earlier for the calculation of the heat of denaturation of methemoglobin: it may be argued that the solutions which were denoted as native in Table I, because no precipitate formed on bringing them to the isoelectric point, were actually partially denatured. However, the slopes of the lines drawn through the experimental points in Fig. 3 are identical for the native and denatured solutions. If in the "native" solutions partial denaturation occurred, it would certainly depend on the *p*H of these solutions and hence the slope would be entirely different from that for the denatured solutions.

The magnitude of the heat of denaturation here reported is about twice as large as that reported by Anson and Mirsky[12] for trypsin and it is interesting to note that the molecular weights of the two proteins stand also in the 2:1 ratio. However, the thermal data on this type of protein reaction are still too meager to attempt their correlation with the structure of proteins.

Dr. Thomas S. Chambers has made preliminary experiments on the denaturation of methemoglobin and participated in the preparation of the stock solutions, for which our thanks are due him. We wish also to thank Dr. W. F. Ross of Harvard and Radcliffe for many valuable suggestions and discussions of the problem. To the Rockefeller Foundation our thanks are due for the financial assistance without which this work would not have been possible.

Summary

1. A calorimeter is described which is suitable for observations on slow reactions with small heat changes.

2. It is shown that denaturation of methemoglobin at *p*H 10 to 12 is a measurably fast reaction accompanied by heat absorption in the initial stages and by heat evolution toward its end. The rate of these processes increases rapidly with *p*H.

3. By an indirect calorimetric procedure the heat of denaturation is determined to be: $\Delta H = 138\ (\pm 14)$ kcal. per mole of methemoglobin, at constant quantity of alkali in the solution. At constant *p*H the heat of denaturation is about 100 kcal.

4. The process of denaturation is shown to be very complex and the precipitability of methemoglobin at the isoelectric point is found to be not a good measure of denaturation.

CAMBRIDGE, MASS. RECEIVED MAY 10, 1940

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[12] Anson and Mirsky, *J. Gen. Physiol.*, **17**, 393 (1934).

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES]

X-Ray Examination of Polyisobutylene[1]

BY C. S. FULLER, C. J. FROSCH AND N. R. PAPE

Polyisobutylene was first studied from the X-ray standpoint by Brill and Halle.[2] These investigators pointed out that when this material was stretched to the maximum the amorphous X-ray diagram was replaced by a fiber pattern, analogous to the case of natural rubber. They found the identity period in the fiber direction to be 18.5 Å. and concluded that the molecules in the stretched state are not planar zigzag but because of the methyl side-groups are probably helical. The authors have re-examined this polymeric substance and in agreement with the work of Brill and Halle find that the reflections appear instantaneously and without orientation phenomena just as in the case of natural rubber. The identity period reported by these authors has been verified and good evidence has been found that the chain molecules in the crystalline regions of the stretched substance assume a coiled form and possess a 1:3 disposition of the methyl groups. Although the present work cannot claim to have arrived at a definite structure for crystalline polyisobutylene, it has been shown that the orthorhombic cell, $a = 6.94$ Å., $b = 11.96$ Å., $c = 18.63$ Å., is in agreement with the observed data.

Material and Procedure Employed.—Polyisobutylene[3] consists of long molecules which in the stretched material may be regarded as essentially linear in form. In the case of the lower molecular weight products there is insufficient interaction between molecules to enable the substance to be held in the stretched condition without relaxation. In the case of the very high molecular weight products, however, the behavior is decidedly rubber-like

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[1] Presented before the Division of Rubber Chemistry of The American Chemical Society at Cincinnati, Ohio, April 12, 1940.

[2] Brill and Halle, *Naturwissenschaften*, **26**, 12 (1938).

[3] Thomas, Sparks, Frolich, Otto and Mueller-Cunradi, THIS JOURNAL, **62**, 276 (1940).

and elongations of 1000% or more may be maintained for sufficient time to secure suitable X-ray data.

The samples employed in this investigation were all of the highest obtainable molecular weight.[4] Strips of suitable dimensions were oriented by stretching and the ends were clamped in order to maintain the samples in the elongated condition. In many cases it was found necessary to give a second stretch to the sample in order to produce sufficient richness and intensity in the fiber pattern. In all instances the force required approached very closely the breaking stress.

Exposures ranging from four to twelve hours were made employing filtered copper radiation. A General Electric X-ray tube operating at 35,000 volts and 25 milliamperes and fitted with a copper target was used. It was found that except in the case of the strongest reflections with long exposure 0.8 mil (0.02 mm.) of nickel foil eliminated the extraneous radiations (copper K-beta and the weak L lines of tungsten) and greatly reduced the continuous radiation. Consequently, it is felt that the reflections observed (Table I) arise from the characteristic K-alpha radiation.

Exposures were made both with the samples perpendicular to the beam and inclined at various angles to the beam in order to detect meridian reflections. Attempts were also made to produce double orientation[5] in the stretched films by stretching while maintaining the width[6] but such orientation was not detected. Finely powdered sodium chloride was used as a standard of reference by dusting directly on the polyisobutylene specimens.

In order to verify certain doubtful reflections K. H. Storks kindly consented to examine a thin film of polyisobutylene by means of electron diffraction. The photographs so obtained showed several features not contained in the X-ray fiber patterns, namely, a weak 100 (see Table I) and a rather strong 0016 reflection. A possible 003 meridian reflection also appears to be present.[7] Unlike the X-ray specimens those employed by Storks showed the presence of double orientation as indicated by the fact that a fluctuation in the intensities of the equatorial reflections occurred on rotation of the specimen around the fiber axis an angle of 45°. The effect of these results on the interpretation of the X-ray data will be discussed below.

