recognition. The alternative assignment of the N–H protons to the otherwise unexplained lines at δ 1.52 or 2.5 is unpalatable since it implies a much larger change in ring current effect than is evidenced by the resonance frequency of the methine protons.

Tetra-benz-tetra-aza-porphin (Phthalocyanine).[16] —The spectrum of this compound dissolved in concentrated D_2SO_4 consists of two lines (half-width $\sim$15 c.p.s.) at δ 8.52 and 9.59 (measured as described in the Experimental Section). In sulfuric acid solution phthalocyanine is almost certainly in the di-cation form, and the four benz-pyrrole rings are thus equivalent through resonance interaction. The two lines must arise from the non-equivalent protons α and β to the pyrrole ring. Since these protons constitute an A_2B_2 or A_2X_2 system, the lines are expected to be split into complex multiplets.[17] The observed width of

15 c.p.s. is large enough to obscure such splitting; indeed, the width probably results partially from unresolved splitting and partially from hindered molecular rotation in the viscous solvent. No N–H line was observed, presumably due to exchange with deuterium in the solvent.

Applications to Porphyrin Structure Studies.— The tabulation of characteristic chemical shifts for a number of porphyrins opens the way for the use of this technique in structure elucidation of porphyrins and related molecules. The differences shown in the spectra of the closely related isomers coproporphyrin-1 and -3 indicate that in suitable cases n.m.r. will be a powerful analytical tool in porphyrin research. Further studies of known porphyrins may permit the development of a more complete relation between chemical shifts and specific locations of functional groups, thereby considerably extending the utility of the technique.

(16) This sample was supplied by Dr. R. Livingston of the University of Minnesota to Dr. E. Charney of the NIH, and Dr. Charney made a portion of it available for this work.

(17) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw–Hill Book Co., New York, N. Y., 1959.

The Crystal and Molecular Structure of S₆ (Sulfur-6)

BY JERRY DONOHUE, AIMERY CARON AND ELIHU GOLDISH

An X-ray crystallographic study of rhombohedral sulfur has been carried out. The crystals consist of hexameric molecules, S₆, with symmetry $\overline{3}m$. Fourier and least squares refinement of the atomic parameters give the following structural quantities: S–S bond length, 2.057 ± 0.018 Å., S–S–S bond angle, 102.2 ± 1.6°, S–S–S–S torsion angle, 74.5 ± 2.5°. These values are compared with those found in orthorhombic sulfur, S₈, and are used in a discussion of the potential function for rotation about the S–S bond together with the S–S–S bending force constant.

Introduction

An allotrope of sulfur discovered by Engel[1] was shown to be a hexamer by Aten.[2] The results of an incomplete X-ray study by Frondel and Whitfield[3] together with the morphological observations of Friedel[4] prompted Donnay[5] to suggest that the substance was rhombohedral, space group $R\overline{3}$ (C_{3i}^2, No. 148) with six atoms in a unit cell having $a = 6.45$ kX., $\alpha = 115°$ 18'. The corresponding hexagonal lattice constants are $A = 10.9$ kX., $C = 4.26$ kX. These conclusions were verified in our preliminary note.[6] We wish now to report the results of our refinement of this structure.

Experimental

Crystals of S₆ were prepared by the method described by Aten.[2] They were mounted in the usual way, and intensity data were collected for the $(hk0)$ and $0kl$ zones in a Weissenberg camera with unfiltered CuKα radiation. The exposure times were limited to about an hour by the instability of the crystals, but the intensity range of the reflections was increased by using small angles of oscillation. Intensities were estimated visually. The $(hk0)$ intensities were corrected for absorption by use of the powder rod formula and the value 0.25 mm. for the radius. No cor-

rection was applied to the $(0kl)$ reflections because the crystal used was much smaller.

The lattice constants were determined from a multiple exposure powder photograph. The hexagonal unit cell was chosen for use in this and all calculations in preference to the rhombohedral one.[7] The powder data, which are given in full elsewhere,[8] give the following results

$A = 10.818 ± 0.002$ Å., $C = 4.280 ± 0.001$ Å.

$$(\lambda\ CuK\alpha = 1.5418\ \text{Å.})$$

In agreement with the results of Frondel and Whitfield[3] it was found that the axis of symmetry was threefold and that there were no vertical planes of symmetry. As predicted by Donnay,[5] only those reflections having $-h+k+l = 3n$ were observed. The space group is therefore established as $R\overline{3}$. The calculated density for 18 sulfur atoms per unit cell is 2.21 g. cm.⁻³, as compared with the observed value[1] of 2.14 g. cm.⁻³.

