Part I

Thermal Data on Some Cyclic Hydrocarbons.

Part II

The Electron Diffraction Investigation of the Molecular Structure of Silicon Tetrabromide, Tribromosilane, and Difluorodibromosilane.

Thesis by

Ralph W. Spitzer

In Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy.

California Institute of Technology

Pasadena, California

1941

Acknowledgment

I should like to express my thanks to Mr. William J. Howell and Dr. Verner Schomaker , who collaborated with me in the electron diffraction work. I am also indebted to Dr. Schomaker for interesting and helpful discussions about the cycloparaffins; to Professors Schumb, Kistiakowsky, and Parks, as well as the Shell Development Company for supplying samples of the materials used in these investigations; to Professor Linus Pauling for suggesting these researches; and particularly to Professor Hugh M. Huffman for constant aid and instruction in the technique of precision calorimetry.

Table of Contents

Part I. Thermal Data on Some Cyclic Hydrocarbons

Page

I. Introduction - 1

II. Experimental

A. Compounds - 1

B. The Calorimeter - 3

C. Calibration, units, etc. - - - - - - - - - - - - - - - - 5

D. Determination of amount of reaction - - - - - - - - - - 7

III. Presentation of the data - - - - - - - - - - - - - - - - - 13

IV. Discussion - 20

Summary - -- 26

Part II. The Electron Diffraction Investigation of the Molecular Structures of Silicon Tetrabromide, Tribromosilane, and Difluorodibromosilane.

A. Introduction - 27

B. Experimental - 27

C. Interpretation - 28

D. $SiBr_4$ - - - - - -- 30

E. $SiHBr_3$ - 34

F. SiF_2Br_2 - 38

G. Previous Work - 45

Summary - 47

Part I

Thermal Data on Some Cyclic Hydrocarbons.

I. Introduction

Recently, Kistiakowsky and coworkers[1] have determined the heats of hydrogenation of many substances, including several cyclic olefins. Their results indicated that information about "steric effects" might be obtained from the heats of formation of cycloparaffins. We have determined the heats of combustion of cyclopentane, cyclohexane, cycloheptane, and cyclooctane, in the liquid state, and at 25°C.

II. Experimental

A. Compounds

Professor Kistiakowsky was kind enough to supply us with pure samples of these substances. They were prepared from the end products of his hydrogenation experiments by careful fractional distillation, and were then sealed into bulbs under vacuum. The physical constants, as determined by Kistiakowsky (except for cyclohexane (b)), are given in Table I. Cyclohexane (b), was kindly supplied by Professor G. S. Parks and was originally prepared by the Shell Development Company.

1. Conn, Kistiakowsky, and Smith. J.Am.Chem.Soc. 61, 1868 (1939). Further references are given in this paper.

Table I

Compound	Freezing Point °C.	Boiling Point °C	n_D^{20}
Cyclopentane	[a]	[a]	1.4060
Cyclohexane	6.42	80.92	1.4260
Cyclohexane (b)	6.35	[a]	[a]
Cycloheptane	12.2	[a]	1.4446
Cyclooctane	14.5	[a]	1.4587

[a] Not given

Professor Kistiakowsky has notified us that, after many distillations, he was unable to purify the cycloheptane and cyclooctane to the point where they melted sharply. He suggests, however, that this does not necessarily indicate the presence of large amounts of impurity, as these substances are characterized by extremely high cryoscopic constants. In his work he found that different samples of the same cycloölefin which had different melting points, gave identical heats of hydrogenation. As the probable impurities would have about the same heat of combustion as the substance itself, small amounts of these impurities should have a negligible effect on the final values.

B. The Calorimeter

The calorimetric system has been described previously[2]. A brief description of the apparatus and technique may be in place here.

The bomb type calorimeter was used in connection with the "ordinary" calorimetric procedure. In this method the calorimeter is surrounded by a jacket whose temperature is kept constant within about .002°C. Heat interchange between calorimeter and jacket is corrected for by observing the rate of change of temperature before and after the combustion, and assuming Newton's law of cooling to hold throughout the experiment. The calorimeter liquid (water) is kept well stirred by a propeller driven by a constant speed motor.

The bomb used in this investigation was of the Parr double valve type. This was substituted for the single valve bomb previously used because the latter tended to allow the leakage of a few cc. of gas during the combustion. While this small leakage would have had no perceptible effect on the observed temperature rise, it might have led to error in the determination of the extent of the reaction by the analytical method, in which the CO_2 produced was absorbed and weighed.

2. a) Huffman and Ellis, J.Am.Chem.Soc. 51, 41 (1935)

b) Dickinson, Bull. Bureau of Standards 11, 243 (1915)

The temperature rise was measured with a calibrated platinum resistance thermometer, a Mueller Thermometer Bridge and high sensitivity galvanometer.

The charge was fired by a weighed fuse made of filter paper, whose heat of combustion was determined to be 3983 calories per gram. The paper was ignited by liberating 1.4 calories of electrical energy in a platinum coil which was in contact with the fuse. The total energy liberated in this process was usually about 20 calories. We believe this method to be superior to the more common iron wire technique, as the products of combustion of the paper are known more exactly than those of the iron fuse.

For photographs of the system see Baumgarten, Thesis, 1941, California Institute of Technology.

C. Calibration, units, etc.

The energy equivalent of the calorimeter was frequently determined by burning Bureau of Standards benzoic acid, standard sample 39e, having for its isothermal heat of combustion per gram under standard conditions[3] at 25°, the value of $-\Delta U_B/m$ = 26,419 N.B.S. international joules[4]. Washburn defines as standard conditions: Initial pressure of oxygen = 30 atmospheres, 3 grams of benzoic acid and 3 grams of water per liter of bomb space. In these experiments the volume of the bomb was 358 cc.; 0.1 gm. of water was added to the bomb, and the sample of benzoic acid weighed about 1.023 grams. Under these conditions $-\Delta U_B/m$ = 26,416 international joules. Results are expressed in defined conventional calories (one defined calorie = 4.1833 international joules).

We have taken the value of the heats of formation of water and CO_2, at 25°, to be 68,317 and 94,030 calories per mole, respectively. Atomic weights used were H = 1.0080, O = 16.0000, C = 12.01.

Correction was made for nitric acid formed in the combustion, using 13,960 calories per mole for the heat of formation of nitric acid. All weights have been reduced to vacuo.

3. Washburn, Bur. Stand. J. Res. 10, 552 (1933)

4. Jessup and Green, ibid. 13, 469 (1934)

The mean of 14 calibrations with benzoic acid gave 3230.3 cal/degree for the energy equivalent of the calorimeter. The standard deviation from the mean was 0.005%. This is indicative of the precision of the method under the most favorable conditions. The larger errors in the experiments on hydrocarbons are due to greater difficulty in determining the extent of the reaction (see section D).

D. Determination of amount of reaction.

The extent of the reaction was determined in two ways:
(1) by direct weighing of the amount of cycloparaffin used, and
(2) by analysis of the gases resulting from combustion.

In method (1) an ampoule holding the cycloparaffin was weighed in a crucible. After the combustion, the crucible containing the melted ampoule was weighed again. The difference of these two weights, corrected to vacuo, gave the mass of cycloparaffin burned. In method (2) the CO_2 formed was absorbed in Ascarite and weighed. The detailed procedure was as follows:

A sample of the material to be burned was placed in a beaker into which dipped the stem of a very thin-walled soft glass ampoule whose sides were flattened. The beaker was placed in a desiccator which was then evacuated, and the liquid was allowed to boil, in order to remove dissolved air. Air was let into the desiccator, and the ampoule filled with liquid. The ampoule was then sealed without a bubble. The presence of a bubble in the ampoule would have caused the glass to become distorted when placed under pressure, and might have resulted in breakage.

