

AN ABSTRACT OF THE THESIS OF

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Title: ELECTRON-DIFFRACTION INVESTIGATION OF
GASEOUS MOLECULES
PART I: 2, 3-DICHLOROBUTADIENE AND
2, 3-DIBROMOBUTADIENE
PART II: METHYLDIAZENE

Abstract approved: Redacted for privacy
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The molecular structures of 2, 3-dichlorobutadiene and 2, 3-dibromobutadiene have been investigated by electron diffraction. Both molecules exist in the trans configuration and for 2, 3-dichlorobutadiene there is no evidence of deviation from coplanarity (C_{2h} symmetry). For 2, 3-dibromobutadiene the results are consistent with a nonplanar model of C_2 symmetry arising from a small ($\sim 17^\circ$) rotation about the conjugated single bond. The electron-diffraction analysis led to the following values for the principal distances and bond angles, assuming symmetric $C=CH_2$ groups; the parenthesized values are 2σ : 2, 3-dichlorobutadiene, $C=C = 1.346 \text{ \AA} (0.003)$,

$C-C = 1.465 \text{ \AA} (0.005)$, $C-H = 1.100 \text{ \AA} (0.010)$, $C-Cl = 1.747 \text{ \AA} (0.002)$,
 $\angle C-C-Cl = 114.7^\circ (0.3)$, $\angle C-C=C = 126.9^\circ (0.2)$, and $\angle C=C-H = 120^\circ$ (assumed); 2,3-dibromobutadiene, $C=C = 1.342 \text{ \AA} (0.006)$,
 $C-C = 1.451 \text{ \AA} (0.011)$, $C-H = 1.098 \text{ \AA} (0.026)$, $C-Br = 1.909 \text{ \AA} (0.004)$,
 $\angle C-C-Br = 116.1^\circ (0.6)$, $\angle C-C=C = 126.1^\circ (0.6)$, and $\angle C=C-H = 120^\circ$ (assumed). The 2,3-dichlorobutadiene structure is not unusual with the conjugated carbon chain very similar to that of butadiene; on the other hand 2,3-dibromobutadiene is notable because of the likely coplanarity of the molecule.

The molecular structure of N-deuterated methyldiazene ($CH_3N=ND$) has also been investigated by gaseous electron diffraction. The results for a nozzle temperature of $0^\circ C$. support a trans configuration for the molecule. Assuming C_{3v} symmetry for the methyl group, the electron diffraction analysis gave the following values for the principal parameters: $r(C-H) = 1.097 \text{ \AA} (0.007)$,
 $r(N-C) = 1.469 \text{ \AA} (0.003)$, $r(N=N) = 1.245 \text{ \AA} (0.002)$, $r(N-D) = 0.989 \text{ \AA} (0.018)$, $\ell(C-H) = 0.051 \text{ \AA} (0.006)$, $\ell(C-N) = 0.049 \text{ \AA} (0.003)$, $\ell(N=N) = 0.032 \text{ \AA} (0.003)$, $\ell(N-D) = 0.057 \text{ \AA}$ (assumed),
 $\angle HCN = 108.4^\circ (1.9)$, $\angle CNN = 112.3^\circ (0.4)$, and $\angle NND = 110.3^\circ (5.1)$. The distances and amplitudes are r_a and ℓ_a values, the parenthesized quantities are 2σ . The three rotational constants calculated from the structure defined by the values of the geometrical parameters determined from electron diffraction are in excellent agreement with those evaluated experimentally from microwave spectroscopy.

Electron-Diffraction Investigation of Gaseous Molecules
Part I: 2,3-dichlorobutadiene and 2,3-dibromobutadiene
Part II: Methyldiazene

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ELECTRON-DIFFRACTION INVESTIGATION OF GASEOUS MOLECULES

PART I: 2,3-DICHLOROBUTADIENE AND 2,3-DIBROMOBUTADIENE

PART II: METHYLDIAZENE

ELECTRON DIFFRACTION METHOD

Since scattering theory applicable to electron diffraction and the general procedure of molecular structure determination by electron diffraction has been described in numerous other works (Brockway, 1936; Glauber and Schomaker, 1953; Waser and Schomaker, 1955; Mott and Massey, 1949; Iwasaki, Fritsch and Hedberg, 1964; Hedberg and Iwasaki, 1964) only a brief description will be given here.

