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 ± 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.

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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

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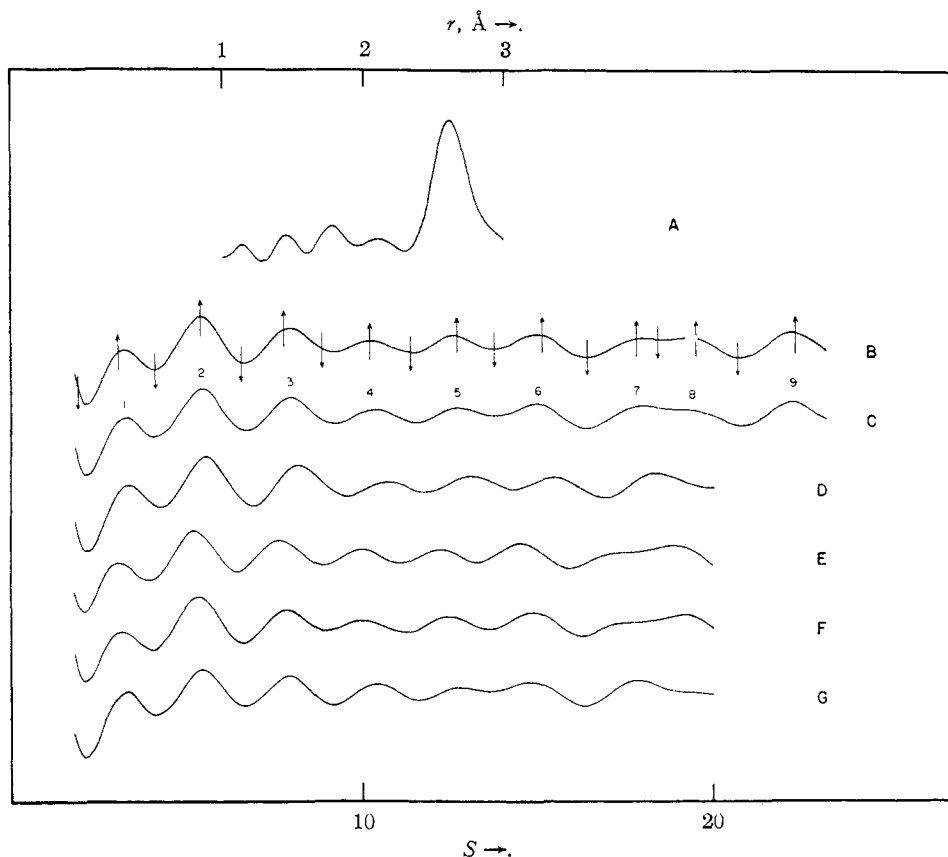
(4) L. O. Brockway, Rev. Mod. Phys., 8, 231 (1936).

Fig. 1.—Dimethylchloramine: Curve A, radial distribution curve; B, $\rho = 1.76/1.47$ and $\alpha = 108°$; C, $\rho = 1.78/1.47$ and $\alpha = 106°$; D, $\rho = 1.74/1.47$ and $\alpha = 104°$; E, $\rho = 1.80/1.47$ and $\alpha = 110°$; F, $\rho = 1.76/1.47$ and $\alpha = 110°$; G, $\rho = 1.82/1.47$ and $\alpha = 104°$.

quite good, showing nine easily measurable rings in the case of the dimethylchloramine and ten easily measurable rings for the methyldichloramine.

Interpretation

The measured s_0 values of the features of the photographs and the corresponding coefficients C_n of the radial distribution[5,6] functions are given in columns 3 and 4 of Tables I and II. The theoretical intensity curves[3] were calculated by the equation

$$I(s) = \sum_{i,j} \frac{(Z_i - f_i)(Z_j - f_j)}{(Z - f)_{Cl}} e^{-a_{ij}s^2} \frac{\sin l_{ij}s}{l_{ij}s}$$

in which account is taken of the variation with s of the relative importance of the various terms as caused by variation of the ratios of the scattering factors, $(Z_i - f_i)/(Z_j - f_j)$, and of the temperature factors $e^{-s^2(a_{ij} - a_{kl})}$. The symbols have their usual significance.[4] The a_{ij}'s were given the values 0.0022 for C—H, 0.0050 for N—H and 0.0

(5) L. Pauling and L. O. Brockway, This Journal, **57**, 2684 (1935).
(6) V. Schomaker, A. C. S. Meeting, Baltimore, Md., April, 1939.

for the other terms. Terms involving distances dependent on the rotation of the methyl groups about C–N bonds were omitted since they are known to have very severe temperature factors.

