individual schedule used. It is believed that the optimum schedule for A may increase the total possible antimony dosage.

TABLE I

Schedule[a]	Fouadin	A[b]
1/3 LD_{50} 1x/day × 14 days[c]	0.2 worms/mouse[d]	1.4 worms/mouse
1/3 LD_{50} 2x/day × 14 days	0.3 worms/mouse	0.0 worms/mouse
1/3 LD_{50} 2x/day × 7 days	4.5 worms/mouse	14.0 worms/mouse

[a] Drugs administered by intraperitoneal injection. [b] A has twice the efficacy of tartar emetic. [c] LD_{50}/20 g. mouse: fouadin, 18.1 mg.; A, 1.66 mg.; tartar emetic, 0.92 mg. [d] Average number of worms per mouse on autopsy two weeks after therapy; controls had approximately 50 worms per mouse.

Summary

Aromatic stibonic acids have been prepared in pure form from several of the sulfonamides. One of these, *p*-sulfonamidobenzenestibonic acid, displays biological activity against *Schistosoma mansoni* in the mouse.

BOULDER, COLORADO

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Molecular Structure of the Two Dimethylhydrazines by Electron Diffraction

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Introduction

The N–N internuclear distance in which the two atoms are bound together by a single covalent bond has been measured for hydrazine by Giguere and Schomaker.[1a] This distance was used by Schomaker and Stevenson,[2] along with the O–O[1a] and F–F[3] distances, as an example of the inadequateness of the simple additivity rule of covalent radii proposed by Pauling.[4] Schomaker and Stevenson suggested that in compounds between atoms differing greatly in electronegativity there is appreciable resonance between ionic and covalent structures (as is known from other considerations) and this resonance leads to shorter interatomic distances. In those bonds which involve like atoms this resonance is at a minimum value. It has been considered worthwhile to extend the results to include a measurement of the N–N single covalent bond distance in the dimethylhydrazines.

By combining the results of the hydrazine investigation with those of dimethylamine[5] one might expect to predict the parameters of asymmetric dimethylhydrazine. The values so predicted were found to fit the observed data well. It was also desired to determine the effects, if any, of the methyl substitution.

The symmetric dimethylhydrazine is of interest because the orientation of the two methyl groups in respect to each other has been a point of discussion. West and Killingsworth[6] determined the electric moment to be 1.35*D*. This would suggest that the *trans* form, which would have no moment, could not be predominant. Penney and Sutherland[7] found hydrazine also to have a dipole moment. They showed that as a result chiefly of the hindrance of rotation about the N–N bond by the interaction of the unsymmetrical wave functions of the two nitrogen atoms the most stable arrangement of hydrazine is that in which the bond angles H–N–H are about 110° and in which one amino group is twisted in respect to the other 90° from the *cis* position. Assuming this same structure for the symmetric dimethylhydrazine West and Killingsworth show that by adding the bond moments for the different bonds of the molecule an electric moment is found which agrees fairly well with the measured value. They also found a Raman spectrum for symmetric dimethylhydrazine which had no strong vibration near 1,000 cm.$^{-1}$, the position at which a symmetrical vibration of the two halves of the molecule along the N–N bond would be expected to fall. This led those investigators to choose for symmetric dimethylhydrazine the structure suggested by Penney and Sutherland.

Boersch[8] investigated the structure of azomethane but was unable to decide between the *cis* and *trans* orientations for the two methyl groups. His work did allow him to exclude the linear model.

It was hoped that an electron diffraction study of symmetric dimethylhydrazine would throw some light on the relative position of the two methyl groups despite the small contribution of the C–C scattering to the total molecular scattering.

Experimental

The asymmetric dimethylhydrazine was prepared by the method of Hatt[9] as the hydrochloride. The melting point of 82.0° indicated high purity. The free dimethylhydrazine was obtained by distillation from a strongly alkaline solution. The product was redistilled at atmospheric pressure. After standing a few hours over pow-

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[1a] Paul A. Giguere and V. Schomaker, THIS JOURNAL, **65**, 2025 (1943).

[2] V. Schomaker and D. P. Stevenson, *ibid.*, **63**, 37 (1942).

[3] Max T. Rogers, V. Schomaker and D. P. Stevenson, *ibid.*, **63**, 2610 (1941).

[4] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

[5] S. H. Bauer, THIS JOURNAL, **60**, 524 (1938).

[6] W. West and R. B. Killingsworth, *ibid.*, **60**, 1 (1938).

[7] W. G. Penney and G. B. B. M. Sutherland, *Trans. Faraday Soc.*, **30**, 898 (1934); *J. Chem. Phys.*, **2**, 492 (1934).

[8] H. Boersch, *Monatsh.*, **65**, 311 (1935).