The filled ampoule was weighed to 0.01 mg. on a Kuhlmann microanalytical balance and placed in a platinum crucible in the bomb, which was filled with oxygen at 30 atmospheres pressure. A weighed quantity of oil was placed on the ampoule to start the

combustion. The heat of combustion of this oil was 10,825 calories per gram.

The oxygen was purified by slow passage, first, through a furnace (A) containing vanadium pentoxide catalyst at 400°, and finally, through Ascarite, and Dehydrite absorbers (B) to remove water and CO_2. (See Figure I).

After the combustion the bomb (D) was emptied through an absorbing train consisting of a drying tube (E) containing Dehydrite and P_2O_5, and three similar Turner absorbers (F, G, H), each of which contained Ascarite, Dehydrite, and P_2O_5. The first absorber removed the CO_2 from the gas, the second was used as a check on the completeness of absorption in the first, and the third was used as a tare in weighing. The tare was treated in the same manner as the absorbers in order to minimize corrections due to changes in the conditions under which the absorbers were filled. All three absorbers had almost identical dimensions and were packed to the same extent.

The absorbers were followed in the train by a U-tube (I) containing Ascarite, whose function was to prevent back diffusion of CO_2 from the atmosphere, and finally, by a flowmeter.

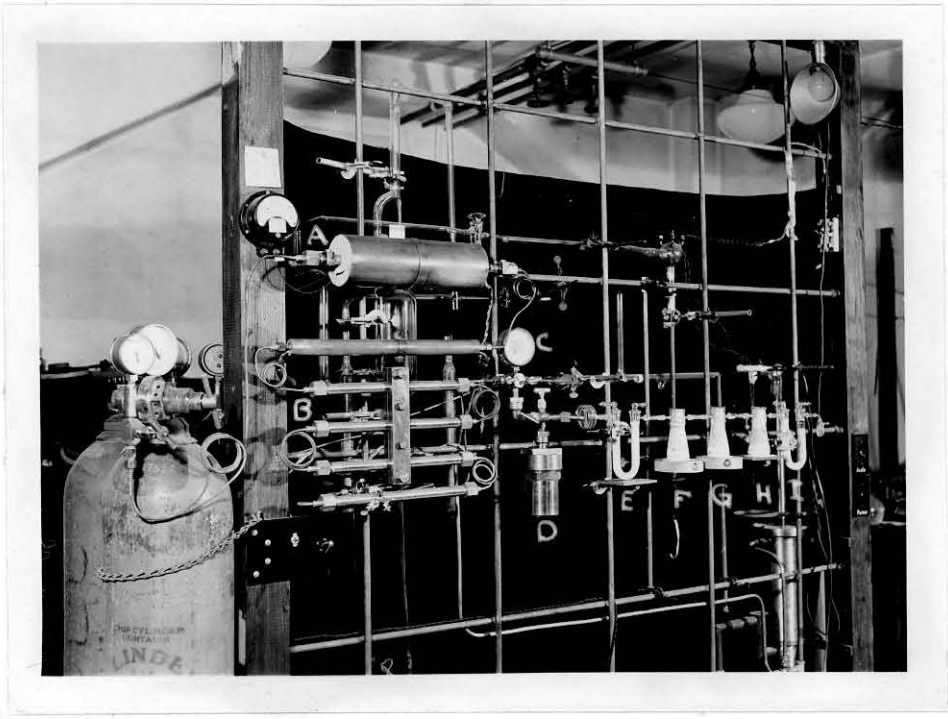

Fig. I

Analytical Train

A. Oxygen purifying furnace
B. Stainless Steel absorbing tubes
C. Pressure gauge
D. Bomb (single valve)
E. U-tube, containing Dehydrite
F, G, H, Turner absorbers
I. Protection tube

Flowmeter, following I is not shown.

The rate of flow of the effluent gas, as determined by the flowmeter (not shown in figure), was kept constant at about 200 cc. per minute by manual regulation. After reduction of the pressure to atmospheric, the bomb was flushed four times by filling with oxygen at ten atmospheres and again emptying through the absorbers. Between the first and second flushings the bomb was heated to 80°C. in order to hasten the attainment of equilibrium between the aqueous and gaseous CO_2. Check experiments showed that this treatment did not drive any of the dissolved nitric acid out of the bomb.

The second absorber gained weight appreciably only in rare instances, indicating that absorption in the first vessel was complete. The increase in weight of the first absorber was corrected for change in volume of the Ascarite by the method described by Rossini[5].

Occasional tests were made for completeness of combustion by connecting to the absorbing train an apparatus similar to that described by Cook[6] for the determination of carbon monoxide, using hemoglobin as detector. In only one run was any carbon monoxide found, and in that experiment other evidences of explosion and spattering were obvious. In check experiments 0.2 cc. of CO was easily detected.

5. Rossini, Bur. Stand. J. Res. 6, 39 (1931)

6. Cook, Ind. Eng. Chem., Anal. Ed. 12, 661 (1940)

The absorbers were weighed on an analytical balance to 0.05 mg. The weight of CO_2 as calculated from absorbers I - II, and I - III usually agreed within 0.2 - 0.4 mg., leading to an uncertainty of 0.01 to 0.02% in the amount of reaction. CO_2 analyses were made during the calibration runs, and the ratio of CO_2 found to CO_2 calculated, averaged for 13 runs, was 0.99997, with a mean deviation of $\pm$ .00008. The extreme deviation from the mean was -.00022.

After the analysis the crucible containing the fused ampoule was weighed twice; once after drying on a hot plate, and again after ignition. In the first experiments with cyclopentane and cyclohexane a 3 gram crucible was used, and the two weighings described above disagreed by as much as 0.4 mg. Consequently, these weighings were not used at all, and the amount of reaction was calculated solely from the CO_2 produced, as determined by analysis.

In the later experiments on cycloheptane and cyclooctane, either a 10 or 20 gram crucible was used. With this technique the weighings were quite reproducible, and so the importance of the analyses was minimized. We are not certain whether this desirable result was brought about by the substitution of the heavier crucible, or merely by the change to less volatile compounds. In those experiments in which both a reliable analysis and reproducible

weighings on the crucible were made, the two quantities agreed within 0.02 to 0.04%. This introduced the largest error of any step in the experiment. A good determination of the amount of reaction by either method (1) or method (2) was probably reliable to $\pm$ 0.02%.

III. Presentation of the Data

Table II gives the results of the experiments on the hydrocarbons. Values of $-\Delta U_B/m$ which are extraordinarily high and are derived from CO_2 analysis are rejected because of the possibility of undetected leakage. Similarly, those values derived from direct weighing on the ampoule which are much lower than the average are rejected because of the possibility of spattering, etc. These rejected values are enclosed in parentheses. As mentioned above, we have not used the direct weighing values in making our final averages (Table II) for cyclopentane and cyclohexane.

In Table III are given the calculated quantities $-\Delta U_B$, $-\Delta U_R$, $-\Delta H_R$ and $-\Delta H_f^\circ$. These quantities all refer to one mole. $-\Delta U_B$ is the actual heat evolved under the conditions in the bomb, corrected to the constant temperature 25°C. $-\Delta U_R$ is the heat evolved when the reaction occurs with all reactants and products in their standard states at 25°. $-\Delta H_R$ is the change in heat content at one atmosphere assuming the perfect gas law to hold for CO_2 and O_2 and ΔH_f° is the standard heat of formation from the elements at one atmosphere and at 25°.

The errors given in Table III correspond to the "uncertainty interval" defined by Rossini[7], and include an estimate of the uncertainty in the value of the heat of combustion of benzoic acid (.023%) and in the heats of formation of H_2O and CO_2 (.015% and .012%).