Dimethylmonochloramine.—The radial distribution curve, curve A of Fig. 1, for this molecule, shows three significant maxima at 1.46, 1.78 and 2.61 Å. corresponding to the N–C, N–Cl and C–Cl distances, respectively, and giving 107° for the C–N–Cl bond angle.

If one assumes that in the methyl groups the H–C–N angle is $109^1/_2°$, the C–H distance is 1.09 Å. and that the C–N–C angle is 108°, as it is in dimethyl- and trimethylamine, it is possible to determine the other structural parameters $\rho = $ N–Cl/N–C and $\alpha = \angle$ C–N–Cl from the comparison of the appearance of the theoretical curves with that of the photographs. Theoretical curves were calculated for seventeen models with $1.74/1.47 \leq \rho \leq (1.80/1.47)$ and $104° \leq \alpha \leq 112°$. The appearance of the photographs is well reproduced by the curves for the models for

TABLE I

Max.	Min.	Cn	s_0	sc^a	sc^b	sc^a/s_0	sc^b/s_0
	1	− 4	1.91	2.12	2.12	(1.110)[c]	(1.110)
1		6	3.05	3.21	3.20	(1.052)	(1.049)
	2	− 7	4.09	4.03	4.07	0.985	0.995
2		9	5.38	5.35	5.33	0.994	0.991
	3	−11	6.53	6.65	6.64	1.018	1.017
3		13	7.75	7.90	7.94	1.019	1.025
	4	−10	8.84	9.08	9.13	1.027	1.033
4		10	10.19	10.30	10.10	1.011	0.991
	5	− 9	11.35	11.40	11.30	1.004	.996
5		8	12.69	12.60	12.50	0.993	.985
	6	− 9	13.75	13.70	13.70	.996	.996
6		8	15.09	14.83	14.90	.983	.987
	7	−10	16.38	16.40	16.30	1.001	.995
7		8	17.79	17.80	17.90	1.001	1.006
	8	− 2	18.41	...	...	...	...
8	1	1	19.48	...	...	...	...
	9	− 6	20.68	20.70	20.70	1.001	1.001
9		5	22.34	22.20	22.20	0.994	0.994
					Average	1.003 ± 0.012	1.001 ± 0.012

[a] From curve for model with ρ = 1.78/1.47, α = 106°, Curve C. [b] From curves for model with ρ = 1.76/1.47, α = 108°, Curve B. [c] Values in parentheses omitted from average.

1.75/1.47 $\angle$ ρ $\angle$ 1.79/1.47 and 105 $\angle$ α $\angle$ 109, (see curves B and C, Fig. 1). Curves for models with the parameters outside the indicated ranges fail to reproduce the proper relative intensities of the fourth, fifth and sixth maximum, and the asymmetric form of the seventh maximum. Theoretical curves for the best models and the closely related unsatisfactory models are shown in Fig. 1.

Quantitative comparison of the photographs with the curves of satisfactory qualitative appearance (see columns 6 and 7 of Table I) gives the following values of the structural parameters for dimethyl chloramine: C–N = 1.47 ± 0.02 Å.; N–Cl = 1.77 ± 0.02 Å.; $\angle$ C–N–Cl = 107 ± 2°; C–H = 1.09° assumed; $\angle$ H–C–N = 109.5° assumed; $\angle$ C–N–C = 108° assumed.

Methyl Dichloramine.—The radial distribution curve for methyldichloramine, curve A of Fig. 2, has significant maxima at 1.74 Å. and 2.82 Å. If these peaks are assumed to correspond to the N–Cl and Cl–Cl distances respectively, the Cl–N–Cl angle is calculated to be 108°.