TABLE I

	Observed					
Ref.	Int.	*d*	*h*	*k*	*l*	Calcd. *d*.
			0	1	0	11.96
A_1[2]	W.	6.88	1	0	0	6.94
			1	1	0	6.00
2	V. S.	5.98	0	2	0	5.98
			1	2	0	4.53
			0	3	0	3.99
3	W.	3.47	2	0	0	3.47
			1	3	0	3.46
4	W.	3.31	2	1	0	3.33
			2	2	0	3.00
5	S.	2.98	0	4	0	2.99
6	W.	2.73	1	4	0	2.75
			2	3	0	2.62
			0	5	0	2.39
			3	0	0	2.31
			3	1	0	2.27
7	M.	2.24	2	4	0	2.24
			1	5	0	2.24
			3	2	0	2.16
			3	3	0	2.00
			0	6	0	1.99
8	M.	1.97	2	5	0	1.97
			1	6	0	1.92
			0	0	1	18.63
			0	1	1	10.07
I_1	S.	6.47	1	0	1	6.50
			1	1	1	5.71
2	S.	5.69	0	2	1	5.69
3	M.	4.40	1	2	1	4.40
			0	3	1	3.90
			2	0	1	3.41
4	M.	3.39	1	3	1	3.40
5	M.	3.25	2	1	1	3.28
			2	2	1	2.96
6	M.	2.94	0	4	1	2.95
7	M.	2.71	1	4	1	2.72
8	W.	2.57	2	3	1	2.60
9	W.	2.36	0	5	1	2.37
10	W.	2.27	3	0	1	2.30
11	W.	2.24	3	1	1	2.25
			2	4	1	2.25
			1	5	1	2.25
12	W.	2.12	3	2	1	2.14
			3	3	1	1.99
			0	6	1	1.98
13	W.	1.95	2	5	1	1.96
14	W.	1.88	1	6	1	1.91
			3	4	1	1.82
II_0	W.	9.33	0	0	2	9.32
			0	1	2	7.35
1	W.	5.58	1	0	2	5.57
2	M.	5.05	1	1	2	5.05
			0	2	2	5.03
3	V. S.	4.07	1	2	2	4.07
4	M.	3.66	0	3	2	3.67
5	M.	3.25	2	0	2	3.25
			1	3	2	3.24
6	M.	3.13	2	1	2	3.14
			2	2	2	2.86
7	M.	2.83	0	4	2	2.85
6	W.	2.62	1	4	2	2.63
9	W.	2.50	2	3	2	2.52
10	W.	2.34	0	5	2	2.32
			3	0	2	2.25
			3	1	2	2.21
11	M.	2.18	2	4	2	2.20
			1	5	2	2.20
12	M.	2.08	3	2	2	2.10
			3	3	2	1.96
			0	6	2	1.95
13	W.	1.90	2	5	2	1.93

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[4] The authors wish to thank Mr. F. J. Malm for his aid in securing suitable samples for this work.

[5] Mark and v. Susich, *Kolloid-Z.*, **46**, 11 (1928).

[6] Gehman and Field, *J. App. Physics*, **10**, 564 (1939).

[7] An indication of this reflection has also been found on one of the X-ray photographs.

TABLE I (*Continued*)

Observed Ref.	Int.	*d*	*h*	*k*	*l*	Calcd. *d*.
$_{14}$	W.	1.85	1	6	2	1.88
			3	4	2	1.80
III$_0$?	W.	6.11	0	0	3	6.21
			0	1	3	5.51
			1	0	3	4.63
$_{1}$	V. S.	4.32	1	1	3	4.32
			0	2	3	4.31
$_{2}$	M.	3.66	1	2	3	3.66
$_{3}$	W.	3.33	0	3	3	3.36
			2	0	3	3.03
$_{4}$	W.	3.01	1	3	3	3.02
$_{5}$	M.	2.92	2	1	3	2.94
			2	2	3	2.70
$_{6}$	M.	2.68	0	4	3	2.69
$_{7}$	S.	2.50	1	4	3	2.51
$_{8}$	S.	2.39	2	3	3	2.41
$_{9}$	W.	2.20	0	5	3	2.23
			3	0	3	2.17
$_{10}$	M.	2.11	3	1	3	2.13
			2	4	3	2.13
			1	5	3	2.13
$_{11}$	M.	2.01	3	2	3	2.04
			3	3	3	1.90
			0	6	3	1.90
$_{12}$	M.	1.85	2	5	3	1.88
$_{13}$	W.	1.81	1	6	3	1.83
			3	4	3	1.76
IV$_0$	W.	4.68	0	0	4	4.66
			0	1	4	4.34
$_{1}$	M.	3.87	1	0	4	3.87
$_{2}$	M.	3.68	0	2	4	3.68
			1	1	4	3.68
$_{3}$	M.	3.25	1	2	4	3.25
$_{4}$	S.	3.03	0	3	4	3.03
$_{5}$	S.	2.77	2	0	4	2.78
			1	3	4	2.78
			2	1	4	2.71
$_{6}$	M.	2.50	2	2	4	2.52
			0	4	4	2.52
			1	4	4	2.37
$_{7}$	M.	2.26	2	3	4	2.28
$_{8}$	M.	2.12	0	5	4	2.13
			3	0	4	2.07
			3	1	4	2.04
			2	4	4	2.04
$_{9}$	S.	2.02	1	5	4	2.03
			3	2	4	1.96
			3	3	4	1.84
			0	6	4	1.83
$_{10}$	W.	1.81	2	5	4	1.81
			1	6	4	1.77
			0	0	5	3.73
V$_1$	V. S.	3.56	0	1	5	3.56
$_{2}$	V. S.	3.31	1	0	5	3.28
			1	1	5	3.17
$_{3}$	V. S.	3.16	0	2	5	3.16
$_{4}$	S.	2.87	1	2	5	2.88
			0	3	5	2.72
			2	0	5	2.54
$_{5}$	M.	2.53	1	3	5	2.53
			2	1	5	2.48
			2	2	5	2.34
$_{6}$	M.	2.33	0	4	5	2.33
$_{7}$	M.	2.20	1	4	5	2.21
$_{8}$	M.	2.12	2	3	5	2.14
$_{9}$	W.	2.00	0	5	5	2.01
			3	0	5	1.97
			3	1	5	1.94
			2	4	5	1.94
$_{10}$	W.	1.91	1	5	5	1.93
$_{11}$	W.	1.84	3	2	5	1.87
			3	3	5	1.76
			0	6	5	1.76
$_{12}$	W.	1.73	2	5	5	1.74
			1	6	5	1.70
VI$_0$	W.	3.15	0	0	6	3.11
			0	1	6	3.01
			1	0	6	2.83
$_{1}$	S.	2.76	1	1	6	2.76
			0	2	6	2.76
			1	2	6	2.56
$_{2}$	W.	2.44	0	3	6	2.45
			1	3	6	2.31
			2	0	6	2.31
$_{3}$	M.	2.27	2	1	6	2.27
			2	2	6	2.16
$_{4}$	M.	2.14	0	4	6	2.15
$_{5}$	W.	2.04	1	4	6	2.06
			2	3	6	2.00
			0	5	6	1.90
			3	0	6	1.86
$_{6}$	W.	1.82	3	1	6	1.83
			2	4	6	1.83
			1	5	6	1.83
			3	2	6	1.77
			0	0	7	2.66
			0	1	7	2.60
			1	0	7	2.49
VII$_1$	S.	2.43	1	1	7	2.43
			0	2	7	2.43
			1	2	7	2.30
$_{2}$	W.	2.21	0	3	7	2.21
			2	0	7	2.11
			1	3	7	2.11
$_{3}$	W.	2.08	2	1	7	2.08
$_{4}$	W.	1.98	2	2	7	1.99
			0	4	7	1.99
			1	4	7	1.91
$_{5}$	W.	1.85	2	3	7	1.87
			0	5	7	1.78
VIII$_0$	S.	2.33	0	0	8	2.33
$_{1}$	V. S.	2.30	0	1	8	2.29
$_{2}$	V. S.	2.21	1	0	8	2.21
$_{3}$	V. S.	2.16	1	1	8	2.17
			0	2	8	2.17
$_{4}$	M.	2.07	1	2	8	2.07
			0	3	8	2.01

