51 daltons; Space group *Fddd* (No. 70), $Z = 16$)

	T (Kelvin)			
	78^a	100^a	200^b	$298^{b,c}$
a (Å)	10.3801 (24)	10.3849 (15)	10.84191 (16)	10.4633 (17)
b (Å)	12.7465 (37)	12.7549 (23)	12.8208 (22)	12.8786 (23)
c (Å)	24.3961 (23)	24.4098 (15)	24.4474 (43)	24.4784 (45)
cos α	−0.0003 (2)	−0.0003 (1)	0.0003 (2)	0.0006 (3)
cos β	−0.0003 (2)	−0.0004 (1)	0.0001 (2)	−0.0001 (2)
cos γ	−0.0003 (4)	−0.0003 (2)	−0.0005 (2)	−0.0003 (2)
V_{cell} (Å^3)	3227.85	3233.29	3265.71	3298.53
$\rho_{\text{x-ray}}$ (g cm^{-3})	2.111	2.108	2.087	2.066
μ (cm^{-1})^d	20.16	20.13	19.93	19.73

[a] Lattice dimensions from least-squares refinement based on optimized setting angles for the 22 reflections in the {12 0 0}, {0 12 0}, {0 0 24}, {2 8 36}, and {8 2 36} forms. λ 0.709 26 Å (Mo Kα_1). [b] Lattic dimensions from least-squares refinement based on optimized setting angles for the 22 reflections in the {12 0 0}, {0 16 0l}, {0 0 24}, {7 7 17}, and {8 8 13} forms. λ 0.709 26 Å (Mo Kα_1). [c] Cf. a = 10.4646 (1) Å, b = 12.8660 (1) Å, c = 24.4860 (3) Å. A. S. Cooper, W. L. Bond, and S. C. Abrahams, *Acta Crystallogr.*, **14**, 1008 (1961), as cited by J. Donohue in "Elemental Sulfur, Chemistry and Physics", B. Meyer, Ed., Interscience, New York, N.Y., 1965, p 17. [d] Based on mass absorption coefficient μ/ρ = 9.55 cm^2 g^{-1} for sulfur at λ 0.7107 Å (Mo Kα). "International Tables for X-Ray Crystallography", Vol. 3, Kynoch Press, Birmingham, 1968, p 162.

vestigation of sulfamic acid, which has been the subject of a preliminary communication,[12b] a study of ammonium and sodium thiocyanate[13] and an analysis of S_4N_4 presently underway.

Experimental Section

X-ray Data Collection and Processing. Well-formed crystals of orthorhombic sulfur were grown by slow evaporation of carbon disulfide solutions. X-ray data were collected on an automated Picker FACS-1 diffractometer using Mo Kα radiation (λ 0.709 26 Å). A large data set collected on a crystal of 0.5 mm maximum linear dimension showed poor agreement between intense symmetry-related reflections. Since the discrepancies were most pronounced for the strongest reflections, anisotropy of extinction was suspected and confirmed by a much better agreement obtained with a smaller specimen crystal. The specimen used for both room and low temperature data collection showed only very small extinction effects (see below under refinement). Its total volume was 0.0072 mm^3, with largest dimension equal to 0.25 mm. It exhibited the forms {111}, {001} and the planes $(\bar{1}\bar{1}3)$, $(1\bar{1}3)$, and $(11\bar{3})$. At room temperature 6479 reflections were measured, including a full sphere (eight symmetry equivalents in the orthorhombic space group) below $2\theta = 30°$, and a hemisphere (four equivalents) up to $2\theta = 60°$ ($S = \sin\theta/\lambda = 0.705$ Å^{-1}). For low temperature data collection the crystal was sealed in a thin-walled glass capillary, which was mounted in a low temperature cryostat described elsewhere.[18] Reflections (11125) were collected at 100 K, including a full sphere of reflections below $2\theta = 30°$ and two symmetry equivalents (1 quadrant) up to $2\theta = 100°$ ($S = 1.08$ Å^{-1}). Crystal data including cell dimensions at four temperatures, are summarized in Table I.

For each reflection the full profile of a $\theta/2\theta$ step-scan was recorded on magnetic tape and analyzed to give the integrated intensity and its standard deviations.[19,20] An extensive analysis for multiple reflection, including an intensity estimate, indicated no significant effect for the general crystal orientation selected for data collection.