If the methyl group is assumed to have the structure given above, there remain three structural parameters which may be conveniently taken as the ratio ρ = N–Cl/N–C and the angles α = $\angle$ Cl–N–Cl and β = $\angle$ Cl–N–C. Theoretical curves were calculated for twenty molecular models in which the parameters were varied within the following ranges, 1.70/1.47 $\leq$ ρ $\leq$ 1.78/1.47, 104° $\leq$ α $\leq$ 112 and 104° $\leq$ β $\leq$ 112°. The structure sensitive features of the curves were

found to be the weak fourth maximum, the inner shoulder on the seventh maximum and the outer shoulder on the eighth maximum. The appearance of the photographs is very well represented by curve B of Fig. 2. The only curves which reproduce at all satisfactorily the appearance of the photographs are those for models whose parameters are, 1.72/1.47 $\angle$ ρ $\angle$ 1.76/1.47, 107° $\leq$ α $\leq$ 109° and 108° $\leq$ β $\leq$ 110°. The quantitative comparison for the two most satisfactory curves is given in Table II. Curves for the closely related unsatisfactory models are also shown in Fig. 2. The final results for the structure of methyldichloramine are: N–Cl = 1.74 ± 0.02 Å.; $\angle$ Cl–N–Cl = 108 ± 1°; $\angle$ C–N–Cl = 109 ± 1°; C–N = 1.47 Å. assumed; C–H = 1.09 Å. assumed; $\angle$ H–C–N = 109½ assumed.

TABLE II

Max.	Min.	Cn	s_0	sc^a	sc^b	sc^a/s_0	sc^b/s_0
	1	− 3¹	1.84	1.88	1.87	(1.022)[c]	(1.016)
1		5	2.90	2.92	2.88	1.007	0.993
	2	− 7	3.91	3.78	3.77	(0.967)	(0.964)
2		9	5.08	5.01	5.03	0.986	0.990
	3	−11	6.31	6.33	6.34	1.003	1.005
3		11	7.51	7.63	7.70	1.014	1.022
	4	− 6	8.60	8.86	8.90	(1.031)	(1.034)
4		6	9.54	9.50	9.40	0.996	0.985
	5	−10	10.55	10.60	10.52	1.005	0.997
5		10	11.82	11.89	11.83	1.006	1.001
	6	−10	12.87	13.23	13.30	(1.028)	(1.033)
6		2	14.02	...	...	...	...
	7	− 1	14.75	...	...	...	...
7		6	15.60	15.30	15.50	0.981	0.994
	8	− 7	16.73	17.00	17.00	1.016	1.016
8		6	18.19	18.60	18.30	1.023	1.006
	9	− 1	19.19	...	...	...	...
9		1	20.33	...	...	...	...
	10	− 4	21.38	21.10	21.20	0.987	0.992
10		4	22.55	22.50	22.70	0.998	1.007
					Average	1.002 ± 0.010	1.001 ± 0.009

[a] From curve for model with ρ = 1.74/1.47, α = 108° and β = 110°, Curve C. [b] From curves for model with, ρ = 1.74/1.47, α = 108° and β = 108°, Curve B. [c] Values in parentheses omitted from average.