[9] H. H. Hatt, "Organic Syntheses," **16**, 22 (1936).

dered barium oxide it was vacuum distilled at room temperature through a long tube of powdered barium oxide and condensed in a Dry Ice–acetone-bath. The product was a clear, colorless, sirupy liquid boiling at 62–64°.

The symmetric dimethylhydrazine was also prepared by the method of Hatt[10] and treated in the manner described above. The clear, colorless liquid boiled at 81–83°.

Both compounds were vacuum distilled immediately before use in the electron diffraction experiments. After use in the camera the purity was checked by refractive indices. The following values were found: asymmetric n^{20}_D 1.4081, symmetric n^{20}_D 1.4277. The literature values are: n^{22}_D 1.4075,[11] n^{20}_D 1.4209.[6]

The impurities most likely to appear in the samples are ammonia, the other isomer of dimethylhydrazine, and methylhydrazine. The possible impurities would have very little effect on the patterns since their concentrations would be low as indicated by the boiling points and they have the same or smaller molecular weights than the substance studied.

The diffraction patterns were measured from at least seven different plates for each compound. Camera distances of about 10 and 25 cm. were used with a de Broglie wave length for the electrons of about 0.06 Å. The photographs used were obtained by means of two electron diffraction cameras. One of these was built in this Laboratory originally for the study of diffraction from crystal surfaces.[12] The camera was redesigned for use with gases and gave clear, well-defined photographs of heavily scattering gaseous molecules such as carbon tetrachloride or microcrystalline magnesium oxide deposited on copper mesh which was used as a voltage standard. However, because of the set camera distance, 25 cm., features of gas photographs falling at values of s greater than 16 could not be recorded on the photographic plate. In order to have more data than are afforded by this limitation photographs were also taken with a diffraction camera built by Dr. L. O. Brockway of the University of Michigan. This apparatus was used by the author with the kind permission and help of Dr. Brockway at Ann Arbor. Both cameras are similar to that described by Brockway.[13]

Interpretation and Results.—The interpretation of the electron diffraction photographs was accomplished by use of the simplified scattering formula

$$I_0 = \sum_i \sum_j z_i z_j \frac{\sin sr_{ij}}{sr_{ij}}$$

where

$$s = (4\pi/\lambda) \sin \theta/2$$

r_{ij} = distance between i^{th} and j^{th} atoms of the molecule. For both compounds all terms were included except those containing a non-bonded hydrogen atom. The C–N and N–N distances were tenatively taken as 1.47 Å., the value reported for these distances in other molecules.

Asymmetric Dimethylhydrazine.—The models for which theoretical curves for asymmetric dimethylhydrazine were calculated are given in Table I. Figure 1 gives curves and Table II presents a summary of the data for the most suitable models.

TABLE I

MODELS TESTED FOR ASYMMETRIC DIMETHYLHYDRAZINE

		C–N/N–N			
	θ	0.965	1.000	1.035	1.060
Using <C–N–C =	105°	XVIII	XVII		
<C–N–N = <θ	108°	III	I	II	
	111°	XVI	V	XV	
	113°	XI	VIII	IX	X
	115°		VII		
	120°		VI		
	<C–N–C				
Using <C–N–N =	108°		XIII	XIV	
113°	113°	XI	VIII	IX	X
	120°		XII		
Using <C–N–N =	105°		XIX		
111°	108°		IV		
	111°		V		
	115°		XX		

TABLE II

SUMMARY OF DATA FOR ASYMMETRIC DIMETHYLHYDRAZINE

Max.	Min.	V s_c/c_o	XV s_c/s_o	IV s_c/s_o	I s_c/s_o
1		0.971	0.981	0.974	0.981
	2	0.983	0.997	0.986	0.994
2		1.034	1.034	1.034	1.052
	3	0.989	1.004	0.991	0.998
3		1.000	1.010	1.000	1.007
	5	1.006	1.008	1.005	1.010
5		0.997	1.009	1.000	1.007
Average		0.997	1.006	0.999	1.007
Average deviation		0.014	0.010	0.019	0.014
Average C–N		1.466	1.479	1.468	1.480
Average N–N		1.466	1.429	1.468	1.480

Final values: C–N = 1.47 ± 0.03Å. <C–N–C = 110° ± 4°
N–N = 1.45 ± 0.03Å. <C–N–N = 110° ± 4°

The visual appearance of the photographs is very like curve I of Fig. 1. The distinguishing qualitative features of the photographs are

a shelf ending at about s = 3
deep first minimum
sharp first maximum
pronounced shelf on outer side of diffuse maximum 2
sharp maximum 3, darker than maximum 2
broad minimum 4, lightest on inner edge
asymmetric maximum 4
faint maximum 5

In comparing the theoretical curves to the observed values of s for the maximum and minimum several interesting effects were observed. As has been the experience of other investigators in this field it was found that the inner features on the theoretical curves occur at lower values of s than that measured on the plates. This is due to the rapid decrease in background near the central spot. This error affects minimum 1, maximum 1 and minimum 2 on some of the models. Maximum 2, however, is measured lower than the values given in the calculated curves. This is because of the St. John effect.[14] St. John and Ware studied the

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(10) H. H. Hatt, "Organic Syntheses," **16**, 18 (1936).