Derivation of the Structure.—The general position of the space group is 18-fold. There are thus three positional parameters to be determined. The required molecular symmetry is $\overline{3}$. Trial values for x and y were obtained by assuming S₆ molecules having bond lengths 2.04 Å. and bond angles 104° and then applying the method of Knott.[9] F values for the $(hk0)$ reflections were calculated, and the signs of all 25 of them could be assigned with confidence. The form factor for

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(2) A. Aten, Z. physik. Chem., 88, 321 (1914).

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(4) C. Friedel, C. R. Acad. Sci. Paris, 112, 834 (1891).

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(7) M. J. Buerger, "Elementary Crystallography," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 106.

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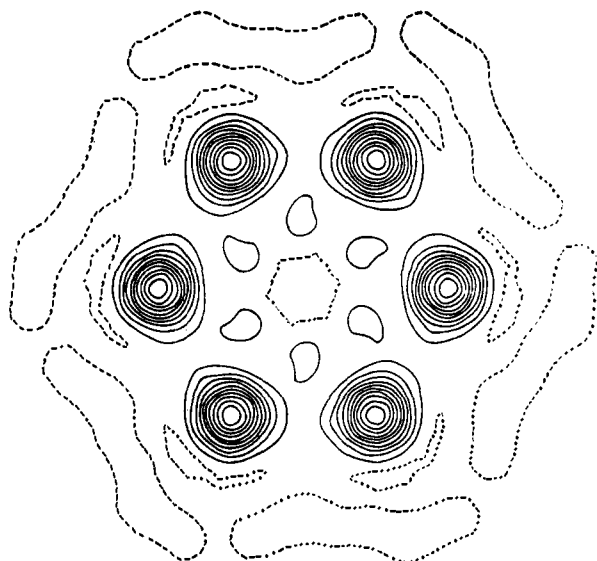
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Fig. 1.—Electron-density projection on (001). Contours at intervals of 2.5 e.Å.$^{-2}$; the zero contour is dashed.

sulfur determined experimentally by Abrahams[10] in his refinement of the structure of orthorhombic sulfur was used in these calculations. New values for x and y were obtained from a projection of the electron density on (00.1), which is shown in Fig. 1. This figure differs from the one given in our preliminary note because the coefficients used have now been corrected for absorption. It is interesting that this correction leads to changes of only 0.001 Å. in x and 0.004 Å. in y. A projection made with calculated F values was then used to estimate the series termination corrections. These corrections were −0.001 Å. in x and −0.012 Å. in y.

The $(hk0)$ data were next treated by the method of least squares, with the two positional parameters, the scale factor and an isotropic temperature factor, B, as variables. The peak shape in Fig. 1 shows that anisotropic temperature factors are not required. Two cycles of least squares led to changes of − 0.011 Å. in x and − 0.024 Å. in y, and of + 0.423 Å.^{2} in B. The changes in x and y between the first and second cycles of least squares were both 0.001 Å., showing that convergence had been attained. The progress of the refinement of the x and y parameters is presented in Table I.

TABLE I

VALUES OF x AND y OBTAINED BY VARIOUS METHODS

	x	y
Knott's method	0.145	0.189
Fourier uncor. for absorption	.1459	.1904
Fourier cor. for absorption	.1460	.1900
Fourier cor. for absorption and termination errors	.1459	.1889
Initial least squares values	.1458	.1896
Least squares values after the first cycle	.1447	.1873
Least squares values after the second (and last) cycle	.1448	.1874
Final values	.1454	.1882
σ	.0012	.0016

The assumed trial model allows two values for the z parameter, ca. + 0.1 or − 0.1. Structure
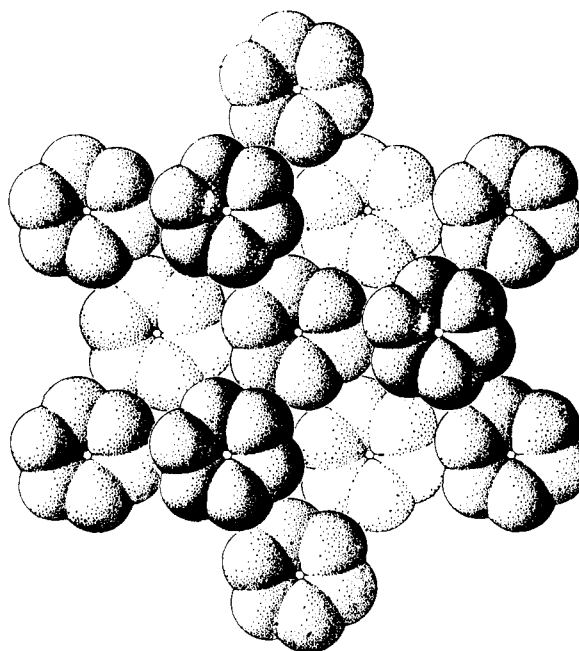
(10) S. C. Abrahams, Acta Cryst., 8, 661 (1955).