Discussion

The nitrogen–chlorine distances in dimethylchloramine and methyldichloramine are 0.08 and 0.05 Å. greater than the 1.69 Å. sum of the covalent radii of nitrogen and chlorine. These new results increase our conviction that there is a general tendency for bond distances between highly electronegative atoms to be greater than the corresponding covalent radius sums. It may be noted, however, that the lengthening of the nitrogen–chlorine distance is less in methyldichloramine than in dimethylchloramine. This would suggest that the lengthening is subject to a satura-
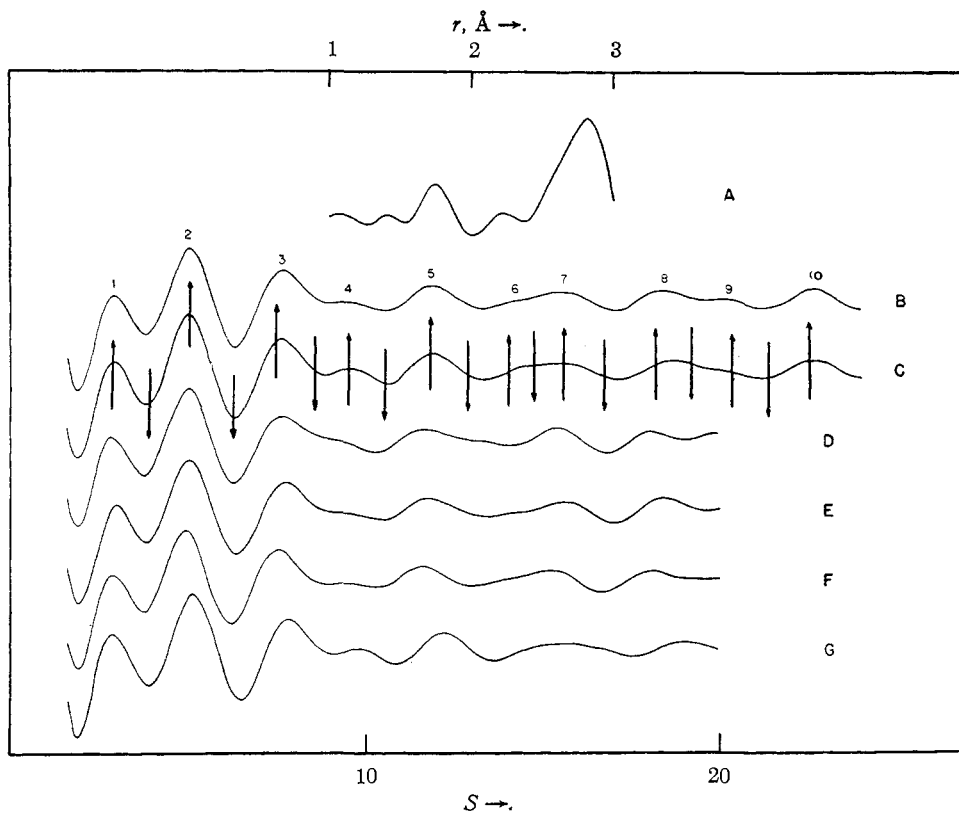
r, Å →.

Fig. 2.—Methyldichloramine: Curve A, radial distribution curve;   B, ρ = 1.74/1.47, α = 108° and β = 108°;   C, ρ = 1.74/1.47, α = 108° and β = 110°;   D, ρ = 1.74/1.47, α = 112° and β = 108°;   E, ρ = 1.74/1.47, α = 108° and β = 106°;   F, ρ = 1.78/1.47, α = 108° and β = 108°;   G, ρ = 1.70/1.47, α = 108° and β = 108°.

tion effect like that observed in the successively substituted chloroethylenes. Thus we would expect the lengthening of the chlorine–oxygen distance to be greater in hypochlorous acid and the alkyl hypochlorites than it is in chlorine monoxide. (However, this prediction regarding the relative bond distances in these molecules can be made without reference to the covalent radius table.) It is also to be noted that the bond angles in the methylchloramines are very nearly the same as in ammonia and its methyl derivatives (108°), and that the carbon–nitrogen distance found for dimethylchloramine is just that (1.47 Å.) reported for di- and trimethylamine.

Summary

An electron-diffraction investigation of the molecular structures of A, dimethylchloramine and B, methyldichloramine yields for the structural parameters of A, N–Cl = 1.77 ± 0.02 Å., C–N = 1.47 ± 0.02 Å. and C–N–Cl = 107 ± 2°, and B, N–Cl = 1.74 ± 0.02 Å., Cl–N–Cl = 108 ± 2° and C–N–Cl = 109 ± 2°. In both molecules the N–Cl distance is greater than the value predicted by the covalent radius table of Pauling and Huggins, 1.69 Å. The C–N distance in dimethyl chloramine, and the bond angles in both molecules are normal.