7. Rossini, J. Wash. Acad. Sci. 29, 440 (1939)

Table II

Experimental Data at 25°

Cyclopentane

Comb.No.	$\frac{\text{Mass } CO_2}{3.13774}$	Mass, direct weighing	Total heat evolved, cal.	Cal. from HNO_3	Cal. from oil	Cal. from paper + EIT	$-\Delta U_B/m$ cal/g from CO_2	Dev. cal.	$-\Delta U_B/m$ from dir. weighing	Dev. cal.
2	.58926	.58932	6699.0	1.0	83.6	25.2	11,192.4	-1.8	11,194.7	+4.4
4	.50942	.50941	6446.3	2.3	723.5	27.1	11,188.3	-5.9	11,188.7	-1.6
6	.53246	.53282	6453.6	0.5	481.0	16.8	11,196.3	+2.1	11,189.0	-1.3
7	.53013	.53044	6479.7	0.5	532.1	16.8	11,198.3	+4.1	11,191.9	+1.6
8	.57205	.57232	6568.5	1.9	151.3	17.3	11,197.9	+3.7	11,192.8	+2.5
9	.56121	.56161	6474.8	1.4	173.1	25.3	11,192.1	-2.1	11,184.4	-5.9
						Mean	11,194.2	±3.3	11,190.3	± 2.9
				Cyclohexane						
1a	.47119	.47133	6485.7	0.8	1233.5	25.7	11,103.6	-3.3	11,100.3	-2.8
2a	.46314	-----	6471.7	1.5	1305.9	25.6	11,108.7	+1.8		
3a	.53034	.53099	6470.73	0.8	559.5	24.2	11,109.2	+2.3	11,098.3	-4.8
5a	.54997	.55010	6493.3	1.3	365.5	23.4	11,108.5	+1.6	11,105.9	+2.8
7a	.58345	.58333	6666.2	1.9	165.1	26.1	11,104.4	-2.5	11,106.7	+3.6
8a	.47647	-----	6454.0	0.8	1153.8	16.6	11,107.0	+0.1		
						Mean	11,106.9	±1.9	11,103.1	±3.5

Table II (cont.)

Cycloheptane

Comb. No.	Mass CO_2 / 3.13774	Mass, direct weighing	Total heat evolved, cal.	Cal. from HNO_3	Cal. from oil	Cal. from paper + EIT	$-\Delta U_B/m$ cal/g from CO_2	Dev. cal.	$-\Delta U_B/m$ from dir. weighing	Dev. cal.
2		.50619	6514.2	1.2	846.2	17.5			11,173.5	+2.5
3	.53788		6455.2	1.5	431.9	18.4	11,173.4	+2.3		
4		.52937	6471.4	0.5	570.1	19.3			(11,160.3)	
6		.54399	6485.9	0.5	396.3	18.0			(11,176.5)	
10		.51118	6488.9	0.9	765.2	21.1			11,167.7	-3.3
11	.52230	.52308	6481.3	1.5	623.3	19.5	11,168.7	-2.3	11,173.4	+2.4
12		.53748	6469.9	2.1	440.5	29.7			11,171.1	+0.1
13	.50090	.50129	6470.0	2.1	851.1	22.6	(11,181.7)		11,173.0	+2.0
14		.49895	6488.3	1.3	903.8	17.9			11,168.5	-2.5
15	.46335	.46352	6470.9	0.8	1283.5	16.9	11,172.6	±2.4	11,168.6	-2.4
						Mean of all acceptable values	11,171.0	±2.1		

Cycloöctane

1		.60593	7015.3	0.7	220.7	21.8			11,189.2	-2.4
4		.57089	6540.6	1.1	120.3	38.1			11,191.0	-0.6
5	(.61346)	.61337	6977.7	1.2	101.5	16.4	(11,192.8)		11,194.4	+2.8
6	(.60906)	.60940	6981.8	2.4	148.6	18.4	(11,197.8)		11,191.5	-0.1
7		.60510	6947.2	2.7	162.5	17.6			11,191.7	+0.1
						Mean			11,191.6	±1.2

Table III

Summary of Derived Data at 25°

Substance	Formula	Molecular wt.	Density	$-\Delta U_B$ kcal/mole	$-\Delta U_R$ kcal/mole	$-\Delta H_R$ kcal/mole	$-\Delta H_f^\circ$ kcal/mole	$d\frac{\Delta U_R}{dT}$ cal $mole^{-1}$ deg^{-1}
Cyclopentane	C_5H_{10}	70.130	0.7460	785.05 ± .28	784.88 ± .28	786.36 ± .28	25.37 ± .33	56
Cyclohexane	C_6H_{12}	84.156	0.7781	934.71 ± .27	934.50 ± .27	936.27 ± .27	37.79 ± .32	67
Cycloheptane	C_7H_{14}	98.182	0.8100	1096.79 ± .31	1096.55 ± .31	1098.62 ± .31	27.79 ± .37	78
Cyclooctane	C_8H_{16}	112.208	0.8304	1255.79 ± .35	1255.50 ± .35	1257.86 ± .35	40.88 ± .43	89

Table IV

Substance	$-\Delta H_R$(liq.)	ΔH(vap.)	$-\Delta H_R^g$(gas phase)	$-\Delta H_R^g/n$	$\Delta H_f^g/n$
Cyclopentane	786.4	*(6.8)	793.2	158.6	-3.75
Cyclohexane	936.3	7.9	944.2	157.4	-4.95
Cycloheptane	1098.6	*(8.9)	1107.5	158.2	-4.15
Cyclooctane	1257.9	*(10.0)	1267.9	158.5	-3.85

*estimated

In order to compare the heats of combustion of the gaseous hydrocarbons, it was necessary to estimate heats of vaporization at 25°, since experimental values are available only for cyclohexane. These values were estimated by a variety of methods and are probably unreliable by about 200 - 300 calories for cyclopentane and perhaps 400 - 500 calories for cycloheptane and cyclooctane. The results of this calculation are summarized in Table IV. $-\Delta H_R^g/n$ is the heat of combustion per CH_2 group at one atmosphere.

Table V

Substance	-ΔH for hydrogenation at 82°C.	-ΔH(liq.)* 25°C.	$-\Delta H_f^\circ$(l) Liquid
Cyclopentene	26.915	26.7	1.3 ± 0.5
Cyclohexene	28.592	28.4	- 9.4 ± 0.5
Cycloheptene	26.515	26.3	-11.5 ± 0.6
Cyclooctene	23.525	23.3	-17.6 ± 0.6

*Assumed to be the same as for the gaseous reaction

Table V gives the heats of formation of the corresponding monocycloölefins in the liquid state. These have been calculated from our data plus the hydrogenation values of Kistiakowsky[1], et al. We have corrected his values to 25° by using ΔC_p = -4 cal. per degree,

and assumed that the heats of vaporization of the corresponding olefin and paraffin are the same at 25°. These two assumptions probably introduce an additional uncertainty of 200 - 300 cal. per mole. We have not attempted to calculate heats of formation of such compounds as the diolefins, since the larger uncertainty in the correction terms would probably render these values worthless. Parks gives the heat and free energy of formation of benzene in his review paper[8].

The only modern data on any of these substances are those of Moore, et al[9], who give for liquid cyclohexane at 25°, $-\Delta U_R$ = 934.62 ± 0.31 cal per mole, in almost perfect agreement with our value. Comparisons with older values are not significant because they cannot be calculated to a comparable basis and are much less precise than the modern work. Kharasch[10] lists all data available to 1929.

8. Parks, Chem. Rev. 27, 75 (1940)

9. Moore, Renquist and Parks, J. Am. Chem. Soc. 62, 505 (1940)

10. Kharasch, Bur. Stand. J. Res. 2, 359 (1929)

IV. Discussion

We see from Table IV that in the gaseous state, at 25°, cyclohexane is more stable than cyclopentane by 1.2 kcal., more stable than cyclooctane by 1.0 kcal, and more stable than cycloheptane by 0.8 kcal per CH_2 group, all $\pm$ 0.1 kcal. It will be shown that these effects are qualitatively in accord with one of the theories that have been advanced to explain phenomena related to those discussed here.