In an apparatus of the usual geometry, a high-energy (40-50 kV) monochromatic beam of electrons is caused to intersect a tiny jet of gas at a 90° angle in a highly evacuated chamber. The scattered electron intensity (in the form of cones coaxially symmetric with respect to the undiffracted beam) is allowed to impinge on a photographic plate perpendicular to the undiffracted beam. Because the scattered intensity falls off very rapidly with increasing scattering angle, it is convenient to modify it with a device known as a "sector" mounted parallel to and immediately above the photographic plate. The sector, which is rotated in its own plane about an axis coincident with the undiffracted beam during the exposures, has a spiral shape which serves to diminish the small-angle intensity

seen by the plate relative to the large-angle intensity; in this way a single photographic plate will provide useful intensity data over a many-fold larger range of scattering angle than could otherwise be attained. The relation between the angular distribution of total scattered intensity $I_t(s)$ and that striking the photographic plate is, apart from a scale factor

$$I_t(s) = I_p(s) \cdot H^3 \times 10^{-8} / \alpha(r) \cos^3 2\theta \quad (1)$$

where $\alpha(r)$ is the sector function ($\alpha(r) \approx kr^3$ with r the radial coordinate measured on the sector), $\cos^3 2\theta$ takes account of the fact that the plate is flat and not everywhere equidistant from the scattering point, (2θ is the scattering angle), and $H^3 \times 10^{-8}$ is a convenient factor for scaling intensities gathered from experiments with the gas jet nozzle tip at different distances from the plate.

The total scattered intensity can be represented by the equation

$$I_t(s) = k \sum_{i+j} \frac{|A_i| |A_j|}{s^5 r_{ij}} V_{ij} \cos |\Delta \eta_{ij}| \sin r_{ij} s + k \sum_i \frac{Z_i^2}{s^4} \quad (2)$$

$$+ k \sum_i Z_i S_i + I_{\text{ext}}$$

$$= I_M + I_a + I_i + I_{\text{ext}} \quad (2a)$$

where I_M , I_a , I_i , and I_{ext} represent respectively the molecular structure sensitive scattering, atomic scattering, incoherent scattering, and extraneous or apparatus scattering. The meaning of the symbols in Equation (2) are as follows.

$V_{ij} (= \exp(-\langle \delta l_{ij}^2 \rangle s^2 / 2))$ with $\langle \delta l_{ij}^2 \rangle$ the mean-square amplitude of vibration of atoms i and j is a vibration factor (harmonic oscillator approximation).

- A_i is the (modified) electron scattering amplitude for atom i .
- r_{ij} is the internuclear distance between atoms i and j .
- l_{ij} is the root-mean-square amplitude between atoms i and j .
- $\Delta\eta_{ij}$ is the phase shift factor between atoms i and j .
- S_i is the incoherent scattering factor.
- $s = 4\pi \sin\theta/\lambda$ is the electron-diffraction variable.
- λ is the wave length of the electrons.
- Z_i is the atomic number of atom i .

The last three terms in equation (2) can be regarded as background, B_t , since they are not sensitive to molecular structure; thus

$$I_M = I_t - B_t. \quad (3)$$

The total background, B_t , can be manually subtracted to yield the experimental molecular intensity. This molecular intensity, I_M , is multiplied by s^4 for convenience because the intensity decreases rapidly with s , which gives

$$I_m = s^4 I_M$$

$$\text{or } s I_m = k \sum_{i+j} \frac{|A_i| |A_j|}{r_{ij}} V_{ij} \cos |\Delta n_{ij}| \sin r_{ij} s \quad (4)$$

All scattering amplitudes, A_i , and phases, η_i , used here were obtained from Cox and Bonham's table (Cox and Bonham, 1967) for an accelerating voltage of 44.0 kV by an interpolation procedure (Gundersen and Hedberg, 1969).