TABLE I (*Concluded*)

Observed Ref.	Int.	d	h	k	l	Calcd. d
$_5$	W.	1.92	2	0	8	1.93
			1	3	8	1.93
			2	1	8	1.91
$_6$	W.	1.83	2	2	8	1.84
			0	4	8	1.84
			1	4	8	1.78
			0	0	9	2.07
			0	1	9	2.04
			1	0	9	1.98
IX$_1$	V. W.	1.96	1	1	9	1.96
			0	2	9	1.96
$_2$	V. W.	1.88	1	2	9	1.88
			0	3	9	1.84
			2	0	9	1.78
			1	3	9	1.78
			2	1	9	1.76
			2	2	9	1.70
			0	4	9	1.70
$_3$	V. W.	1.64	1	4	9	1.65
$_4$	V. W.	1.62	2	3	9	1.62
			0	5	9	1.57
			3	0	9	1.54
X$_0$	W.	1.85	0	0	10	1.86
$_1$	W.	1.84	0	1	10	1.84
			1	0	10	1.80
$_2$	W.	1.77	1	1	10	1.78
			0	2	10	1.78
			1	2	10	1.72
$_3$	W.	1.70	0	3	10	1.69
			2	0	10	1.64
			1	3	10	1.64
$_4$	W.	1.62	2	1	10	1.63
$_5$	W.	1.57	2	2	10	1.58
			0	4	10	1.58
			1	4	10	1.54
			0	0	11	1.69
			0	1	11	1.68
XI$_1$	M.	1.66	1	0	11	1.65
$_2$	M.	1.63	1	1	11	1.63
			0	2	11	1.63
			1	2	11	1.59
$_3$	M.	1.57	0	3	11	1.56
			2	0	11	1.52
			1	3	11	1.52
$_4$	W.	1.50	2	1	11	1.51
			2	2	11	1.48
$_5$	W.	1.46	0	4	11	1.47
			1	4	11	1.44

Results

Figure 1 shows the diffraction effects observed for perpendicular incidence on (a) unstretched polyisobutylene, and (b) the same sample elongated approximately 1400%. Figure 2 illustrates the patterns obtained for various inclinations of the fiber axis to the beam direction as noted on this figure. A tabulation of the observed reflections together with the observed *d*-values and relative intensities is given in the first three columns of Table I.

It is evident from Fig. 1(b) that the molecules of polyisobutylene form well-defined crystalline regions and the breadth of the reflections shows these regions to be very small. As evidenced by the richness of the patterns, an arrangement of the chain molecules is present which permits of a large number of strongly reflecting atomic planes. The average identity period in the fiber direction as taken from the more reliable measurements of Table I is 18.63 ± 0.05 Å., a value which agrees well with that of 18.5 Å. reported previously by Brill and Halle.[2]

By means of the inclined photographs of Fig. 2, meridian reflections have been located on the second, fourth, sixth, eighth and tenth layer-lines. It is significant that the odd orders are absent except for the possible 003 reflection mentioned above. The eighth layer-line reflection is particularly strong and indicates a division of the fiber period by relatively strong planes spaced 2.33 Å. apart. The significance of this in regard to the molecular structure will be considered below.

Chain Configuration.—Whenever a substance consisting of long-chain molecules is subjected to a stress it is common to find that the molecules are aligned with their long axes in the direction of the stress. If the substance is already crystalline, orientation phenomena occur, and the molecules are completely aligned when orientation is perfect. On the other hand, if the substance crystallizes on stretching as in the case of natural rubber, the first crystals which form already are oriented completely in the direction of the stress. The latter is the case with polyisobutylene and it may be taken as axiomatic that the chain molecules in the oriented specimens are aligned in the direction of stretch (vertical in Figs. 1 and 2). The fiber period of 18.63 Å., therefore, corresponds to the distance at which the structure repeats along the chain direction. Since the chains are essentially continuous, elements of the chains must repeat at this distance. It does not follow from this, however, that the molecule must always assume its most extended form. Packing considerations may require more folded or coiled arrangements.[8]

To arrive at a plausible chain configuration for polyisobutylene in the crystalline state, it is neces-