In order to explain these data we assume with Schomaker that a configuration of two neighboring carbon atoms which are arranged so that the directions of the three bonds (other than the carbon-carbon bond) attached to each are opposed to one another (as in the D_{3h} form of ethane), is less stable than a configuration which allows the attached bonds to be staggered (as in the D_{3d} form of ethane). In the future, for brevity, we will refer to the pairs of atoms themselves as opposed or staggered.

There is only one reasonable model for cyclopentane--that which makes the carbon atoms all coplanar and, hence, opposed. Cyclopentane, therefore, should be at least as unstable as any other cyclic hydrocarbon, insofar as the property under discussion determines the stability of these systems. This agrees with the observed values.

For the cyclohexane molecule, at least two configurations are possible: the rigid "chair" model of symmetry D_{3d}, and the various "tub" models of lower symmetry. These two types should be in tautomeric equilibrium; we later attempt to calculate the equilibrium constant. Although the Raman data have not been interpreted completely enough to lead to general agreement on the symmetry of the molecule which is present in the largest amounts, the latest workers[11] agree that the "tub" molecules are not present in detectable concentration. If we assume, then, that most of the cyclohexane molecules are in the chair form, we see by examination of the model, that all the carbon atom pairs are staggered. This should make cyclohexane the most stable of these substances, as is indeed observed.

Dr. Schomaker has suggested that the energy difference per CH_2 group between cyclopentane and cyclohexane might be expected to be quite closely related to the potential restricting the internal rotation of ethane, since in moving from one position of equilibrium to another, the ethane molecule changes from one staggered state to another by assuming an intermediate opposed state. (This is true if our assumption that staggering leads to stabilization is correct.) The three kilocalories required for this process in ethane compares rather poorly with the 1.2 kilo-

11. a) Langseth and Bak, J. Chem. Phys. 8, 403 (1940)

b) Saksena, Proc. Ind. Acad. Sci. Sect. A, XII, 321 (1940)

calories observed for the cycloparaffins. However, for these two quantities to be compared directly, several conditions would have to hold:

1. The strength of the bonds in the various cyclic molecules would have to be equal.

2. The energy of vibration, rotation, and translation per CH_2 group would have to be the same. It is very easy to see that this cannot be true. A rough calculation indicates that the energy content of cyclohexane, due to these effects, is about 0.4 kcal. higher per CH_2 group than that of cyclopentane.

3. Whatever interaction is responsible for the hindering potential would have to be the same in all these cases.

It is probable that none of the above conditions holds strictly. Condition (1) is probably nearly true. Since the source of the hindering potential is not known, it is difficult to estimate the extent of the validity of (3). It is certainly true that the difference between cyclopentane and cyclohexane does not parallel, strictly, the difference between the two forms of ethane. The symmetry around the carbon-carbon bond is different in the two cases; the number of hydrogen interactions is different; the cycloparaffins include second neighbor carbon interactions which are lacking in ethane. It is therefore not surprising that the interaction potential in cycloparaffins is different from that in ethane.

The value of 1.2 kcal for the energy difference between the cyclopentane and cyclohexane rings is roughly confirmed by the following calculation:

Parks[8] gives $-\Delta H_R$ for liquid methylcyclohexane, methylcyclopentane and ethylcyclopentane, as 1090.4, 940.4 and 1096.4 kcal per mole, respectively. If we arbitrarily subtract 156.0 kcal from these values for each carbon atom external to the ring (the heat of combustion of long-chain normal paraffin liquid hydrocarbons increases about 156 kcal per CH_2 group added[12]) and then divide by the number of carbon atoms in the ring, we get 155.7, 156.9 and 156.9, respectively, for these three compounds, giving a difference of 1.2 kcal per CH_2 group between cyclohexane and cyclopentane rings. This value is not very sensitive to change of a few kilocalories in the assumed value of the heat of combustion of the extra-ring carbons. At any rate, it indicates that in cycloparaffins the difference in energy between opposed and staggered carbon pairs (if, indeed, this is responsible for the relative stabilities of cyclopentane and cyclohexane) is of the order of 1 rather than 3 kcal.

The heats of combustion of cycloheptane and cyclooctane fit into this scheme quite well. Since structural information on these compounds is lacking, we constructed mechanical models, and

12. a) Rossini, Bur. Stand. J. Res. 13, 21 (1934)
    b) Jessup, ibid. 18, 115 (1937)

discovered that there were only a few configurations that could not be ruled out on the basis of the simplest considerations.

The only configuration which the cyclooctane molecule can assume without involving extremely improbable hydrogen contacts (of the order of 1.6 Å apart) is the Archimedean antiprism form, in which the carbon atoms are almost perfectly opposed. The predicted value of the energy per CH_2 group is, therefore, the same as that for cyclopentane, and this is the value observed.

It is impossible to decide on a unique structure for cycloheptane. All configurations show at least moderate hydrogen repulsions and have from two to four carbon pairs which are at least partially staggered. Without further knowledge about the repulsion energies of hydrogen atoms, it is impossible to make a quantitative prediction. At any rate, cycloheptane should be considerably less stable than cyclohexane.

We may now return to a consideration of the equilibrium between the two forms of cyclohexane. The symmetrical tub form has two staggered pairs replaced by opposed, leading to destabilization of 2.4 kcal per mole. In addition, two of the hydrogen atoms are separated by only 1.84 Å, considerably less than the 2.4 Å given by the van der Waals diameter of hydrogen.

This may add about 1.5 kcal. The energy content of the tub form is, therefore, probably at least 4.0 kcal per mole greater than that of the chair form. The tub form, however, has the higher entropy: $R\ln 3 = \frac{2.2}{0.96}$ entropy units due to its lower symmetry and possibly another entropy unit due to lower vibrational frequencies--a total of $\frac{3.2}{2.0}$ entropy units. At 25°, then,

$$\Delta F = 3.\# \text{ kcal per mole}$$

$$K = \cancel{3} \; 10^{\#} = \frac{(\text{tub})}{(\text{chair})}$$

Despite the approximate nature of this calculation, it indicates that the equilibrium concentration of the tub form is inconsiderable, and accounts for the failure of the spectroscopists to obtain evidence of its existence.

We would like to conclude with a few comments concerning the assertion of Langseth and Bak[11a,13] that cyclohexane exists in the planar form. We believe that the present work rules out this possibility. Langseth and Bak assert that the opposed position of carbon atoms is the more stable, and therefore cyclohexane assumes the planar configuration despite the strain in the bond angles. However, cyclopentane would also possess the extra stability due to opposition of carbon atoms, but would have negligible strain energy; hence the cyclopentane would be more stable, contrary to experiment.

13. Schomaker and Stevenson, J. Chem. Phys. 8, 637 (1940)

Summary

1. The heats of combustion of cyclopentane, cyclohexane, cycloheptane and cyclooctane have been determined in the liquid state at 25°.

2. The technique of making the measurements is described.

3. The heats of combustion per CH_2 group in the gaseous state at 25° of these substances are as follows:

	$-\Delta H_R/n$
Cyclopentane	158.6 kcal.
Cyclohexane	157.4
Cycloheptane	~~158.2~~ 158.2
Cyclooctane	158.5

4. It is concluded that the "opposed" configuration of a carbon-carbon bond is less stable by 1.2 kilocalories than the "staggered" configuration in cycloparaffins.

. It is shown that cyclohexane almost certainly has the "chair" structure, and that cyclooctane probably has the Archimedes antiprism configuration.

Part II

The Electron Diffraction Investigation of the Molecular Structure of Silicon Tetrabromide, Tribromosilane, and Difluorodibromosilane.