Symmetry equivalent reflections were averaged after absorption correction (μ = 19.73 cm^{-1}) rejecting 69 room temperature and 193 low temperature reflections with exceptionally large deviations from the average to give 1309 and 4077 independent data for room and low temperature structure refinement, respectively. Internal consistency agreement factors (analogous to $R(F^2)$) between symmetry related reflections were 2.5 and 3.8% at the two temperatures, the higher low temperature value being due to the larger number of weak high order reflections in this set.

Neutron Data Collection and Processing. Neutron data were collected at 298 K on a Hilger-Ferranti four-circle diffractometer at the DR reactor of the Danish Atomic Energy Commission Research Establishment at Risø. An approximately spherical single crystal of 6.6 mm diameter was mounted in an aluminum brace. The (002) reflection of a Be monochromator provided an incident neutron beam of λ 1.070 Å and a flux of about 0.8 × 10^6 neutrons cm^{-2} s^{-1}. Reflections (4400) were collected up to S = 0.68 Å^{-1} corresponding in nearly all cases to two symmetry equivalents. Intensity profiles were analyzed as describe elsewhere.[20] Averaging of symmetry-equivalent reflections after absorption correction (μ = 0.011 cm^{-1}) indicated an internal agreement factor of F^2 of 2.0% and gave 963 reflections for the least-squares refinement.

Least-Squares Refinement. Both room and low temperature data were refined by full-matrix least squares including adjustment of an isotropic extinction parameter and using as weights $w = 1/\sigma^2$ where $\sigma^2(I) = c^2I^2 + \sigma^2_{\text{counting}}$ with c = 0.03 and 0.02 for the room and low temperature data, respectively. As refinements minimizing $\sum w(F_o - |kF_c|)^2$ and $\sum w(F_o{}^2 - k^2F_c{}^2)^2$ give very similar results only refinements on F^2 will be reported here. Anomalous dispersion values for sulfur were taken from ref 23 ($\Delta f' = 0.1$, $\Delta f'' = 0.2$), and as reported by Wagenfeld[24] ($\Delta f' = 0.15$, $\Delta f'' = 0.13$). Since parameters agree within one standard deviation, except for the scale factor k which differs by 1–2σ, only the former treatment will be described. Two sets of scattering factors were used (a) those listed in ref 23, which are based on isolated atom Hartree–Fock (HF) calculations, and (b) isolated atom Hartree–Fock scattering factors for the core electrons (K and L shell) as given by Fukamachi[25] combined with scattering factors based on molecule-optimized Slater-type atomic orbitals with exponential value from Hehre, Ditchfield, Stewart, and Pople,[26] which are referred to hereafter as STO scattering factors. A third refinement in which the radial dependence of the sulfur valence shell was varied is described below. To minimize the effect of bonding on the x-ray atomic parameters, further refinements were performed using only the high-order reflections above S = 0.65 Å^{-1}. The room-temperature x-ray data were also refined after correction for thermal diffuse scattering according to a procedure described by Stevens,[27] using elastic constants from ref 28.

Standard deviations from the neutron refinement were derived as described for the x-ray data with c = 0.02. Refinement was again performed on F^2 and included an isotropic extinction parameter. In neither the x-ray or neutron data sets was extinction severe, the transmission factor y being always larger than 0.79 and 0.74 (but generally much closer to one) in the x-ray and neutron cases, respectively. Results of the refinements are summarized in Table II.

Experimental Determination of the Absolute Scale. Since the scale factor obtained by least-squares refinement depends on the choice of atomic scattering factors, information on the scattering factors may be obtained by an experimental determination of the absolute scale of the diffraction data. Measurements of the scale factor were made at room and low temperature using three different methods. The results which have been described in detail[29] are 2.19 (2) and 2.03 (2) at the two temperatures. Here and elsewhere in this article k is defined by $F(\text{obsd}) = kF(\text{calcd})$. The room temperature value agrees well with the scale factor from the refinement with optimized STO valence scattering factors, but the low temperature result appears too low in comparison with the least-squares values. The low temperature scale factor from the STO valence scattering refinement was selected in the calculation of the 100 K density maps.