The determination of a molecular structure by electron diffraction involves the discovery of a trial structure by analysis of radial distribution curves followed by refinement of the trial structure using least squares methods. The radial distribution curve is the Fourier sine transform (Waser and Schomaker, 1953) of the intensity curve and is related to the probability of finding a certain internuclear distance, r_{ij} , in a molecule. For the purpose of calculating experimental radial distribution curves, a composite intensity curve is made by suitably averaging and joining experimental curves from the individual plates. The composite curve is converted to a "constant coefficient" curve $I'_m(s)$, by multiplying each point by the factor $Z_A Z_B / A_A A_B$ in order that the peaks of the radial distribution have essentially the easy-to-interpret Gaussian shape.

The radial distribution function is calculated according to

$$D(r) = \sum_{s_{\min}}^{s_{\max}} I'_M(s) \exp(-Bs^2) \sin rs \Delta s \quad (5)$$

where the factor $\exp(-Bs^2)$ reduces series termination effects. A convenient value of the coefficient B is calculated from the expression $e^{-Bs^2} = 0.1$ at $s = s_{\max}$. The trial structure is usually derived from the radial distribution curve using

$$A \propto n_{ij} Z_i Z_j / r_{ij} \quad (6)$$

where A is the area of a peak in the curve and n_{ij} is the frequency that the distance r_{ij} occurs in the trial structure. The initial root-mean-square amplitudes of vibration, l_{ij} , are calculated from the expression

$$1/2 = \exp[-\Delta r_{1/2}^2 / (2l_{ij}^2 + 4B)] \quad (6)$$

where $\Delta r_{1/2}$ is the half-width of the peak at half height, and B is the damping factor defined above. When more than one molecular distance contributes to a peak in the radial distribution curve, it may be necessary to resolve the peak into its components, in order to obtain a satisfactory trial structure.

Structure refinement in this laboratory is based upon adjustment of theoretical to experimental intensity curves. The procedure (Hedberg and Iwasaki, 1964; Iwasaki, Futsch, and Hedberg, 1964) makes use of intensities in the form of Equation (4) and as adapted to the present computational facilities (CDC 3300 computer) adjusts

distance parameters, amplitude parameters, and the mole fractions of three molecules.

PART I

2, 3 DICHLOROBUTADIENE AND 2, 3 DIBROMOBUTADIENE

INTRODUCTION

Since bond lengths have been more widely used than any other molecular property to provide insight into the nature of chemical bonding, the dependency of bond lengths on their environment has been well studied. Herzberg and Stoicheff (1955) and later Costain and Stoicheff (1959; Stoicheff, 1962) were the first to systematize the existing experimental data for the carbon-carbon bonds for 33 different compounds. Costain and Stoicheff derived the empirical formulas

$$r(C-C) = 1.299 + 0.040n \quad n = 2, 3, 4 \dots 6$$

$$r(C=C) = 1.226 + 0.028n \quad n = 2, 3, 4$$

where n is the number of adjacent bonds. Since then, better experimental results have been published, especially during the last decade, that do not fit the empirical rules of Stoicheff et al. especially for certain conjugated systems and when heteroatoms are present.

The first to discuss the problem of carbon-carbon bonds was Pauling (1960) in his book Nature of the Chemical Bond which was first published in 1939. Since that time molecular structure refinements have increased in quality, and it became obvious that significant differences existed in the carbon-carbon single bond lengths,

whereas, the length of the double and triple bonds were found to be remarkably constant from one molecule to another (Lide, 1962; Traetteberg, 1969).