A. Introduction

The interatomic distances in the halides of the fourth, fifth and sixth group elements are, in general, considerably shorter than the distances given by the sums of the corresponding Pauling-Huggins covalent radii[1]. This discrepancy appears to be resolved, in part, by the introduction of a correction for the ionic character of the bonds[2], but large disparities still exist for second row fluorides, while, for the heavier of these halides, the agreement is not precise. The Si-Br distances reported here are all 2.16 $\pm$ 0.03 Å.--0.06 Å shorter than the distance calculated by Schomaker and Stevenson[2].

B. Experimental

The apparatus and technique employed have been described by Brockway[3]. The wavelength of the electrons was determined frequently from transmission photographs of gold foil (a_o = 4.070 Å), and was about 0.061 Å.

We are indebted to Professor Schumb of Massachusetts Institute of Technology for supplying us with the samples.

1. L. Pauling and M. L. Huggins, Zeit. f. Krist. 87, 205 (1934)
2. V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. 63, 37 (1941)
3. L. O. Brockway, Rev. Mod. Phys. 8, 231 (1936)

C. Interpretation

The improved radial distribution method described by Schomaker[4] was used in conjunction with the correlation method of interpreting the photographs. The simplified theoretical intensity curves were calculated for a variety of models, using the formula:

$$I(s) = \frac{1}{(Z_{Si}-f_{Si})(Z_{Br}-f_{Br})}\sum_{i,j}(Z_i-f_i)(Z_j-f_j)e^{-a_{ij}s^2}\frac{\sin sl_{ij}}{sl_{ij}}$$

in which Z_i is the atomic number of atom i; f_i, the atom form factor[5]; l_{ij}, the interatomic distance; and a_{ij} is one half the mean square amplitude of vibration of atom i against atom j.

Since the calculation of a_{ij} from spectroscopic data is not at present feasible for polyatomic molecules having large moments of inertia, an attempt was made to determine these temperature factor constants by including them as extra parameters in the correlation treatment. a_{Si-Br} was arbitrarily set equal to zero, so that the quantities actually determined were $a_{ij} - a_{Si-Br}$; for brevity, we call these quantities a_{ij}.

4a. V. Schomaker, Thesis, California Institute of Technology, 1938;

b. V. Schomaker, Am. Chem. Soc. Meeting, April 1939.

5. L. Pauling and J. Sherman, Zeit. f. Krist., 81, 1 (1932).

The radial distribution formula used was

$$D(r) = \sum_n C_n \frac{\sin s_n r}{s_n r}$$

$$C_n = I_n s_n^{-as_n^2}$$

$$e^{-as_{max}^2} = 0.1$$

where I_n is a relative intensity, estimated for the various peaks so as to show no average dependence on s, and s_{max} is the value of $s = \frac{4\pi}{\lambda} \sin \frac{\phi}{2}$ for the last observable feature on the photograph. ϕ is the scattering angle.

D. Silicon Tetrabromide

The two parameters to be determined were ℓ, the Si-Br distance and a, the temperature factor constant for Br-Br vibration. The Br-Si-Br angle was assumed to be exactly tetrahedral.

The photographs showed a rather heavy background which tended to make the measurements less precise than usual. The difficulty of measurement was enhanced by the slight, but deceptive, asymmetry of some of the peaks. In all, 26 features were measured and used in the radial distribution curve; of these, only 15 were used in the quantitative visual comparison. The observed values of s are given in Table I, together with values of I_n and C_n used in the radial distribution function, and values of s_{calc}/s_o.

The curves D, E and F (Figure I) correspond to a = 0, 0.001, and 0.003 respectively. None of the curves shows marked disagreement with the photographs, but the best representation of their appearance would be given by some curve between B and C. This fixes the value of a between 0.001 and 0.003. Figure Ia shows the radial distribution curve for $SiBr_4$.

The average value for the Si-Br distance obtained from 15 features by the correlation method was 2.145 Å with an average deviation of 0.9%. This gives 3.50 Å for the Br-Br distance. The

radial distribution method gives $l_{Si-Br} = 2.16$ Å; $l_{Br-Br} = 3.51$ Å. Since the Br-Br distance is the more reliable, we base our value of ℓ on it. The estimated best values are:

$$l_{Br-Br} = 3.51 \pm 0.03 \text{ Å}$$

$$l_{Si-Br} = 2.15 \pm .02 \text{ Å}$$

$$.001 < a_{Br-Br} < .003$$

TABLE I

Max.	Min.	I_n	C_n	s_o	$s_{calc.}$	s/s_o
	1	3	-2	1.54		
1		2	2	2.39		
	2	2	-2	3.25		
2		7	10	4.11		
	3	10	-17	5.00	4.91	(.983)
3		5	10	5.99	5.87	.980
	4	5	-10	6.78	6.70	.988
4		4	9	7.63	7.49	.982
	5	10	-23	8.53	8.36	1980
5		10	24	9.45	9.35	.989
	6	7	17	10.37	10.32	.996
6		4	10	11.19	11.23	1.004
	7	3	-7	12.08	11.87	.983
7		6	14	12.71	12.80	1.007
	8	10	-22	13.84	13.80	.997
8		10	+21	14.66	14.77	1.008
	9	3	-6	15.65	15.65	1.000
9		4	7	16.49	16.30	.989
	10	7	-11	17.26	17.22	.998
10		10	15	18.23	18.22	.998
	11	10	-13	19.41	19.30	(.994)
11		5	6	20.19	20.10	(.996)
	12	1	-1	21.05	20.90	(.993)
12		5	5	21.60	21.55	(.998)
	13	6	-5	22.85	22.61	(.990)
13		9	7	23.71	23.80	(1.004)
					Av.	.993 Dev. .008

l_{Si-Br} assumed = 2.16 l_{Si-Br} assumed x .993 = 2.145 $\pm$ 0.02Å

Ratios enclosed in parentheses were not used in quantitative comparison

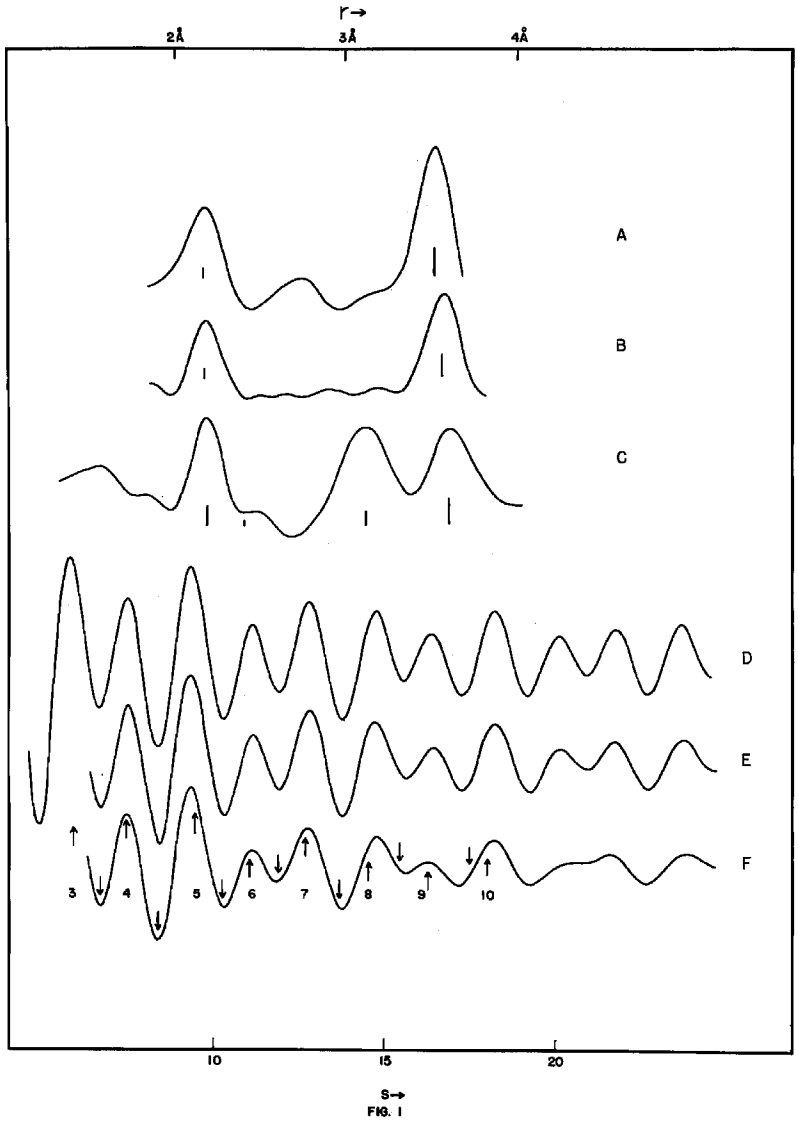

Fig. I

A - Radial Distribution curve, $SiBr_4$
B - " " " " $SiHBr_3$
C - " " " " SiF_2Br_2

Vertical bars indicate interatomic distances finally chosen. Heights of bars are proportional to $Z_i Z_j$ times number of interactions.