Table II. Survey of Refinement Results[b]

A. Room Temperature Parameters[a]

	Scattering factors				
	HF (isolated atom)	HF core STO valence	HF after TDS correction	HF high order $S >$ 0.65 Å^{-1}	Neutron diffraction $b = 0.2847 \times 10^{-12}$ cm^{-1}
k	2.297 (5)	2.229 (5)	2.300 (5)	[2.20][a]	
S(1) x	0.855 78 (4)				0.855 87 (10)
y	0.952 69 (3)				0.953 15 (7)
z	0.952 69 (3)				0.951 52 (3)
S(2) x	0.784 05 (4)				0.784 26 (9)
y	0.030 24 (3)				0.030 02 (7)
z	0.076 26 (2)				0.076 21 (3)
S(3) x	0.707 18 (3)				0.707 28 (10)
y	0.979 67 (3)				0.980 04 (8)
z	0.004 09 (2)				0.004 10 (4)
S(4) x	0.785 97 (3)				0.785 99 (9)
y	0.907 65 (3)				0.908 01 (8)
z	0.129 54 (1)				0.129 51 (3)
$g \times 10^4$	5.6 (6)	7.7 (7)	4.7 (5)		
$\Sigma w\Delta^2$ ($N_{\text{obsd}} - N_{\text{var}}$)	1.29	1.33	1.33	1.58	2.19
$R(F)$	2.0	2.0	2.0	5.3	4.1
$R_w(F)$	2.7	2.7	2.7	4.9	2.1
$R(F^2)$	2.4	2.3	2.3	7.4	5.5
$R_w(F^2)$	5.4	5.5	5.2	10.2	4.1
		Temperature Parameters $U_{ij} \times 10^4$			
S(1) 11	608 (2)	590 (3)	619 (3)	584 (11)	561 (7)
22	391 (2)	374 (2)	401 (2)	380 (8)	343 (5)
33	335 (2)	320 (2)	341 (2)	331 (5)	284 (4)
12	35 (2)	34 (2)	35 (2)	25 (8)	39 (5)
13	52 (2)	52 (2)	52 (2)	54 (7)	46 (4)
23	78 (1)	78 (1)	78 (1)	76 (4)	
S(2) 11	581 (2)	567 (3)	593 (3)	572 (12)	534 (8)
22	370 (2)	353(2)	380 (2)	366 (7)	324 (5)
33	424 (2)	406 (2)	431 (2)	402 (7)	379 (5)
12	7 (2)	7 (2)	6 (2)	19 (7)	25 (6)
13	40 (2)	40 (2)	40 (2)	36 (8)	40 (4)
23	−90 (1)	−91 (1)	−90 (2)	−87 (6)	−93 (4)
S(3) 11	438 (2)	420 (2)	449 (3)	422 (10)	394 (6)
22	490 (2)	472 (2)	501 (3)	475 (10)	427 (6)
33	412 (2)	396 (2)	418 (2)	398 (7)	383 (5)
12	98 (2)	97 (2)	99 (2)	95 (8)	101 (5)
13	−50 (1)	−50 (2)	−50 (2)	−50 (8)	−56 (4)
23	18 (1)	18 (2)	18 (2)	22 (6)	16 (4)
S(4) 11	336 (2)	319 (2)	347 (2)	323 (8)	286 (5)
22	622 (2)	604 (3)	634 (3)	614 (11)	583 (7)
33	335 (2)	319 (2)	341 (2)	323 (6)	290 (4)
12	−17 (2)	−17 (2)	−18)2)	−15 (8)	−9 (5)
13	61 (1)	60 (1)	61 (2)	60 (6)	59 (4)
23	33 (1)	34 (1)	33 (2)	37 (6)	29 (4)

B. Low Temperature (100 K) Parameters[c]

	Scattering factors			
	I HF	II HF core STO valence	III HF $S > 0.65$ Å^{-1}	IV HF >0.75 Å^{-1}
k	2.203 (3)	2.17 (2)		
S(1) x	0.85576 (3)			
y	0.95367 (2)			
z	0.95063 (1)			
S(2) x	0.78417 (3)			
y	0.03215 (2)			
z	0.07599 (1)			
S(3) x	0.70603 (3)			
y	0.98106 (2)			
z	0.00361 (1)			
S(4) x	0.78528 (3)			
y	0.90851 (2)			
z	0.12969 (1)			
$g \times 10^4$	5.7 (4)	7.3 (3)		

Table II (*Continued*)