Fig. 2.—The structure viewed along [001].

factor calculation of the $(0kl)$ reflections gave for the former an R value of 19%, for the latter, 50%. Starting from the value + 0.1, the z parameter, the scale factor, and temperature factor dependent on l^2 were refined by least squares. This procedure gave an optimum value for z of + 0.1055, σ = 0.0020, and a B value of − 0.89 Å.^{2} relative to the f curve of Abrahams.[10]

The observed and calculated structure factors are presented in Table II. The conventional discrepancy figures are $R(hk0)$ = 13.2%, $R(0kl)$ = 11.3%, R (over-all) = 12.5%. These could doubtless be made smaller by the pointless device of constructing an empirical f-curve different from that of Abrahams.

Discussion

The S_6 molecule is a puckered ring with the chair conformation. The S–S bond length is 2.057 ± 0.018 Å., the S–S–S bond angle, ϑ, is 102.2 ± 1.6°, and the S–S–S–S torsion angle, φ, is 74.5 ± 2.5°. The uncertainties quoted are standard errors. These values, together with the corresponding values for S_8 in orthorhombic sulfur,[10−13] and the significance levels of the differences, are compared in Table III. It should be noted that while the bond lengths are not significantly different, the bond angles are and the torsion angles highly so.

The intermolecular contacts are listed in Table III. Each sulfur atom is virtually equidistant from three sulfur atoms in neighboring molecules so that each molecule has eighteen such contacts. The next shortest distances are 3.75 Å. (6 per molecule) and 3.85 Å. (12 per molecule). The large number of nearly equal short intermolecular contacts leads to a very efficient packing, as shown in Fig. 2. In the case of orthorhombic sulfur, the number of such contacts per molecule is smaller

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TABLE II
OBSERVED AND CALCULATED STRUCTURE FACTORS

h k l	$F_{calcd.}$	$F_{obsd.}$	h k l	$F_{calcd.}$	$F_{obsd.}$	h k l	$F_{calcd.}$	$F_{obsd.}$
1 1 0	61.4	84.3	7 1 0	8.7	<16.0	0 2 4	23.7	<69.7
1 4 0	-84.9	74.3	7 4 0	-32.0	37.9	0 5 4	30.0	<64.6
1 7 0	-50.0	59.8	8 2 0	-29.4	37.1	0 8 4	47.7	48.0
1.10.0	-14.0	12.5	8 5 0	-1.9	<6.7	0 1 5	-66.7	<55.9
2 2 0	-145.9	149.8	9 0 0	-51.9	58.8	0 4 5	4.1	<45.2
2 5 0	-98.1	91.3	9 3 0	46.1	40.8	0 1 $\bar{1}$	210.9	179.8
2 8 0	35.2	43.8	10.1.0	1.0	<9.3	0 4 $\bar{1}$	-132.6	156.6
3 0 0	-156.6	143.0	12.0.0	-17.0	11.2	0 7 $\bar{1}$	6.9	<65.8
3 3 0	29.4	32.6	0 2 1	54.6	62.5	0.10.$\bar{1}$	-65.6	74.8
3 6 0	-23.4	26.2	0 5 1	97.2	129.0	0 2 $\bar{2}$	-87.0	74.3
3 9 0	45.1	38.3	0 8 1	13.1	<69.4	0 5 $\bar{2}$	-6.9	<61.4
4 1 0	147.0	130.0	0.11.1	-43.7	<43.7	0 8 $\bar{2}$	-91.0	104.3
4 4 0	-27.1	37.3	0 1 2	70.1	60.3	0.11.$\bar{2}$	16.2	<36.3
4 7 0	70.6	76.0	0 4 2	113.5	112.5	0 3 $\bar{3}$	-64.5	64.5
5 2 0	191.7	163.8	0 7 2	11.2	<69.2	0 6 $\bar{3}$	-5.9	<69.7
5 5 0	-36.7	46.8	0.10.2	34.5	<53.8	0 9 $\bar{3}$	-54.7	57.8
5 8 0	14.9	10.6	0 0 3	-102.1	92.3	0 1 $\bar{4}$	-91.7	81.8
6 0 0	100.5	90.0	0 3 3	129.6	119.1	0 4 $\bar{4}$	-14.2	<67.7
6 3 0	-25.2	39.4	0 6 3	-47.8	<69.7	0 7 $\bar{4}$	-9.2	<51.3
6 6 0	-13.2	11.7	0 9 3	92.2	87.9	0 2 $\bar{5}$	8.2	<54.0
						0 5 $\bar{5}$	-24.5	<36.6