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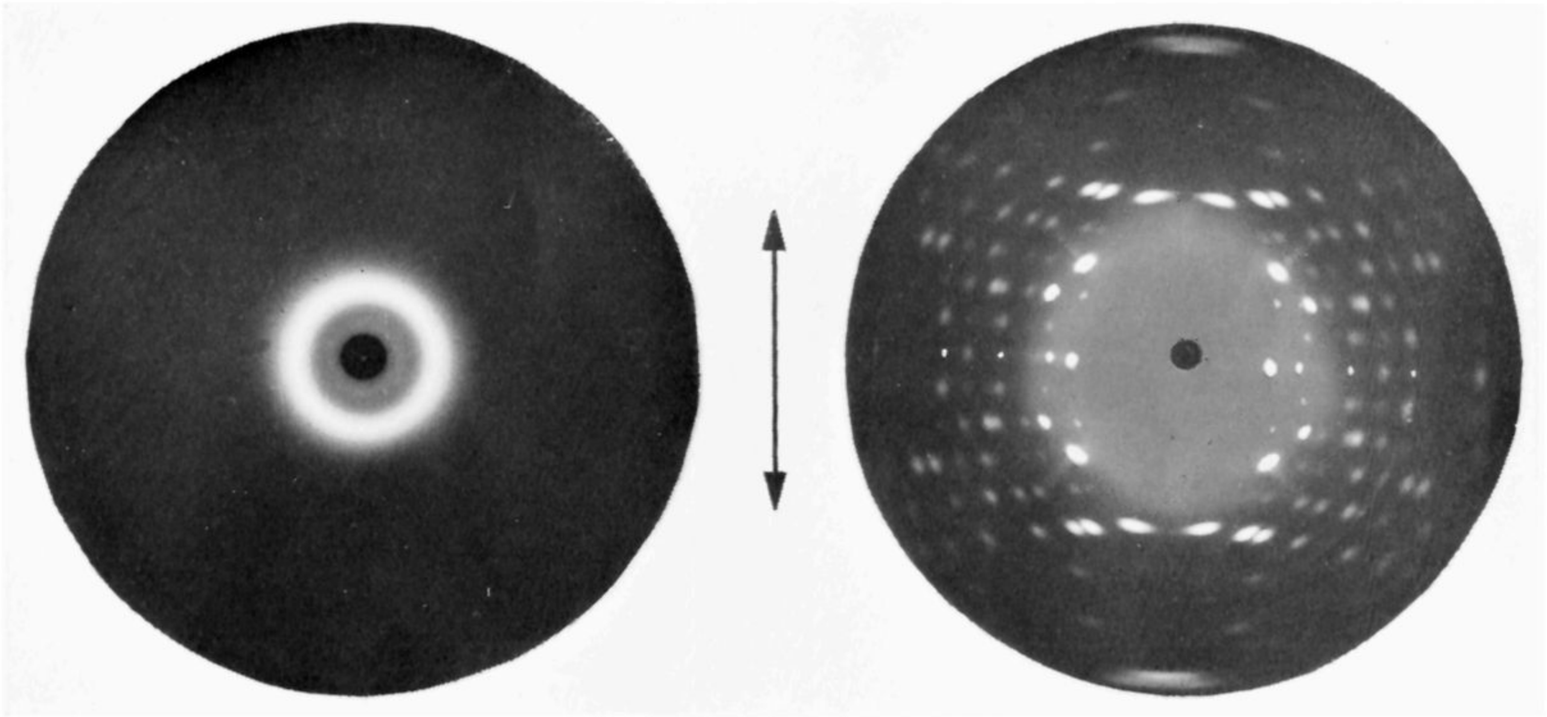
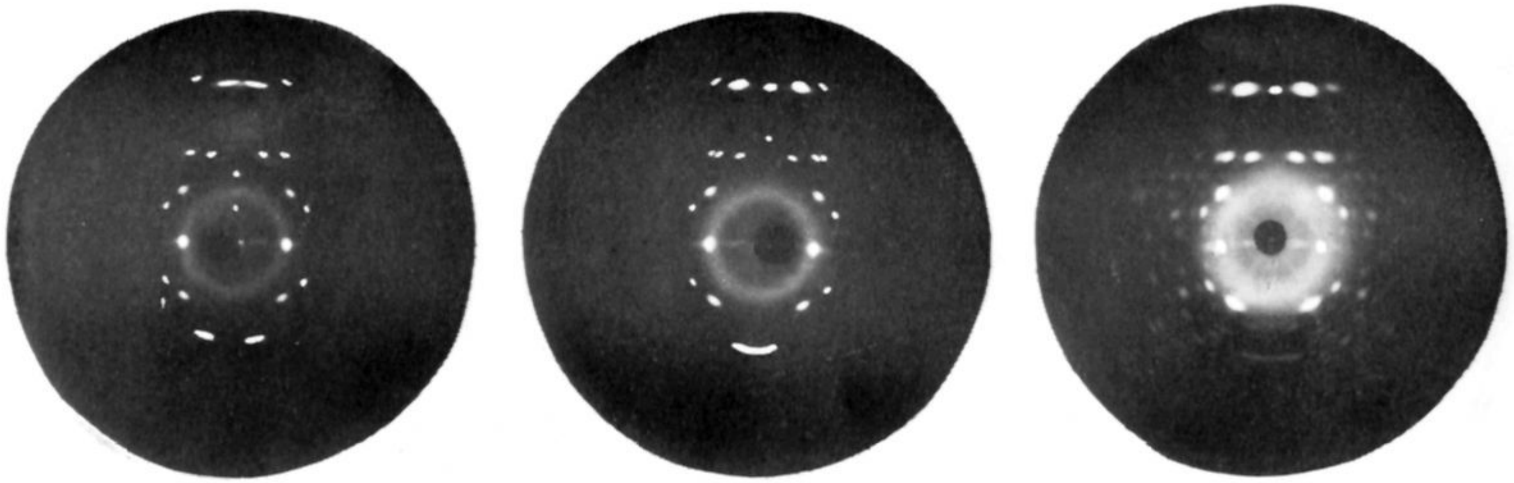
[8] Fuller, *Chem. Rev.*, **26**, 143 (1940).