(11) I. M. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1934.

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(14) C. E. St. John and L. W. Ware, *Astrophys. J.*, **44**, 35 (1916).

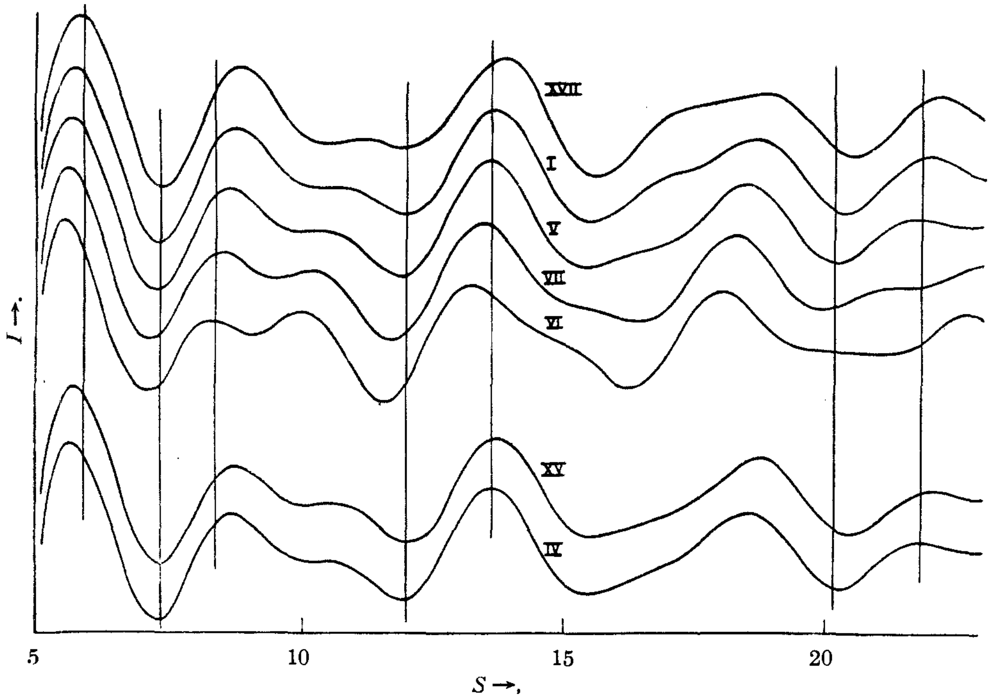

Fig. 1.—Theoretical curves for asymmetric dimethylhydrazine.

measurements of asymmetric spectral lines and found that in subjective measurements one makes an error toward the side of the line having the greater contrast. In our case, the shelf on the outside of maximum 2 constitutes a side of less contrast. Minimum 3 and maximum 3 are sharp features. Minimum 4 is broad and maximum 4 is asymmetric. These features cannot be measured accurately on the photographic plate. In some models the value taken from the calculated curve for minimum 4 is found to agree with the observed values, but since the minimum is broad no faith is put in this agreement. Maximum 5 was found to be very sensitive to structure changes and helped to eliminate a great many of the models tested.

An interesting set of theoretical curves is shown in Fig. 1 where $\theta = <\text{C–N–C} = <\text{C–N–N}$ is varied from 105° in model XVII to 120° in model VI. The shelf on maximum 2 rises to be a second distinct peak higher than maximum 2 itself as the deepest part of minimum 4 shifts from left to right making maximum 3 asymmetric instead of maximum 4. During this transition maximum 5 and minimum 5 shift inward and lose their identities.

This variation of the curves with change in parameters is a good example of the method used to determine the correct values. The models decided upon as fitting the qualitative and quantitative data the best are I, V, IV, and XV.

Pauling's table of covalent radii predicts a single bond distance of 1.40 Å. for the N–N linkage. Models were not calculated for this distance, but models II, XV and IX used an N–N value of 1.42 Å. and model X used 1.38 Å. Of these only one, XV, is satisfactory. The models tested indicate a N–N distance larger than 1.40 Å.