B. Low Temperature (100 K) Parameters[c]

	Scattering factors			
	I HF	II HF core STO valence	III HF $S > 0.65$ Å^{-1}	IV HF >0.75 Å^{-1}
$\Sigma w\Delta^2/(N_{obs} - N_{var})$	1.45	1.32	1.17	1.16
$R(F)$	2.9	2.9	5.1	6.4
$R_w(F)$	3.3	2.6	3.9	4.9
$R(F^2)$	2.8	2.8	6.4	8.4
$R_w(F^2)$	5.5	5.0	7.3	9.2
		Temperature Parameters $U_{ij} \times 10^4$		
S(1) 11	335 (1)	322 (1)	333 (2)	333 (4)
22	202 (1)	190 (1)	199 (2)	197 (3)
33	183 (1)	172 (1)	179 (1)	194 (2)
12	24 (1)	24 (1)	24 (1)	25 (2)
13	27 (1)	27 (1)	25 (1)	26 (2)
23	42 (1)	42 (1)	42 (1)	45 (2)
S(2) 11	330 (2)	319 (2)	329 (2)	330 (4)
22	193 (1)	181 (1)	190 (2)	188 (3)
33	227 (1)	216 (1)	223 (2)	220 (2)
12	9 (1)	9 (1)	10 (1)	11 (2)
13	16 (1)	17 (1)	17 (2)	19 (2)
23	−47 (1)	−47 (1)	−47 (1)	−47 (2)
S(3) 11	244 (1)	233 (1)	246 (2)	245 (3)
22	263 (1)	251 (1)	257 (2)	255 (4)
33	220 (1)	209 (1)	216 (2)	211 (2)
12	59 (1)	57 (1)	57 (1)	57 (2)
13	−30 (1)	−29 (1)	−28 (1)	−24 (2)
23	4 (1)	4 (1)	6 (1)	6 (2)
S(4) 11	180 (11)	170 (1)	179 (2)	175 (2)
23	329 (1)	316 (1)	328 (2)	324 (4)
33	185 (1)	174 (1)	180 (1)	176 (2)
12	−4 (1)	−4 (1)	−4 (1)	−4 (2)
13	33 (1)	33 (1)	32 (1)	33 (2)
23	21 (1)	21 (1)	18 (1)	19 (2)

[a] Not varied. [b] Positional parameters from all x-ray refinements are identical within the experimental errors. [c] The expression for the temperature factor is $\exp[-2\pi^2(U_{11}a^{*2}h^2 + 2U_{12}a^*b^*hl + \ldots)]$. For numbering of atoms, see Figure 1. [d] Positional parameters from all x-ray refinements are identical within the experimental errors.

Table III

		298 K X-ray		100 K X-ray	
Bond lengths and angles	Neutron	All data	$\sin\theta/\lambda >$ 0.65 Å^{-1}	All data	$\sin\theta/\lambda >$ 0.65 Å^{-1}
S(1′)-S(1)	2.044 (3)	2.041 (1)	2.042 (6)	2.046 (1)	2.046 (2)
S(1)-S(3)	2.050 (3)	2.049 (1)	2.049 (6)	2.052 (1)	2.053 (2)
S(3)-S(2)	2.045 (3)	2.047 (1)	2.045 (6)	2.051 (1)	2.051 (2)
S(2)-S(4)	2.046 (3)	2.048 (1)	2.050 (6)	2.051 (1)	2.051 (2)
S(4)-S(4′)	2.045 (3)	2.044 (1)	2.042 (6)	2.050 (1)	2.049 (2)
S(1′)-S(1)-S(3)	108.4 (1)	108.40 (4)	108.5 (2)	108.35 (4)	108.4 (1)
S(1)-S(3)-S(2)	107.4	107.37	107.6	107.29	107.3
S(3)-S(2)-S(4)	108.1	107.95	108.1	107.97	108.0
S(2)-S(4)-S(4′)	109.1	109.03	109.2	109.01	109.1

Results and Discussion

Refinements Results. Atomic coordinates from the x-ray and neutron refinements (Table II) agree within two standard deviations for the x and z parameters, but discrepancies for the y parameters range up to about $6\sigma = 0.005$ Å for S(1). The coordinate differences could be due to asphericity shifts observed previously in light-atom molecules, but the shifts were not reduced in the high-order x-ray refinement which suggests that other sources of error affect the parameters. Bond lengths before and after correction for thermal shortening based on a rigid body model are given in Table III and are not significantly different from those published by Caron and Donohue,[17] though the standard deviations are smaller in the present x-ray study. There is also good agreement between our room and low temperature values, indicating the validity of the correction for apparent thermal shortening and suggesting that the x-ray values may be more accurate than the neutron results. It may be noted that at the level of precision of the present experiment, in which least-squares standard deviations in the bond lengths are less than 0.001 Å, other considerations such as the difference between equilibrium bond length R_e and mean bond length R_g will limit the accuracy of the results.