TABLE III
DISTANCES AND ANGLES IN S_6 AND S_8

	S_6	S_8	P^a
Bond length	2.057 ± 0.018 Å.	2.059 ± 0.002 Å.	91
Bond angle	102.2° ± 1.6°	107.9° ± 0.6°	0.08
Torsion angle	74.5° ± 2.5°	98.9° ± 0.7°	≪0.002
Shortest intramolecular non-bonded distance	3.202 Å.	3.312 Å.	
Van der Waals distances shorter than 3.850 Å.,	3.501 Å. (12)	3.374 Å. (2)	
followed by the number of such distances per	3.526 Å. (6)	3.504 Å. (4)	
molecule	3.749 Å. (6)	3.703 Å. (4)	
		3.773 Å. (2)	
		3.803 Å. (4)	
		3.815 Å. (4)	
		3.826 Å. (4)	
		3.828 Å. (4)	

ᵃ Percentage probability that the two distances or angles are different by chance only.

(see Table III), a fact which partially accounts for the lower density of 2.07 g. cm.$^{-3}$ for that substance, as compared with the value 2.21 g. cm.$^{-3}$ for rhombohedral sulfur, although the larger hole in the center of the 8-ring molecule certainly must be a factor here also.

In an earlier discussion, Pauling[14] proposed that the stability associated with the S_8 molecule could be explained on the basis of the "normal" values for the angles ϑ and φ and pointed out that for symmetrical staggered rings containing n atoms (n even), with point-group symmetry $\bar{n}m2$ (not D_{nh}, as stated by Pauling), ϑ and φ are not independent, but are related by the equation

$$\sin^2 \frac{\varphi}{2} = \frac{\cos(2\pi/n) + \cos \vartheta}{1 + \cos \vartheta} \quad (1)$$

This function, for $n = 6$ and 8, is shown in Fig. 3. The data then available suggested that the normal values for the angles were $\vartheta_0 = 105°$, $\varphi_0 = 100°$; the deviations of φ from this value, for $\varphi = 105°$, are, for 6, 8 and 10 membered rings, 30°, 2° and 19°, respectively, and this fact accounted for the stability of the S_8 molecule. The normal value for φ was stated by Pauling to be a consequence mainly

of the repulsion of the pπ electrons, which, "according to simple theory," is proportional to $\sin^2\varphi$. This discussion was modified recently by Pauling[15]: he assumed: (i) that the energy as a function of φ had the simple form $E = A \cos \varphi + B \cos^2 \varphi$; (ii) that φ_0 was 102° as indicated by the data on S_8[16,17]; (iii) that the S_8 molecule was unstrained; (iv) that the S_6 molecule had $\vartheta = 104°$ and $\varphi = 71°$; (v) that all the strain in this molecule was torsion strain; and (vi) that the values given by Rossini, et al.,[18] corresponded to a difference in enthalpy of S_6 and S_8 of 1.10 kcal./mole per S–S bond. These assumptions lead to $A = 1.6$ kcal./mole and $B = 3.9$ kcal./mole (not vice versa as given by Pauling).

However, not only are more accurate data for orthorhombic sulfur available, but also the present study gives values for ϑ and φ in S_6 which are a little different from those assumed above (see Table III). Furthermore there is additional information

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TABLE IV

MOLECULAR CONSTANTS FOR SULFUR

	ϑ_0	φ_0	Bending force constant[a] in: S₆	S₈	c_1	c_2	Barrier[b] to rotation at φ = 0°	180°	Assumptions[c]
A	106.4	91.2	(154)	(154)	12.61	0.53	13.1	12.1	Spectroscopic $\overline{k}$ for S₆ and S₈
B	106.6	(92.0)	133 (=)	133	10.85	.76	11.6	10.1	Obsd. $\overline{\varphi}_0$, $k(S_6) = k(S_8)$
C	(106.9)	(92.0)	122	170	10.52	.73	11.3	9.8	Obsd. $\overline{\vartheta}_0$, obsd. $\overline{\varphi}_0$
D	(106.9)	93.4	108 (=)	108	8.64	1.07	9.7	7.6	Obsd. $\overline{\vartheta}_0$, $k(S_6) = k(S_8)$
E	(106.9)	(94.6)	74	101	7.54	1.21	8.8	6.4	Obsd. $\overline{\vartheta}_0$, φ_0 from Fig. 5
F	(107.9)	(98.9)	65	...	4.90	1.52	6.5	3.5	S₆ strainless

[a] In kcal./rad.²/mole.   [b] In kcal./mole.   [c] Assumed values are in parentheses in body of table.

concerning the normal values ϑ_0 and φ_0, and, finally, the values in the National Bureau of Standards Tables give 1.20 kcal./mole per S–S bond for the enthalpy difference.