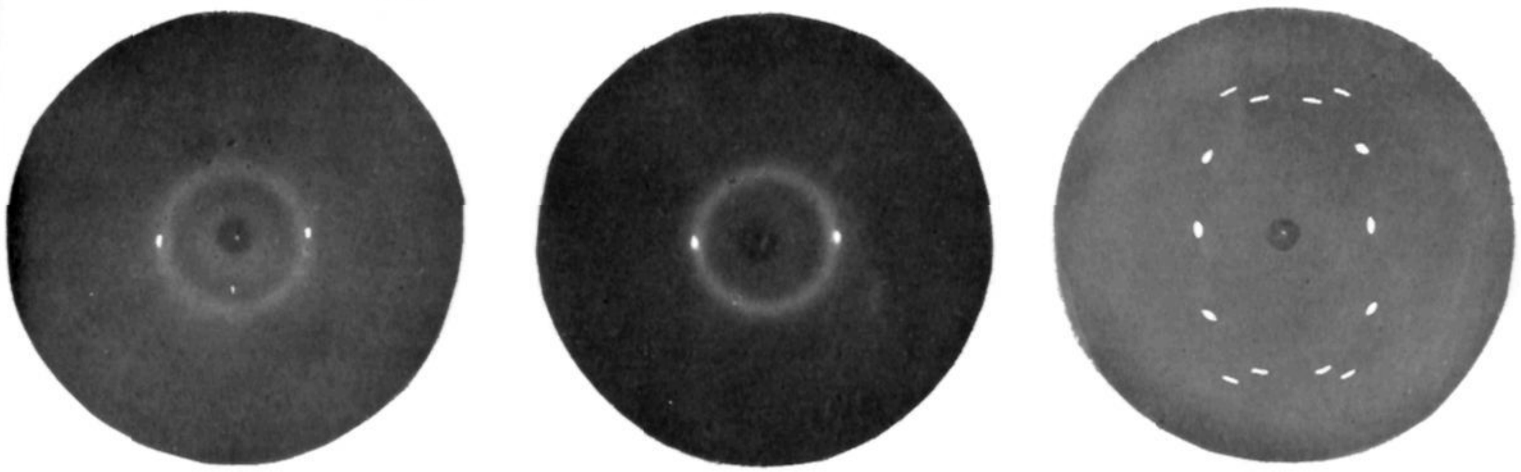
(a) (b)

Fig. 1.—X-ray diffraction photographs of (a) unstretched polyisobutylene, plate distance 3 cm. and (b) polyisobutylene stretched to the maximum, distance 4 cm. The fiber axis is vertical.



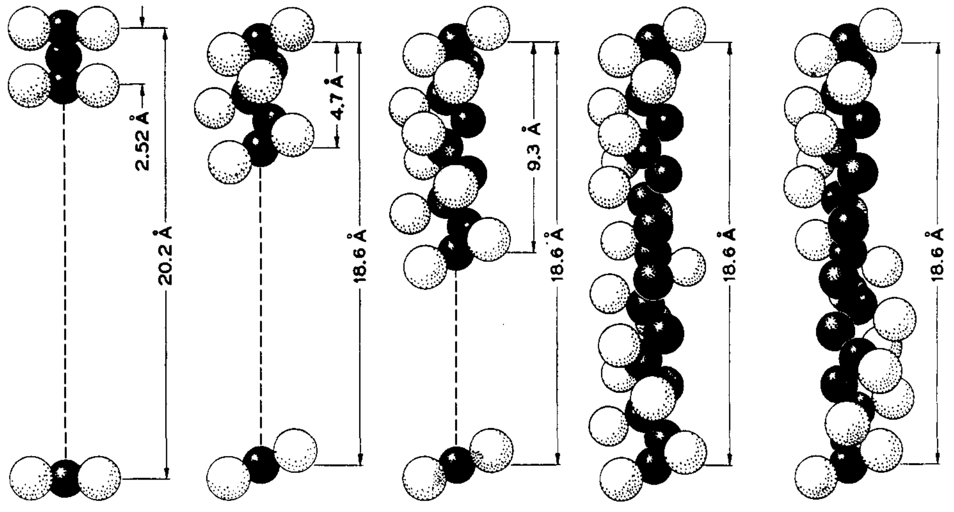
15° 20° 25°

Fig. 2.—Fiber diagrams of polyisobutylene obtained from stretched samples inclined at various angles to the X-ray beam and showing the even order meridian reflections. The fiber axis is vertical. Plate distance 3 cm.



275% 350% 500%

Fig. 6.—Effect of percentage elongation on the fiber pattern of polyisobutylene at 25°. The fiber axis is vertical. Plate distance 3 cm.



(a) (b) (c) (d) (e)

Fig. 3.—Various 1:3 chain configurations: (a) planar zigzag form; (b) to (e) non-planar forms which produce the required shortening. The larger spheres represent methyl groups.

sary first to consider why a disposition of the methyl groups on every other chain carbon rather than on adjacent carbons accords best with the facts furnished by the X-ray patterns. The inclined exposures of Fig. 2 show that only the even orders of the planes perpendicular to the fiber axis (00*l*) are prominent and of these the eighth order is the strongest. This behavior is difficult to explain on the basis of a 1:2 or "head-to-head"–"tail to-tail" arrangement but is readily explained by the 1:3 or "head-to-tail" arrangement of the isobutylene units, *i. e.*, with a disposition of the methyl group pairs on alternate atoms along the chain molecule. Thus, the 1:2 form of chain requires a strong 004 and a weak 008 reflection, whereas the 1:3 form requires a weak 004 and a strong 008 as observed.[9] The planar zigzag 1:3 chain is illustrated in Fig. 3(a). Furthermore, the strong 008 reflection indicates that the methyl group pairs are spaced 2.33 Å. along the fiber direction and hence that there are eight isobutylene units in the fiber period.

This length (2.33 Å.) for the isobutylene unit is considerably less than that required for a planar zigzag arrangement of the carbon atoms, namely, 2.52 Å., as is shown in Fig. 3(a). The usual strong layer-line reflection occurring at 2.15 Å. in patterns of zigzag structures[10] is also absent from the patterns of polyisobutylene. The polyisobutylene chain does not, therefore, have a planar zigzag form of chain as in the paraffins[11] and certain other long-chain substances.[8]

A scale model of the polyisobutylene chain constructed on the basis of the 1:3 arrangement of the methyl groups shows that successive methyl group pairs must assume a staggered packing in order to permit the chain to assume a fully extended linear form. The tightness of the packing also requires that the line joining the carbon atoms of each methyl group pair form an angle of approximately 22.5° with the plane perpendicular to the molecule axis. Assuming that the steric conditions are such as to necessitate a staggered arrangement of the methyl groups, there are four possibilities to be considered. These are shown in Figs. 3(b) to (e). Of these various structures those represented in (b) and (c) can be discarded immediately since they do not reproduce the observed fiber period. The remaining helical configurations of Fig. 3 agree with the observed fiber period (18.63 Å.) and the requirement of eight isobutylene units in the repeating length as suggested by the strong eighth-order meridian reflection and density considerations (see below). It is very difficult, however, to choose between these two configurations on the basis of the available X-ray evidence. As will be shown in the next section, the extinctions favor the form of chain shown in Fig. 3(e) in which the methyl group pairs complete one revolution about the chain axis in the fiber period distance.