Thermal motion parameters with the STO scattering factors

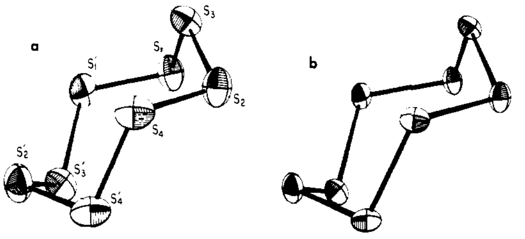

Figure 1. The sulfur molecule and the atomic thermal motion ellipsoids (50% probability ellipsoids). Primed atoms are symmetry related to unprimed atoms with the same number: (a) at 300 K, (b) at 100 K.

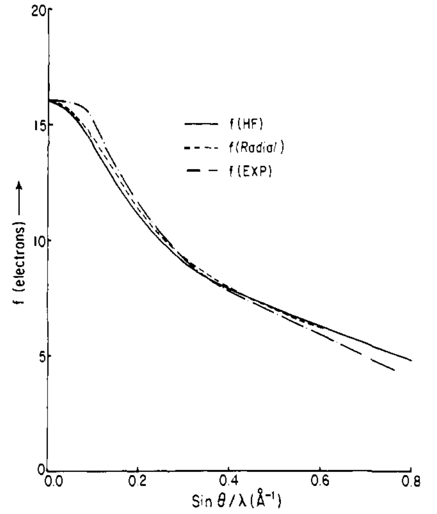

Figure 2. Experimental scattering factor f(exp) compared with the isolated atom scattering factor f(HF) and the results of the orbital exponent refinement f(radial). Orbital exponent refinements results with two different starting sets (see text) coincide in this figure.

are smaller thn values obtained with HF scattering values (Table II) as observed in previous studies.[30] ORTEP[31] plots of the x-ray thermal vibrations (with HF scattering factors) are given in Figure 1. The 100 K diagonal elements of the thermal displacement tensor are typically 50–60% of the room temperature values, so that the reduction is considerably less than the ratio of absolute temperatures. Nevertheless, reasonable fit to a rigid body analysis is obtained at both temperatures, but, as Pawley and Rinaldi have shown,[32] in the case of a highly symmetric molecule such as cyclooctasulfur internal modes can be easily absorbed in a rigid body description of the molecule.

The neutron thermal parameters U_{ii} are smaller than the corresponding x-ray values, the average of the ratio's $(U_{ii})_N/(U_{ii})_X$ being 0.89 (0.92 when comparison is made with the high order refinement). Systematic discrepancies of the same sign between x-ray and neutron thermal parameters have been observed before,[33] but the effect observed here is larger than would be expected for sulfur atoms which have a relatively unperturbed core of ten electrons. The neutron values are also considerably smaller than the temperature factors from the STO x-ray refinement.

The Radial Dependence of the Sulfur Atom Density. As the sulfur crystal contains only one type of atom, it provides an excellent opporunity for analysis of the radial dependence of the sulfur atom density, or, in other words, for an experimental determination of the scattering factor of the bonded sulfur atom. Two approaches have been followed here. The first is based solely on the x-ray data and allows the atomic scattering factor to contract or expand through the use of a parameter (κ) such that true valence scattering factor f at $\sin\theta/\lambda = S$ is given by

$$f_{\text{val}}(S) = f'_{\text{val}}(S/\kappa)$$

where f' is the valence scattering factor of the isolated (free-space) atom.[34] Simultaneous refinement of the parameter κ along with the other structural parameters shows the valence shell to be *contracted* relative to the isolated atom Hartree-Fock orbitals, with κ = 1.028(11) and 1.040(5) (weighted average 1.038(5)) for room and low temperature data, respectively, but *expanded* relative to the molecule optimized STO orbitals[26] for which κ = 0.956 (9) and 0.977 (5) at the two temperatures (weighted average of 0.972 (4)). It is very satisfying that the κ-corrected HF and STO scattering factors practically coincide (Figure 2); the most appropriate scattering factor being intermediate between the two starting curves. This is further demonstrated when the best single ζ values for the atom (ζ = 1.91 for the isolated atom; ζ = 2.05 a_0^{-1} according to ref 26) are multiplied by the respective κ values of 1.038 and 0.972. This leads to orbital exponents of 1.983 and 1.992 a_0^{-1}, respectively. The average value of 1.99 a_0^{-1} is clearly the best experimental single ζ value in the S_8 molecular environment. As might be expected, the temperature parameters from the κ refinement are intermediate between values listed in Table II from the HF and STO refinements.