The average value of seven different S–S–S bond angles as observed in BaS₄·H₂O,[19] Cs₂S₆[20] and (CH₃)₂S₃[21] is 106.9°. The observed equilibrium values for S₆ and S₈, as shown in Fig. 4, then imply a value for φ_0 of about 94.6°. Observed values of S–S–S–S, C–S–S–S, C–S–S–C and Cl–S–S–Cl torsion angles show a rather wide scatter: five values in the two polysulfide ions mentioned above average to 74.6°; six values in neutral molecules and in ions where the charge is not on the sulfur atoms, viz., diglycylcystine,[22] S₂Cl₂,[23] (CH₃)₂S₃, cystine,[24] cystine dihydrochloride[25] and cystine dihydrobromide[26] average to 92.0°. Distortions apparently occur in the crystals containing the polysulfide ions.

Although the S₆ molecule is strained relative to the S₈ molecule, it would be a remarkable coincidence if the S₈ molecule were not strained at all relative to the normal values of both ϑ and φ. Indeed, the average values quoted above do in fact lead to a small strain in the S₈ molecule.

We assume that the energy per atom of a sulfur ring is given by the function

$$E(\vartheta, \varphi) = c_1 \cos 2\varphi + c_2 \cos \varphi + \frac{1}{2}k(\vartheta_0 - \vartheta)^2 \quad (2)$$

The strain energy is then given by the expression

$$E_{strain} = E(\vartheta, \varphi) - E(\varphi_0, \varphi_0) \quad (3)$$

There are thus six constants to be evaluated: ϑ_0, φ_0, $k(S_6)$, $k(S_8)$, c_1 and c_2. The experimentally observed quantities are: (i) the equilibrium angles in S₆, (ii) the equilibrium angles in S₈, and (iii) the difference in enthalpy between S₆ and S₈. In addition, the values $\vartheta_0 = 106.9°$ and $\varphi_0 = 92.0°$ are suggested by the limited molecular structure data, but the more reliable value of $\vartheta_0 = 106.9°$ implies the slightly different value for φ_0 of 94.6°. Furthermore, the S–S–S bending force constant may be estimated from the spectroscopic data of

Stammrich, Forneris and Sone[27] for SCl₂ and of Linton and Nixon[28] for S(SiH₃)₂; the respective values are 173 kcal./rad.²/mole and 135 kcal./rad.²/mole. A summary of the values of molecular constants, as obtained under various assumptions, is presented in Table IV, where it may be
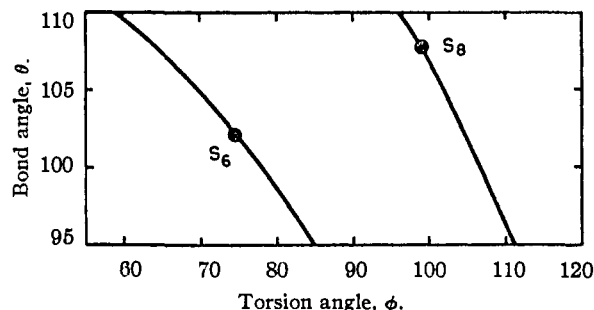

Fig. 3.—Bond angle vs. torsion angle for staggered rings with point symmetry $\overline{3}m2$ containing six and eight atoms.

seen that while the values of ϑ_0 and φ_0 do not vary widely, those of the other constants do. Although it is difficult to choose, on the basis of the limited available data, just which set is the most reasonable, it seems very unlikely that the true value of any particular constant lies outside the limits of the table. The strain energies of the equilibrium conformations of various sulfur rings calculated by the use of the constants of Table IV are shown in Table V.

TABLE V

STRAIN ENERGIES OF SULFUR RINGS IN KCAL./MOLE/S-S BOND

Assumptions	S₆	S₈	S₁₂	S₁₀
A	19.4	1.5	0.3	2.3
B	17.2	1.4	.2	1.8
C	17.6	1.4	.2	1.8
D	14.4	1.3	.1	1.3
E	12.5	1.3	.1	1.0
F	9.8	1.2	.0	0.4

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