It is logical to assume, therefore, that the chain

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[9] It is assumed that the chain is uniform and that the methyl groups on adjacent chains are opposed. If they are unopposed, only the 0016 reflection would appear strong.

[10] Fuller and Frosch, *J. Phys. Chem.*, **43**, 323 (1939).

[11] Muller, *Proc. Roy. Soc.* (London), **A120**, 437 (1928).

configuration in polyisobutylene is that of a helix in which the successive methyl group pairs pack together in a staggered arrangement. This necessitates successive partial rotations of the methyl group pairs an angle of 45° around the molecule axis. In this manner coincidence results after eight such rotations. In Fig. 3 no attempt has been made to illustrate the actual packing, which in reality is quite close.

X-Ray Structure.—The difficulties of working out of the X-ray structure of crystalline high molecular organic substances on the basis of data furnished by the fiber pattern alone has been the subject of much discussion.[5,12,13] As is well known, these difficulties arise chiefly through the fact that the orientation in these substances giving rise to the fiber pattern is generally of the uniaxial type and does not allow the identity periods other than that along the fiber axis to be uniquely determined. The production of selective uniplanar orientation[14] which is possible in certain instances, notably in natural rubber,[5,6] is of some further assistance in this regard. Even in these cases, however, there has been considerable disagreement among investigators in the past even as to what crystal system should be assigned to these structures.[5,15–20]

Two other factors frequently further complicate the situation. Very often as in the case of natural rubber relatively few reflections occur so that the indexing of the patterns and the determination of the space group on the basis of the missing spectra are particularly hazardous. Second, the fuzziness of the reflections present makes accurate measurement impossible and often leads to confusion due to the overlapping of spectra.

The justification for suggesting in this investigation a unit cell and possible space group for the crystalline components in stretched polyisobutylene is based on the following arguments. First, the chemical structure of the substance is well established and consists of isobutylene units combined into chain molecules.[2] This information together with the knowledge that the fiber period comprises eight isobutylene units simplifies the working out of the structure since we are enabled to start with a linear unit of pattern in which are combined together in a known manner a large fraction of the total number of atoms involved in the unit cell. Second, an extremely rich pattern involving reflections from over 100 planes is given by polyisobutylene and these reflections are sufficiently sharp and intense in most cases to enable quite accurate measurements to be made.

Obviously, the analysis of the structure cannot proceed in as straightforward a manner as in the case of the analyses based on single crystals and the problem of determining the numerous atomic parameters is an exceedingly complicated one. To show the various lattice possibilities, consider the planar net (Fig. 4) which arises from the equatorial reflections. Inspection shows that a hexagonal cell (h) can be chosen since within the limit of error the spacing corresponding to reflection A_2 in Table I is equal to that of A_3 multiplied by $\sqrt{3}$. It is not possible, however, to index the observed reflections on the basis of this cell. In addition, the required three or sixfold axes parallel to the chains are lacking. This latter fact excludes larger hexagonal cells, *e. g.*, a = 13.88 Å., c = 18.63 Å. (fiber axis) (H in Fig. 4), which are capable of accounting for the observed reflections.

The smallest orthorhombic cell, 0 in Fig. 4, must on the basis of the density contain two molecules per cell. The axes are: a = 6.94 Å., b = 11.96 Å., c = 18.63 Å. (fiber axis). Again it is possible to account for all of the observed reflections. These indices and the calculated d-values are given in Table I. If we neglect the weak 100 and 003 reflections, the indices so obtained show the following restrictions on h, k and l: (hkl) present in all orders, (h00) only present when h is even, (0k0) only present when k is even, (00l) only present when l is even. These extinctions suggest the space group $D_2^4 - P_{2_12_12_1}$. This space group requires three twofold screw axes at right angles to one another. This condition is met along c by the chain configuration arrived at above and shown in Fig. 3(e). If the central molecule in the cell, 0, of Fig. 4 is displaced along c (*i. e.*, perpendicular to the plane of the paper) a distance of one-half a repeating unit, it then becomes possible to provide twofold screw axes parallel to the other two directions in accordance with the above space group requirements.

Alternatively, if the central molecule of cell 0 of Fig. 4 is not exactly centered on the a-axis and

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[12] Katz, *Trans. Faraday Soc.*, **32**, 77 (1936).

[13] Mark, *Ber.*, **59**, 2982 (1926).

[14] Sisson, *J. Phys. Chem.*, **40**, 343 (1936).

[15] Meyer and Mark, *Ber.*, **61B**, 1939 (1928).

[16] Lotmar and Meyer, *Monatsh.*, **69**, 115 (1936); *Rubber Chem. and Tech.*, **10**, 203 (1937).

[17] Morss, THIS JOURNAL, **60**, 237 (1938).

[18] Clews, *Rubber Tech. Conf.*, Preprint No. 34.

[19] Sauter, *Z. physik. Chem.*, **43B**, 292 (1939).

[20] Misch and Van der Wijk, *J. Chem. Phys.*, **9**, 127 (1940).

a two-fold screw does not exist along the chain as the appearance of the 100 and 003 reflections would require, then the space group $D_2^4 - P_{2_12_12_1}$ is not present. In this case a shift of the middle molecule one-half the fiber period could conceivably meet the symmetry requirements of the space group P_{22_12}.

The above space groups are satisfied as to symmetry for any orientation of the molecules in azimuth (Fig. 4) as long as molecule A and molecule B are 180° out of phase. No attempt has been made in the present work to determine whether the observed intensities can be accounted for by a particular orientation.