There has been much interest in the theories proposed to describe the existing experimental bond length measurements (Bastiansen and Traetteberg, 1962). Different theories emphasized different concepts. Pauling (1939), Mulliken (1959a, b), and others have emphasized conjugation and hyperconjugation, or resonance and electron delocalization, in their theories in order to explain the observed shortening of single bonds adjacent to multiple bonds. Dewar and Schmeising (1959, 1960), Brown (1959), and Mikhailov (1965), have suggested that the bond lengths in molecules with multiple bonds are determined primarily by changes in the hybridization state of the carbon atoms involved in the bond. Dewar, the most dedicated defender of the hybridization theory, has dismissed the possible importance of conjugation or resonance stabilization in all molecules for which no more than one classical (unexcited) structure can be written.

Other contributions have been made by Pauling (1939) and Bartell (1962) correlating bond lengths with intramolecular repulsions. Electronegativity has also been included in discussions of possible factors pertaining to bond lengths, but this effect must be considered simultaneously with hybridization changes since the

electronegativity of a carbon atom changes with its hybridization state.

Since butadiene is one of the favorite examples cited in the above theories, it is a much studied compound. Part I of the present thesis is a study of two substituted butadiene compounds, 2,3-dichlorobutadiene and 2,3-dibromobutadiene. In particular, it was hoped that at least one of these compounds would experience enough intermolecular steric interaction to cause a twist about the single bond.

The molecular configuration of 1,3 butadiene has been investigated by a variety of techniques during the past 25 years. Even though the overall coplanar-trans molecular geometry had been confirmed at the time of the study of Stoicheff et al., the electron diffraction value (Almennigen, Bastiansen, and Traetteberg, 1958) for the carbon-carbon single bond ($1.483 \pm 0.01 \text{ \AA}$) in butadiene used in the study (Costain and Stoicheff, 1959) was 0.020 \AA larger than that predicted by the empirical formula, whereas the observed carbon-carbon double bond value ($1.337 \pm 0.01 \text{ \AA}$) compared favorably with the predicted value of 1.338 \AA . Traetteberg and Haugen (1966) reinvestigated butadiene by the method of electron diffraction and obtained values of $1.343 \pm 0.001 \text{ \AA}$ and $1.467 \pm 0.001 \text{ \AA}$ for the carbon-carbon double and single bonds, respectively. The latter results for butadiene were consistent with the independent electron diffraction determination of butadiene by Kuchitsu, Fukuyama, and

Morino (1968), and with spectroscopic observations (Traetteberg, Hagen, and Cyvin, 1969).

In 1952, an infra-red spectroscopic study of some chlorinated butadienes by Szasz and Sheppard (1953) included vapor, liquid, and solid phase studies of 2,3-dichlorobutadiene. The only conclusion made regarding the molecular structure was that it was trans-coplanar (C_{2h} symmetry). Hobgood and Goldstein (1964) reported the NMR study of 2,3-dichlorobutadiene. They remarked that the substituents appeared to have withdrawn charge from the diene system, which to them suggested an increase in the electron delocalization compared to butadiene itself. No molecular structure related investigations have been reported for 2,3-dibromobutadiene.

EXPERIMENTAL AND DATA REDUCTION

The sample of 2,3-dichlorobutadiene was kindly provided by Dr. C. A. Stewart, Jr. of the DuPont Co. The sample was in the form of a 40% solution in decahydronaphthalene (decalin) and an inhibitor, phenothiazine. Phenothiazine and decalin have boiling points of 371°C and 185.5°C , compared to 98°C for 2,3-dichlorobutadiene; therefore, a pure sample of 2,3-dichlorobutadiene was easily obtained from the solution by a simple stage of vacuum distillation. The pure sample was stored at -80°C . The purity of the distillate was checked by comparing the gas phase infrared spectrum of the sample with that reported by Szasz and Sheppard (1953).