D, E, F, Theoretical intensity curves for $SiBr_4$. Vertical arrows indicate $s_o \times .993$. Maxima 1 and 2 are not shown but have the same appearance as the corresponding features in the $SiHBr_3$ curves.

E. Tribromosilane

Thirty features were measured, of which twenty were used for the quantitative visual comparison. The photographs were better than those for $SiBr_4$. The values assumed for the Br-Si-Br angle ϑ were 107° (curves A), 109°28' (B), 111° (C), and 113° (D). The curves in Figure II are divided into three groups--curves A, B, C, D, with $\underline{a}$ = 0, A', B', C', and D' with $\underline{a}$ = 0.001 and A", B", C", D" with $\underline{a}$ = 0.003.

In this molecule, as in $SiBr_4$, it may be seen that the effect of changing the temperature factor is quite distinct from the effect of changing the model. This is not true in general; for example, in SiF_2Br_2 it is difficult to decide on a model because the application of the temperature factor produces changes in the curves that cannot be distinguished from changes brought about by varying the structural parameters slightly.

The singly primed curves show the best agreement with the photographs with respect to the effect of the temperature factor, in that the doubly primed group loses too much detail beyond s = 20, and the umprimed group shows many features too sharply. This indicates that $\underline{a}$ = 0.001 is approximately correct. The singly primed curves are not shown below s = 14 because small differences in the temperature factor have virtually no effect in this region.

The curves D, D' and D'' for ϑ = 107° can be eliminated because they show minimum 9 deeper than 10, maximum 11 higher than 12, and minimum 6 deeper than 7. These difficulties persist for all values of a.

The curves A, for ϑ = 113° are unsatisfactory because they show minima 6 and 7 with the same depth, maximum 6 too low compared with 7, maxima 8 and 9 too nearly equal, and minimum 12 too deep compared with 11 and 13.

The curves C for ϑ = 109°28', and B for ϑ = 111° are almost identical. The only respect in which curves C disagree with the photographs is that they show minimum 8 slightly shallower than 6.

Table II gives s_{obs}/s_{calc} for models B and C. In both cases, the Br-Br distance agrees well with the radial distribution value of 3.54 Å, but the tetrahedral model gives a long value for the Si-Br distance. For this reason, as well as the slight qualitative superiority of C, we choose our final model closer to C than B, but assign limits of error which include both. The best values are

$$l_{Si\text{-}Br} = 2.16 \pm 0.03 \text{ Å}$$

$$\measuredangle \text{Br-Si-Br} = 110\tfrac{1}{2} \pm 1\tfrac{1}{2}°$$

$$l_{Br\text{-}Br} = 3.54 \pm 0.02 \text{ Å}$$

$$a_{Br\text{-}Br} = 0.001$$

TABLE II

Max	Min	I_n	C_n	s_o	s_C	s_C/s_o	s_B	s_B/s_o
	1	-3	-1	1.64				
1		4	2	2.35				
	2	-6	-3	3.06				
2		+10	7	3.97				
	3	-10	-9	4.92				
3		6	6	5.97	6.06		6.06	
	4	-4	-4½	6.68	6.94	1.039	6.85	1.026
4		4	5	7.42	7.70	1.037	7.58	1.019
	5	-9	-12	8.45	8.58	15	8.50	06
5		10	14	9.37	9.59	35	9.57	23
	6	-7	-10	10.31	10.70	38	10.61	29
6		4	6	11.18	11.60	37	11.43	22
	7	-3	-4½	11.88	12.20	27	11.98	09
7		7	10	12.77	13.16	30	13.04	21
	8	-10	-15	13.83	14.22	28	14.10	20
8		10	14	14.80	15.28	32	15.16	24
	9	-7	-3	15.58	16.24	50	15.90	27
9		2	3	16.25	16.90	40	16.68	27
	10	-10	-13	17.24	17.72	28	17.54	17
10		10	12	18.19	18.82	35	18.64	25
	11	-8	-9	19.25	19.88	33	19.65	21
11		4	4	20.00	20.88	44	20.54	27
	12	-1	-1	20.70	21.54	41	21.16	22
12		6	5	21.43	22.36	43	22.12	32
	13	-9	-7	22.59	23.40	36	23.20	27
13		5	4	23.44	24.44	43	24.28	36
	14	-1	-1	24.05	25.48	(1.060)	25.16	(1.046)
14		6	-4	24.57	26.26	(1.068)	25.64	(1.044)
	15	-10	-6	25.55	26.84	(1.051)	26.56	(1.040)
15		7	-3	27.01	27.90	(1.032)	27.60	(1.023)
				Av.		1.036 ± .006		1.023 ± .005
				Si - Br dist.		2.18 ± .01 Å		2.15 ± .01 Å
				Br - Br "		3.54 ± .02		3.54 ± .02

C

Br - Si - Br = 109°28'

B

Br - Si - Br = 111°

Assumed ^{l}Si - Br = 2.10

Ratios enclosed in parenthesis not used in quantitative comparisons.