The average density of unstretched polyisobutylene has been determined as 0.915 at 25°. If it is assumed that the same percentage increase in density occurs on stretching as occurs in the case of natural rubber, namely, 2.4%[21] then the density of the crystallized portions of polyisobutylene may be assumed to be 0.937. If this value is substituted in the equation

$$n = abcd/1.65\, mM$$

where a, b and c correspond to the axes of the orthorhombic cell, d to the density, m to the molecular weight of one isobutylene unit (56.0) and m to the number of these units per repeating length in the chain direction; then n, the number of repeating units per cell, is 1.96 when m is 8, as has been assumed above. This is in good agreement with the expected value of 2.0. Values of n of 1.74 and 2.24 are obtained when m is chosen as 7 and 9 units, respectively, instead of 8. It is evident, therefore, that 8 units is in best agreement with the density requirements.

Discussion

It must be admitted that the process by which the chain configuration described above has been obtained is to no little extent intuitive. However, as has been stated, accurate structural models of the polyisobutylene chain enable one to see readily the reasonableness of this configuration. For it is only by a rotation of the methyl group pairs as described that the chain can be made to assume the linear form and less logical configurations which still explain the X-ray results are difficult to accept on the basis of the intimate packing which is required. Because of its cylindrical form a helical 1:3 type of chain is in good agreement with the pseudo-hexagonal nature of the unit cell. It is of interest also that the angle formed between a plane perpendicular to the axis of the helix and the tangent to the helix is closely 67.5° when the methyl group rotations of 45° as described above are carried out. This is precisely the angle required to convert the zigzag spacing of 2.52 Å. (Fig. 3(a)) into 2.33 Å. when projected on the molecule axis. The chain of Fig. 3(e) would be expected to confer optical activity on the crystal. Actually, of course, a mixture of right and left-handed crystals could exist in the polycrystalline mass.

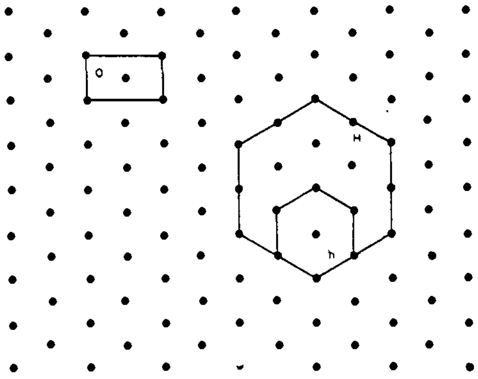

Fig. 4.—A cross section of crystalline polyisobutylene taken perpendicular to the axis of the molecules (c-axis) showing the positions of the molecules which agree with the equatorial reflections and the density. Various unit cells are shown.

If it is assumed that a 1:3 type of chain having the helical form described above and that the two molecules contained in the unit cell are situated with respect to one another in such a way that the methyl substituted carbon atoms fall in common horizontal planes for both chains (Fig. 5), it is easy to show that only the eighth and sixteenth orders of the meridian reflection should appear strong. The fact that other even orders also appear may be due to an incomplete alignment of the atoms of the two molecules in the proper horizontal planes. A mixture of the two types of chains, *i. e.*, the 1:2 and the 1:3 with the latter predominating is also not excluded. The appearance of the 100 reflection (on the electron photographs) and possibly also of the 003 reflection may also be explained on a similar basis. Otherwise the presence of these reflections of course invalidates the $P_{-2_12_12_1}$ space group.

It is of interest to compare briefly the conclusions drawn above in regard to the structure of stretched polyisobutylene with the corresponding

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[21] Davis and Blake, *Chemistry and Technology of Rubber*, 71 (1937).

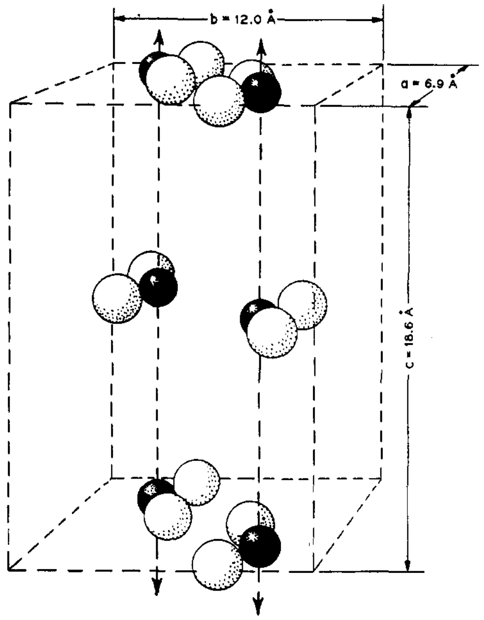

Fig. 5.—Schematic view of the unit cell of polyisobutylene showing a possible chain arrangement. The larger spheres represent methyl groups.

results on natural rubber. The original space group symmetry of three two-fold screw axes perpendicular to one another which was proposed by Meyer and Mark[22] for natural rubber is identical with that suggested by the present work on polyisobutylene. Later work on rubber[16-20] has modified these original conclusions of Meyer and Mark in favor of a less symmetrical space group. Whether the higher symmetry here proposed for polyisobutylene will prove ultimately to be correct will have to await further investigation. The structural formulas of the two compounds, however, furnish a basis for expecting polyisobutylene to assume a more symmetrical chain configuration than rubber, which in turn might be expected to lead to more symmetrical packing in the crystal.

The shortening of the chain as compared to the planar zigzag arrangement is considerably greater for rubber than for polyisobutylene. Thus, in the case of rubber this shortening amounts to 0.35 Å. per pair of chain atoms, whereas for polyisobutylene it is only 0.19 Å. The rubber chain may be considered, therefore, as more folded. On the other hand, if the cross sections of the chains are calculated using for this purpose the cell of Lotmar and Meyer[16] or that of Sauter,[19] the values of 28 Å.^{2} for rubber and 41.5 Å.^{2} for polyisobutylene are obtained. Thus, although the rubber chain is more folded, it nevertheless requires considerably less area than that of polyisobutylene, a fact which is in part due to the presence of only one methyl group every four chain atoms in the case of rubber. It is possible, therefore, as has been suggested,[22] that the rubber chain is flatter.