The second approach is based on the combined x-ray and neutron data. For a centrosymmetric monatomic (i.e., elemental) crystal the x-ray scattering factor in the spherical approximation may be written as

$$F(\mathbf{H}) = f(\mathbf{H}) \sum_{\substack{\text{all} \\ \text{atoms } i}} \cos 2\pi(\mathbf{H}\cdot\mathbf{r}_i)\ T_i(\mathbf{H}) \equiv f(\mathbf{H})G(\mathbf{H})$$

where **H** is the reciprocal space vector represented by the Miller indices h, k, l and $\mathbf{r}_i$ is the position vector of the ith atom. The function G represents the sum of the geometrical cosine terms times the atomic temperature factors T_i, and can be obtained from the neutron diffraction results. Thus,

$$f_{\text{obsd}}(\mathbf{H}) = F(\mathbf{H})/G(\mathbf{H})$$

which, upon averaging of observations in the same $\sin\theta/\lambda$ range gives

$$f_{\text{obsd}}(S) = \langle F(\mathbf{H})/G(\mathbf{H})\rangle_S$$

This function is represented by the broken curve in Figure 2 and it straddles the κ refinement results. The larger values of low S represent a contraction of the density at distances away from the nucleus in real space, while the smaller values at high S represent an expansion of the density near the nucleus, the total effect being more complex than representable by a single κ parameter. The low value of the observed f beyond $\sin\theta/\lambda$ = 0.4 Å^{-1} results mainly from the difference between x-ray and neutron thermal parameters and is therefore sensitive to systematic errors in the thermal parameters or temperature discrepancies between the two experiments.

Electron Density Maps. Electron density maps used here represent deformation densities (i.e., the observed density ρ_{obsd} minus the density corresponding to the sum of spherical atoms centered at the nuclear positions). The designations X–N and X–X refer to maps in which respectively neutron or high-order x-ray atomic parameters are used to calculate the spherical atom density that is subtracted from the observed density.[2a]

The high symmetry of the sulfur molecule, which contains four chemically equivalent but crystallographically distinct atoms, allows averaging of the densities over chemically equivalent groups and a concomitant reduction in the experimental standard deviations. Room temperature X–N maps averaged over all four S–S–S groups and obtained with the experimental scale factor value are shown in Figure 3. They

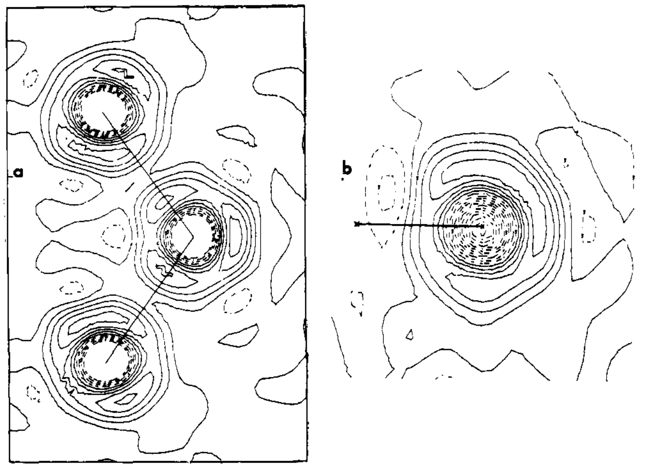

Figure 3. X–N deformation density (300 K) with experimental scale factor each averaged over four chemically equivalent planes in the molecule: (a) in plane of SSS (left- and right-hand sides averaged), (b) in the plane bisecting the two S–S bonds. The horizontal line indicates the projection of the bonds. Contours at 0.10 e Å^{-3}, negative contours broken. Contours below −0.4 e Å^{-3} have been omitted.

indicate a contraction of the density at about 0.6 Å from the nucleus and an expansion near the nucleus, in agreement with the conclusions reached earlier on the basis of the spherically averaged scattering factor curves of Figure 2.

In crystal space it is the region near the nucleus which is very much dependent on the exact value of scale and temperature parameters. This is demonstrated by the densities obtained with different scale factors[29] and also by the X–X maps at both 300 and 100 K (Figure 4) which show a peak rather than a trough at the nucleus when the high order thermal parameters are used. As the high order thermal parameters at room temperature are about 8% higher than the values obtained from the neutron refinement we have repeated the calculation of the low temperature X–X charge distribution after multiplication of each U_{ij} value by the factor 0.92 to analyze the effect of a possible bias in the thermal parameters. The results shown in Figures 4c and d are similar to the room temperature X–N maps.