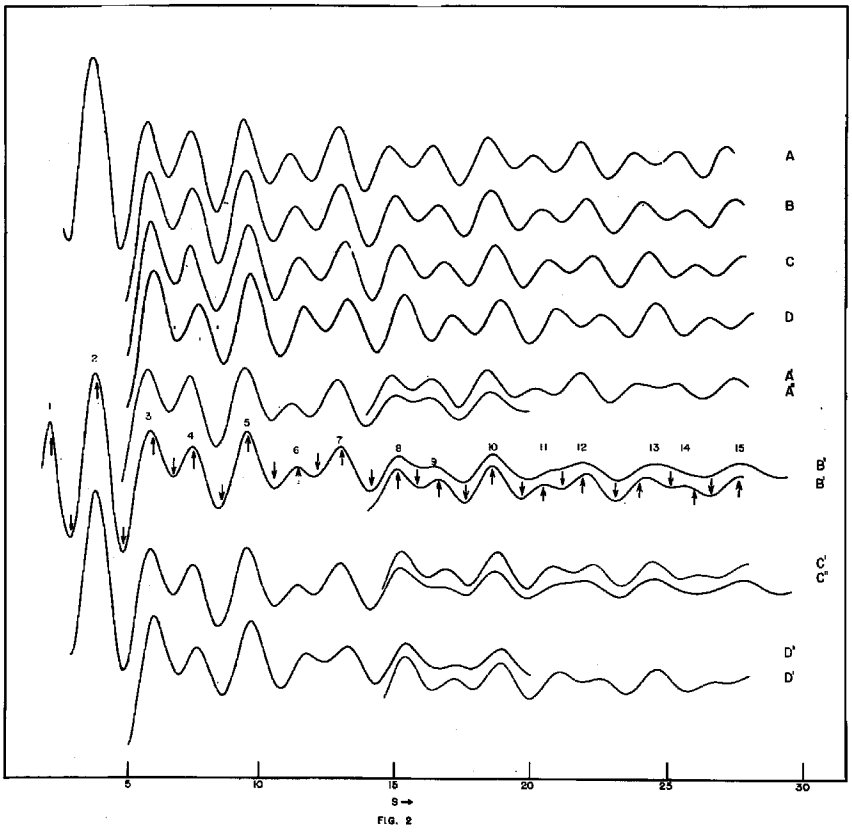

FIG. 2

Fig. II

Theoretical curves for $SiHBr_3$

Si - Br distance assumed to be 2.10 Å

Curves A $\vartheta = 113^0$

B $\vartheta = 111^0$

C $\vartheta = 109^0 28'$

D $\vartheta = 107^0$

The vertical arrows indicate the position of s_0 x 1.023

F. Difluorodibromosilane.

The photographs showed eleven measurable rings. The pattern is well represented by curve J (Fig. III) except for peaks 3 and 9. The exact appearance of these features is doubtful. Maximum 3 is quite broad, and appeared at first glance to be rather more flat topped than the figure indicates. For this reason, two terms, numbers 3 and 4, were put into the radial distribution function to represent the extra width. The arrow at peak 3 (Fig. III) shows the average of measurements 3 and 4.

The appearance of the ninth maximum and adjacent minima was also uncertain; hence s values for these features were not used in the quantitative comparison. In all, the measured positions of 12 features were compared with the theoretical curves. Twenty-three terms were used in the radial distribution function.

Fourteen theoretical curves (Fig. III) were calculated with $l_{Si-Br} = 2.15$ Å, $l_{Si-F} = 1.54$ Å, l_{F-Br} ranging from 3.01 to 3.11 Å and l_{Br-Br} from 3.49 to 3.61 Å. These four parameters are sufficient to define the symmetrical, tetrahedral model. The Si-F distance was assumed, because the appearance of the theoretical curves was insensitive to variations in this distance, and the radial distribution function did not show a well resolved peak which could be

attributed to the Si-F distance. The assumed value of 1.54 Å is equal to the Si-F distance in SiF_4[6]. This assumption may be partially justified by analogy with CF_2Cl_2 and CF_4[7], in both of which the C-F distance is the same. It should be borne in mind, however, that the reported values of the Br-Si-F and F-Si-F angles are dependent on the assumed Si-F distance, and are, therefore, more uncertain than the Br-Si-Br angle.

The models investigated (Table IV) were systematized by locating them on a two-dimensional map of l_{F-Br} against l_{Br-Br}. All models lying outside a closed curve corresponding to the assigned limits of error were inacceptable, and, in general, became progressively worse as their distance from the selected points increased in any direction. The parameters were varied about the values given by the radial distribution curve (Fig. Ic): l_{Si-Br} = 2.15 Å, l_{Br-Br} = 3.56 Å and l_{Br-F} = 3.07 Å.

Since it is impossible, as discussed above, to determine the temperature factor experimentally, the value a_{Br-Br} = 0.001, which is approximately equal to that obtained for Br-Br vibration in $SiBr_4$ and $SiHBr_3$, was adopted here for both a_{Br-Br} and a_{Br-F}. a_{Si-F}, a_{F-F}, and a_{Si-Br} were assigned the same value, again arbitrarily set at zero.

6. L. O. Brockway, J. Phys. Chem. 41, 747 (1937)

7. L. O. Brockway and F. T. Wall, J. Am. Chem. Soc. 56, 2372 (1934)

The curves disagreed with the photographs as follows:

a) Curves A, B, and D show minimum 7 too deep, relative to minima 6 and 8. Curve D also reverses the relative depths of minima 3 and 5, and makes maximum 3 too high compared with 5.

b) In curves K and N, minimum 5 is deeper than 6, contrary to the appearance of the photographs. K also shows the fifth maximum higher than the second. C and G are also unsatisfactory in the latter respect.

c) L and H give maximum 3 too high relative to 5, and minimum 3 deeper than 5.

None of the group E, F, I, J, or M are definitely inacceptable; hence, the assigned limit of error allows the range of parameters covered by these models. The values of s_{calc}/s_{obs}, which vary little from one curve to another, are calculated for curve J.

Curve O, which includes only Si-Br and Si-F interactions, shows the effect of an infinite temperature factor on Br-Br and Br-F vibrations.

The selected best values are:

$$l_{Si-Br} = 2.16 \pm 0.02 \text{ Å}$$
$$l_{Si-F} = 1.55 \text{ Å (assumed)}$$
$$l_{Br-Br} = 3.56 \pm .05 \text{ Å}$$
$$l_{F-Br} = 3.08 \pm .04 \text{ Å}$$
$$l_{F-F} = 2.35 \pm .15 \text{ Å}$$

$\measuredangle$ Br-Si-Br = 110°50' $\pm$ 3°

$\measuredangle$ Br-Si-F = 111°20' $\pm$ 3°

$\measuredangle$ F-Si-F = 98°50' $\pm$ 10°

TABLE III

SiF_2Br_2

Max	Min	I_n	C_n	s_o	$s_{J(calc.)}$	s_J/s_o
	1	-5	-4	1.61		
1		5½	4	2.49	2.46	
	2	-8	-6	3.20	2.23	(1.009)
2		10	9	4.21	4.20	(0.997)
	3	-6½	-8	5.14	5.30	(1.031)
3		5	7	6.23		(0.976)
					(6.50)*	
4		5	7	7.08		
	5	-11	-17	7.89	7.90	1.001
5		10	16	9.03	9.11	1.007
	6	- 5	- 8	10.10	10.23	1.014
6		2½	4	10.91	10.94	1.003
	7	- 6½	-11	11.74	11.80	1.004
7		10	16	12.78	12.80	1.002
	8	-10	-16	13.74	13.90	1.012
8		6	9	14.90	14.92	1.003
	9	- 2	- 3	15.33	15.80	(1.031)
9		2	3	16.72	16.78	(1.004)
	10	- 6	- 8	17.12	17.34	(1.013)
10		10	12	18.18	18.20	1.001
	11	- 8	- 8	19.67	19.70	1.001
11		8	7	21.25	21.33	1.004
	12	-10	- 7	22.71	22.70	1.000
12		10	6	23.96	23.70	(0.973)
					Av.	1.0043 Av. dev. = .003

Assumed $\ell_{Si-Br} = 2.15$ Å

Calculated $\ell_{Si-Br} = 2.16$ Å

*Marked maximum 3 in Fig. III. To be compared with average of observed maxima 3 and 4. (See text)

Ratios enclosed in parentheses not used in making final averages because of uncertainty in measurements.