Natural rubber and polyisobutylene show an analogous effect of elongation on their X-ray fiber patterns. It is well known that the fiber pattern of rubber is very weak at room temperature at elongations of about 100% and becomes progressively more intense as more crystallinity is produced by further stretching.[23] Polyisobutylene of medium degree of polymerization does not show crystallinity on stretching except at elongations above 1000%. Then, just as with rubber, the pattern becomes more intense with further stretching. This difference is perhaps understandable when one considers the behavior of sol and gel rubber in this respect. Thus, it has been found[24] that sol rubber shows no fiber pattern up to 1000% elongation, whereas the gel portion shows crystalline behavior just above 100%. Since polyisobutylene is an essentially saturated linear hydrocarbon in which little if any gel structure exists below a certain degree of polymerization, it is perhaps to be expected that orientation will be effective in lining up the molecular units only at the higher elongations. On the other hand, when the degree of polymerization is sufficiently high a gel apparently is formed and orientation effects are observed in approximately the same elongation range as in natural rubber. This is illustrated in Fig. 6 in which the strong A_2 equatorial reflection is just detected at 275% elongation. It is to be concluded therefore that both natural rubber and polyisobutylene show initial orientation of the molecules in roughly the same elongation range provided the degree of polymerization of the polyisobutylene is sufficiently high.

Finally, it is of interest to compare the amorphous rings of natural rubber and polyisobutylene. The Bragg *d*-value corresponding to the amorphous ring in polyisobutylene is 6.3 Å., which is considerably greater than the value of 4.9 Å. reported for natural rubber. Katz[25] has pointed out that the number of methyl substituents in the chains of various rubbers is related in a definite

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(22) Meyer and Mark, "Der Aufbau," Akad. Verlags ges., Leipzig, 1930.

(23) Katz, *Naturwissenschaften*, **13**, 414 (1925).

(24) Clark, Wolthuis and Smith, *Rubber Age*, **42**, 35 (1937).

(25) Katz, Selman and Heyne, *Z. Kautschuk*, 214 (1927).

way to the diameters of the amorphous rings. These data are given in Table II in which polyisobutylene is also included. It is evident that a progressive increase in the *d*-values with methyl substitution occurs.

TABLE II

	Methyl groups per chain atom	*d*-Value amorphous ring (Å.)
Polybutadiene	0	4.6
Polyisoprene	$^1/_4$	4.9
Polydimethylbutadiene	$^1/_2$	5.4
Polyisobutylene	1	6.3

Summary

1. Fiber patterns of polyisobutylene have been obtained which have enabled complete measurements to be made. It is found in agreement with Brill and Halle that the fiber period is 18.63 ± 0.05 Å.

2. Inclined photographs indicate that 8 isobutylene units are contained in the repeating distance along the chain. This together with other evidence suggests a 1:3 arrangement of the methyl group pairs along the chain and a helical chain configuration.

3. The X-ray structure of polyisobutylene crystals is discussed and it is shown that the data obtained agree with an orthorhombic cell having $a = 6.94$ Å., $b = 11.96$ Å. and $c = 18.63 \pm 0.05$ Å. (fiber axis).

4. The effect of elongation on the X-ray fiber pattern of high molecular polyisobutylene is shown to be analogous to that of natural rubber.

SUMMIT, N. J. RECEIVED MAY 2, 1940

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA, NO. 777]

The Molecular Structures of Dimethyl Chloramine and Methyl Dichloramine

BY D. P. STEVENSON AND VERNER SCHOMAKER

The chlorine–oxygen distance in chlorine monoxide,[1a] the fluorine–oxygen distances in fluorine monoxide[1a,b] and fluorine nitrate,[1c] and the fluorine–fluorine distance in fluorine,[1d] which have been determined from electron diffraction photographs of these molecules, are all considerably greater than the distances predicted by the covalent radius table.[2] In each of these molecules the abnormally great bond distance is that between two highly electronegative atoms. We thought it would be interesting to investigate the structure of other molecules which might involve such anomalously long bonds. In this paper we present the results of an electron diffraction investigation of dimethyl chloramine and methyl dichloramine.[3]

Experimental

The electron diffraction apparatus used in this investigation has been described by Brockway.[4] The camera distance was 10.81 cm. and the wave length of the electrons, determined in the usual way[4] from transmission photographs of gold foil, ($a_0 = 4.070$), was 0.0618 Å.

The two chloramines were prepared by the reaction of stoichiometric amounts of calcium hypochlorite (H. T. H. from the Mathieson Alkali Works), with cold concentrated solutions of the corresponding methylamine hydrochloride. The resulting solutions were acidified by the addition of dilute hydrochloric acid and fractionally distilled. The fractions were collected between 35–50° in the case of the dimethyl chloramine and between 50 and 65° for the methyl dichloramine. The samples were dried with anhydrous sodium sulfate and refractionated. The boiling points were, 45° for $(CH_3)_2NCl$ and 59° for CH_3NCl_2. It was observed that the dimethyl chloramine deposited small crystals after standing twenty-four to forty-eight hours. Accordingly, the sample of this compound was redistilled immediately before taking the photographs.

The photographs were taken with the liquid in the sample tube between 20° and 5° below the boiling point. The photographs so obtained are

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(1) (a) L. E. Sutton and L. O. Brockway, THIS JOURNAL, **57**, 473 (1935). (b) H. Boersch, *Monatsh.*, **65**, 311 (1935). (c) L. Pauling and L. O. Brockway, THIS JOURNAL, **59**, 13 (1937). (d) L. O. Brockway, *ibid.*, **60**, 1348 (1938); M. T. Rogers, D. P. Stevenson and V. Schomaker, in press.

(2) L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

(3) This pair of substituted ammonias appears to be the only sufficiently stable chloramines which are suitable for an electron diffraction investigation, although with sufficient care it might be possible to obtain electron-diffraction photographs of nitrogen trichloride. The structures of nitrosyl chloride and bromide which have been discussed by Ketelaar and Palmer [THIS JOURNAL, **59**, 2629 (1937)], probably do not involve typical nitrogen–halogen bonds.

(4) L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).