Symmetric Dimethylhydrazine.—For symmetric dimethylhydrazine five models were calculated. These are listed in Table III and a summary of data for the acceptable models is given in Table IV. Those values of <C–N–N,

TABLE III

MODELS TESTED FOR SYMMETRIC DIMETHYLHYDRAZINE

	C–C	C-N/N-N 1.000	1.035
<C–N–N = 111°	*trans* 3.73	I	
	Right angle 3.25	II	IV
	cis 2.52	III	
<C–N–N = 108°	Right angle 3.16	V	

TABLE IV

SUMMARY OF DATA FOR SYMMETRIC DIMETHYLHYDRAZINE

Max.	Min.	I s_c/s_0	II s_c/s_0	IV s_c/s_0	V s_c/s_0
1		0.938	0.964	0.980	0.976
	2	0.978	0.966	0.978	0.978
2		1.011	1.000	1.000	1.009
	3	0.981	0.981	0.997	0.980
3		1.005	1.005	1.017	1.018
	5	1.006	1.001	1.027	1.021
5		1.011	1.000	1.022	1.019
Average		0.990	0.990	1.003	1.000
Average deviation		0.019	0.015	0.016	0.019
Average C-N		1.457	1.457	1.474	1.470
Average N-N		1.455	1.455	1.424	1.470

Final values: C-N = 1.47 ± 0.03Å.
N-N = 1.45 ± 0.03Å. <C-N-N = 110° ± 4°

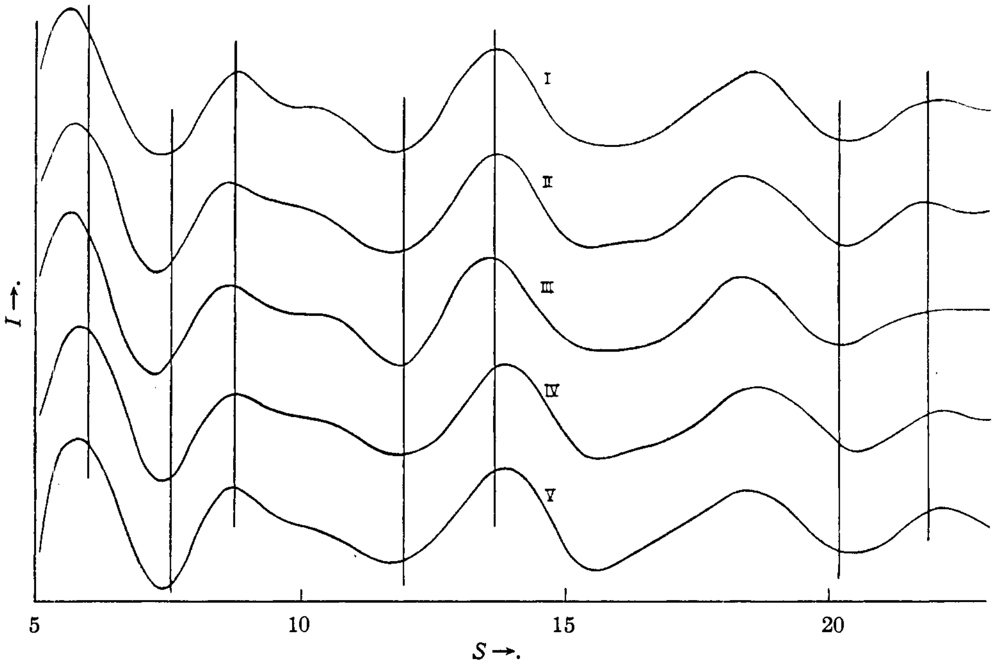

Fig. 2.—Theoretical curves for symmetric dimethylhydrazine.

C–N, and N–N were used which were found to fit the data for the asymmetric compound. The same qualitative features were observed for this compound as for the preceding one. Any differences in the scattering must be attributed to changes in the parameters mentioned above caused by the different position of the methyl group and the longer C–C distance.

It is seen from the curves of Fig. 2 and the data of Table IV that the C–C distance has little effect on the curves until it becomes small. The *cis* form is unlikely because of the flat maximum 5 but the other possibilities cannot be excluded. The term "right angle" means that one C–N bond lies in a plane at right angles to the plane defined by the other carbon and the two nitrogens. Little can be said about the relative position of the carbon atoms except that probably they are not *cis* to each other.

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Summary.—An electron diffraction investigation of the molecular structure of the two dimethylhydrazines has been made. The molecular dimensions are found to be:

C–N = 1.47 ± 0.03Å. N–H = 1.04Å. (assumed)
N–N = 1.45 ± 0.03Å. <C–N–N = 110° ± 4°
C–H = 1.09Å. (assumed) <C–N–C = 110° ± 4°

The value of the C–N distance is in agreement with that found by a number of other investigators for that distance in other compounds. The value of the N–N distance is in agreement within experimental error with that found in hydrazine by Giguere and Schomaker.

On the basis of this study the relative position with respect to each other of the methyl groups in symmetric dimethylhydrazine cannot be ascertained. The evidence presented is unfavorable to the *cis* orientation but other possibilities cannot be distinguished.

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