TABLE IV

Models used in calculating theoretical intensity curves for SiF_2Br_2

l_{Si-F} = 1.54 Å and l_{Si-Br} = 2.15 Å in all models

Label of curve	l_{Br-Br}	l_{F-Br}	l_{F-F}	∠ Br-Si-Br	∠ F-Si-Br	∠ F-Si-F
A	3.51	3.04	2.06	114°10'	113°55'	83°50'
B	3.61	3.08	2.22	114°10'	112°	92°25'
C	3.61	3.05	2.36	114°10'	110°20'	100°10'
D	3.57	3.11	2.12	112°10'	113°55'	87°5'
E	3.57	3.08	2.28	112°10'	112°0'	95°15'
F	3.57	3.05	2.41	112°10'	110°20'	102°40'
G	3.57	3.01	2.55	112°10'	108°10'	112°5'
H	3.53	3.11	2.18	110°10'	113°55'	90°
I	3.53	3.08	2.32	110°10'	112°	97°40'
J	3.53	3.05	2.44	110°10'	110°20'	104°50
K	3.53	3.01	2.58	110°10	108°10'	114°
L	3.49	3.08	2.36	108°30'	112°	99°50'
M	3.49	3.05	2.47	108°30'	110°20'	106°45'
N	3.49	3.01	2.60	108°30	108°10'	115°30'

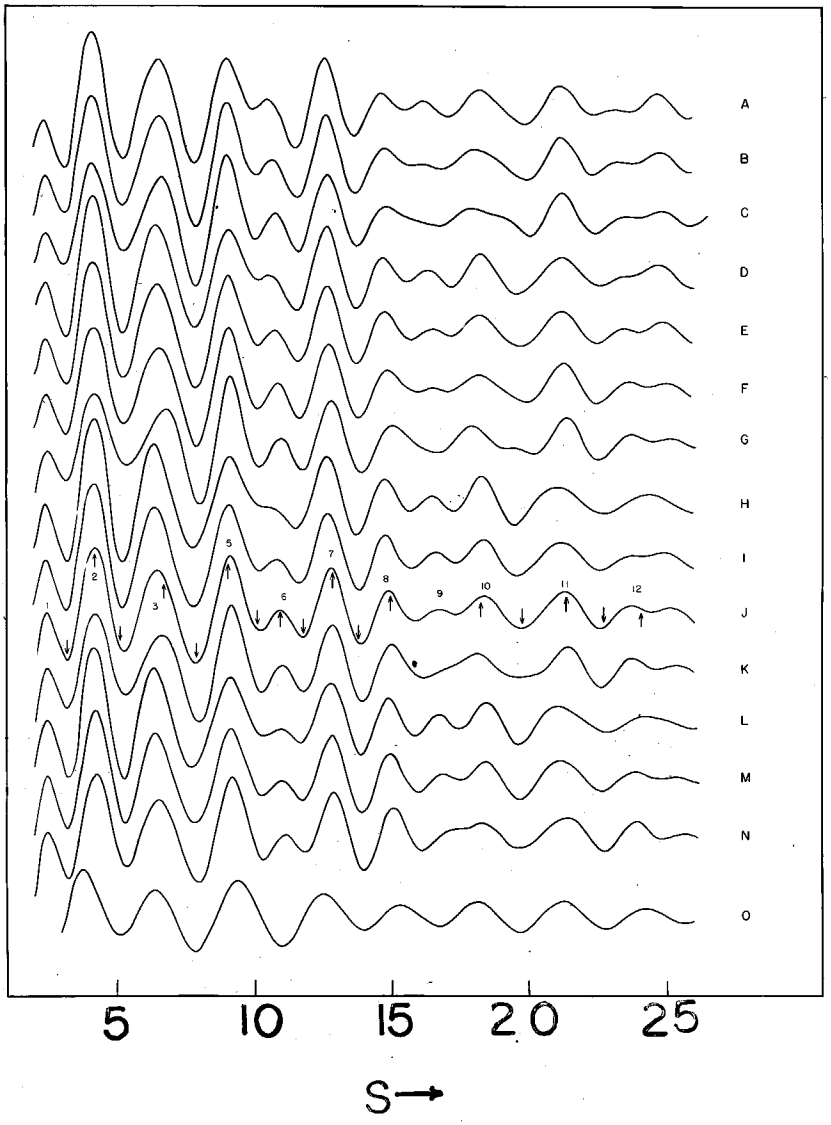

Fig. III

Theoretical Intensity curves for SiF_2Br_2

Vertical arrows indicate $s_0 \times 1.004$

G. Previous Work

Wouters, De Hemptinne and Capron[8] have used the electron diffraction method to determine the structure of $SiHBr_3$. They obtained the results:

$$l_{Si-Br} = 2.19 \pm 0.05 \text{ Å}$$
$$l_{Br-Br} = 3.63 \text{ Å}$$

This value for the Br-Br distance (and consequently, the Si-Br distance) is significantly higher than ours. We believe the present determination to be more reliable for the following reasons:

1. Wouters and coworkers measured only the first five maxima. These are the most difficult to measure accurately. It has been our experience that determinations based on a few measurements--particularly when the minima are neglected--are likely to be inaccurate.

2. The above authors have reported several interatomic distances which appear too high. Their determination of the size of the $SiHCl_3$[9] molecule gives a result 2 - 3% higher than that given by Brockway[3] and Pirenne[10].

Also, in their work on $SiBrCl_3$[9b], in which they report 2.19 Å for the Si-Br distance, De Hemptinne and Wouters also give 2.05 Å

8. Wouters, De Hemptinne, and Capron, Ann. Soc. Sci. Bruxelles, 574 25 (1937)

9. a) De Hemptinne and Wouters, Nature, 138, 884 (1936)
   b) De Hemptinne and Wouters, ibid. 139, 928 (1937)

10. Pirenne, J. Chem. Phys. 7, 144 (1939)

for the Si-Cl distance, compared with 2.01 Å which is usua
found. While these values agree with accepted values within the
assigned experimental error, the above authors seem to have a
slight tendency to give high mean values.

Summary

1. The molecular structures of $SiBr_4$, $SiHBr_3$, and SiF_2Br_2 have been determined by the electron diffraction method.

2. The Si-Br distance in these molecules is 2.16 $\pm$ 0.03 Å.

3. The valence angles are little distorted from the tetrahedral value.

4. The temperature factors have been determined from the appearance of the photographs.

Propositions

1. Semiquantitative predictions can be made about the equilibrium concentrations and rate of interconversion of the molecular species present in cyclohexane. Conclusions drawn from these estimates are in agreement with the experimental data.

2. The equilibrium configuration of the cyclooctane molecule is probably that of the square Archimedean antiprism.

3. The strain energy in cyclobutane, calculated by the Pauling bond strength method, assuming that the bonds are sp^3 single bonds is about 5 kcal. per CH_2 group. This is of the order of magnitude of the observed destabilization of the cyclobutane ring; hence, there is probably little contribution to the ground state of this molecule from hyperconjugated structures.

   A similar calculation for cyclopropane gives a much larger strain energy--about 70 kcal. per CH_2 group. The stability of cyclopropane must, therefore, be due to more complex bonding.

4. A satisfactory statement of the second law of thermodynamics which retains the mathematical advantages of the Caratheodory postulate, but is closely connected with a definite, simple experiment is:

4. (continued)

No change in the generalized forces (pressure, magnetic field etc.) acting on an adiabatic system can lower the temperature of the system while the external parameters (volume, intensity of magnetization) are kept constant.

5. $$\lim_{n \to \infty} \int_0^{2\pi} \left[1 - \left(\frac{x}{2\pi}\right)^n\right]^{1/n} \sum_{m=0}^{\infty} \frac{(2m)!}{2^{2m+1}} \frac{e^{n\pi i/2}}{(m!)^2} \frac{n}{m + \frac{n}{2}} \frac{\cos^n mx}{\cos \frac{n\pi}{2}} dx = 2\pi$$

6. It is possible for a body to have an average angular velocity without at any time possessing angular momentum.

7. The W.K.B. approximation, carried out to two terms, for the energy levels in the treatment of the V-shaped potential gives a result which is in error by only 15% for the lowest energy level and by 2% for the first excited state. The approximation becomes essentially perfect for higher levels.

8. An interesting group of substances has been neglected entirely by structural chemists. The study of bicyclohydrocarbons would be extremely interesting and would provide considerable information about strain energies.

9. Trouton's rule in its original form is more useful, from a practical standpoint, than Hildebrand's improved rule. However, no reasonably accurate method exists for calculating heats of vaporization from data which are commonly available.

10. a) All freshman recitation sections should be taught by the same person--preferably the instructor in freshman chemistry who should be relieved of other teaching duties.

b) 30% H_2O_2, rather than Na_2O_2, should be used in courses in analytical chemistry.

c) Advantage could be taken of the ability of $Al(OH)_3$ to precipitate colloidal NiS.