An estimate of the standard deviations in the density may be obtained with the assumption that the errors in the observed structure factors and the refined parameters are uncorrelated. The variance in the experimental deformation density is then given by[35]

$$\sigma^2(\rho) = \sigma^2(\rho_{\mathrm{obsd}}) + \sigma^2(\rho_{\mathrm{calcd}}) + (\sigma^2(k)/k^2)\rho^2_{\mathrm{obsd}} + R$$

The first term represents the measurement error; the second and third terms allow for errors in the atomic parameters and the scale factor, respectively, while the residual term R accounts for the effect of correlation between the refined parameters. The error is position dependent and its distribution in the plane of the three sulfur atoms is shown in Figure 5. In calculating this function the reduction in error on averaging of the four chemically equivalent S–S–S regions has been taken into account. The error is very large at the nuclear position (~0.77 e Å^{-3}), as already suggested by comparison of Figures 4a and 4c, but diminishes rapidly to about 0.05 e Å^{-3} at the bond midpoint and in the remainder of the interatomic region. At the position of the bond maxima which have a height of 0.43 e Å^{-3} the error is 0.07 e Å^{-3}, so that the observed contraction at 0.6 Å from the nucleus is significant.

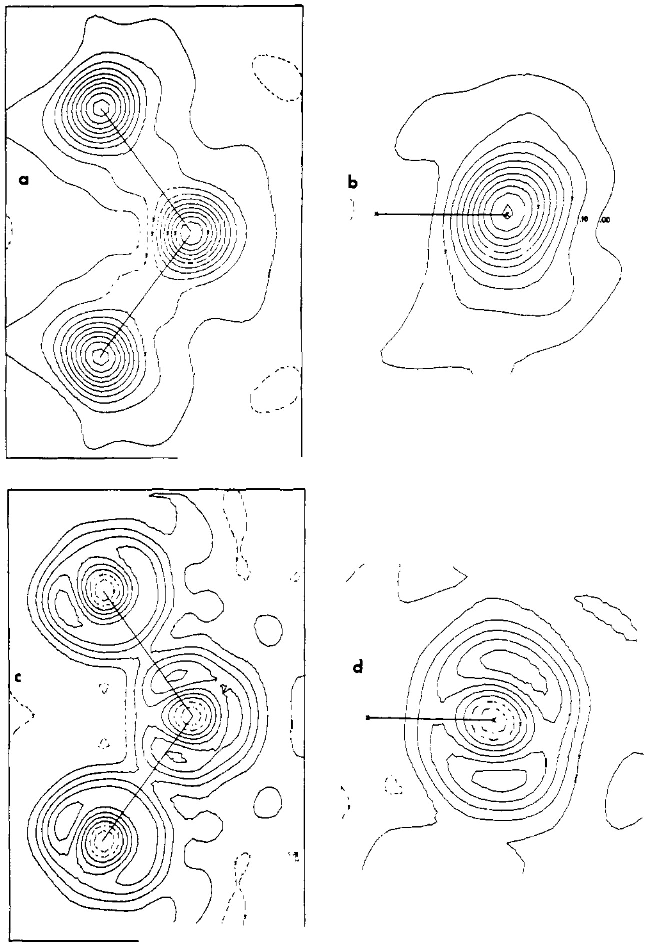

Figure 4. (a) X–X deformation density at 100 K in the plane of SSS with scale factor from HF core, STO valence refinement (Table II). Contours and averaging as in Figure 3a; (b) as 4a bisecting the two S–S bonds; (c) as 4a with $U'_{ij} = 0.92U_{ij}$; (d) as 4b with $U'_{ij} = 0.92U_{ij}$. Note that 4a–b and 4b–c both indicate excess density at 0.6 Å from the nucleus and an extension of the sulfur atom density in the direction perpendicular to the plane of the S–S bonds.

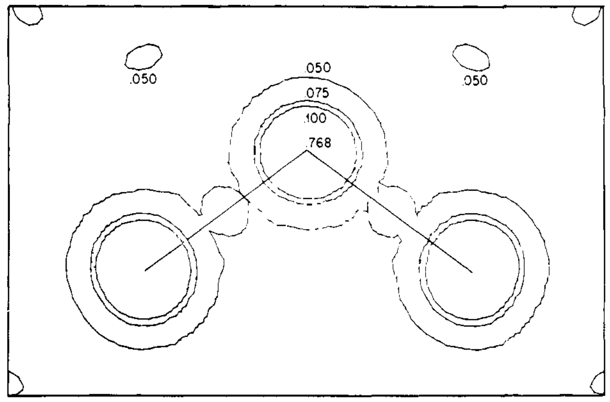

Figure 5. Error function in the plane of SSS for the room temperature X–N map, contours at 0.025 e Å^{-3}. Contours above 0.10 e Å^{-3} have been omitted. The error function is maximum at the nucleus where it has a value of 0.77 e Å^{-3}.

Figure 3b represents the deformation density in the plane bisecting the two sulfur–sulfur bonds and shows that the contraction is not confined to the plane of the bonds. In this room temperature map there is no clear evidence for directional character of the sulfur lone pair electrons, but Figure 4b which is based on the low temperature data shows the deformation density on the sulfur atom to be ellipsoidal in the S–S–S bisecting plane with the longest ellipsoid axis perpendicular to the plane of the bonds. The nature of the deformation density is further illustrated in Figure 4d in which the reduction of the

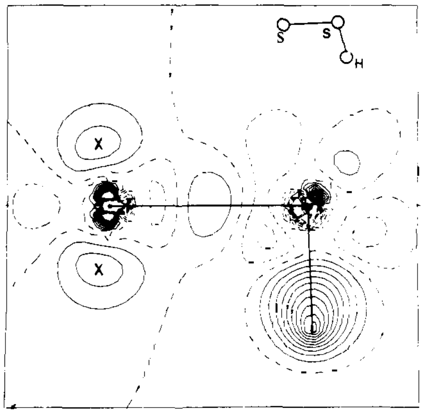

Figure 6. Theoretical deformation density for H_2S_2 according to Rys and Dupuis:[36] Gaussian basis set (12, 7, 1/5, 1) contracted to (7, 5, 1/4, 1); crosses indicate residual density in the sulfur lone pair regions; contours at 0.1 e Å^{-3}; geometry, S–S = 2.055 Å, S–H = 1.327 Å, ∠SSH = 91°20′, dihedral angle (HSS) (SSH) = 90°45′.

thermal parameters has removed the experimentally nonsignificant peak at the nuclear position. In this figure remaining "lone pair" density is seen above and below the SSS planes corresponding approximately to a p atomic orbital. The maxima are slightly asymmetric and extend somewhat towards the back of the sulfur atom suggesting a small s contribution to the lone pair hybrid. We note that though at first sight Figures 4c and d appear very different from 4a and b, the differences occur especially in the region close to the nucleus where the experimental error is very large. The two sets of maps have in common the main features discussed above, i.e., the extension of the density perpendicular to the plane of the bonds and the excess density at 0.6 Å from the nucleus, which are therefore well established.

The distributions 4a and 4b are, of course, the ones that are firmly based on the low temperature experimental results. The source of uncertainty is the as yet unexplained 8% difference between the high-order x-ray and neutron thermal parameters at *room temperature.* This discrepancy if physically significant implies an effect of chemical bonding on the inner shells of the sulfur atom. But, the possibility of unrecognized systematic errors in either the x-ray or neutron room temperature experiment cannot be ruled out at this moment.

An ab initio calculation of the cyclooctasulfur molecule with the extended basis-set required to obtain a reliable deformation density is not available, but comparison may be made with theoretical results on H_2S_2 obtained by Rys and Dupuis of our department[36] and reproduced in Figure 6. The dihedral angle in H_2S_2 is nearly 90°, so the section shown in the figure contains the SS and SH bonds and the plane perpendicular to the second SH bond. The density maximum in the S–S bond (l = 2.055 Å) is low as observed experimentally in the present study of cyclooctasulfur, but no contraction of the density around the sulfur atom appears in the theoretical map except at 90° to both S–S and SH bonds. These peaks (marked ×) are interpreted as the sulfur atom lone pair peaks and are analogous to the experimental maxima in Figure 4d. In both cases, the positions of the maxima are somewhat displaced from the perpendicular to the two bonds formed by the sulfur atom. In this respect both experiment and theory approximately but not exactly support qualitative discussions of sulfur bonding which often assume p hybridization of the sulfur lone pair orbitals.[37] On the other hand, the discrepancy between theory and experiment may very well be due to the different environments of the sulfur atoms in H_2S_2 and S_8 and does not necessarily indicate a shortcoming in either technique.

Finally, no density is observed between two sulfur atoms at 3.33 Å distance indicating the absence of a significant covalent interaction. Several compounds with S···S distances between the values found in cyclooctasulfur (2.05 and 3.33 Å) will be the subject of further studies.

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