Electron diffraction photographs were made using the r^3 sector described earlier on 8x10- and 5x7-in. Kodak process plates. The sample bulb with a 2 mm vacuum stopcock was attached to the electron diffraction apparatus using a 10/30 $\frac{1}{8}$ joint; all joints were lubricated with Kel-F No. 90 halocarbon grease. The sample bulb was maintained at -5° to $+5^{\circ}\text{C}$ in order to obtain a suitable sample vapor pressure. The nozzle-tip temperature was maintained in the range of 17° to 30°C , and the ambient pressure in the apparatus during exposure of the plates was about 3×10^{-6} Torr. An electron beam of 0.16-0.21 μa was used, and exposure times ranged from 45 sec. to 4 min. The average wave length was 0.05720 \AA , as

determined by calibration against gaseous CO_2 in separate experiments [$r_a(\text{CO}) = 1.1642 \text{ \AA}$; $r_a(\text{O} \cdots \text{O}) = 2.3244 \text{ \AA}$]. A total of 15 plates were exposed--ten at the "middle" camera distance (30 cm) and five at the "long" camera distance (75 cm). "Short" camera (12 cm) plates were also exposed, but they were of such quality that no additional data could be extracted from them. The experimental data for the plates used for the structure refinement are summarized in Table 1.

The method of preparation of the 2, 3-dibromobutadiene was similar to that proposed by Berchel and Carothers (1933) for the preparation of 2, 3-dichlorobutadiene. A mixture of 10 grams of 1, 2, 3, 4 tetrabromobutane in 125 ml of methyl alcohol was placed in a three necked flask provided with a magnetic stirrer and reflux condensor. A solution of 3.0 grams potassium hydroxide in 50 ml of methyl alcohol was added through a dropping funnel while the temperature of the mixture was kept at about 10°C . The flow rate of the KOH solution was regulated in such a manner that the addition took about 30 min. After the addition of the KOH-MeOH solution was completed, the reaction mixture was stirred for one-half to two hours at a temperature of $20\text{-}25^\circ \text{C}$. About 0.1 grams of the inhibitor, phenothiazine, were then mixed into the reaction mixture. The solution was filtered, and the filtrate was poured into 400 ml of distilled water. The separation of the oil was facilitated by the

addition of 40-50 ml of ether. The oil and ether solution was dried over CaCl_2 for 12 hours. The ether was removed by vacuum distillation while the sample bulb was kept at -40°C . The distillation time was from four to six hours insuring a pure sample, since the sample purity, not sample yield, was the important aspect of the preparation.

The sample was used with the inhibitor present, since the pure 2,3-dibromobutadiene polymerized almost immediately upon separation from the inhibited solution by vacuum distillation. The inhibited sample was stable enough to permit storage for reasonable times at 0°C . Gas phase infrared spectra were taken using the Beckman IR 7 spectrometer. Both the NaCl and CsI interchange were used in order to obtain a spectral range of 300- to 4000-cm^{-1} . The spectra compared very well with that of dichlorobutadiene in the range of 750- to 4000-cm^{-1} . The carbon halogen stretch for the dibromobutadiene was at $571 \pm 5\text{ cm}^{-1}$ compared to $715 \pm 5\text{ cm}^{-1}$ for dichlorobutadiene.

The sample was attached to the diffraction apparatus in the same manner described earlier for the dichlorobutadiene. The sample was heated to $55\text{-}60^\circ\text{C}$. in order to obtain the proper sample vapor pressure, and the nozzle was heated to $50\text{-}55^\circ\text{C}$. to reduce polymer formation in the nozzle tube. Exposure times ranged from 1 to 3 min. with a beam of 0.22 to $0.48\text{ }\mu\text{A}$. The ambient pressure inside the apparatus during exposure was maintained at $2.9\text{-}4.4 \times 10^{-6}$ Torr. The average wavelength for the experiment was $0.057204\text{ }\text{\AA}$. A total

of 18 plates were exposed. Only long and middle camera distance plates were exposed, since it was obvious from the intensity fall-off of the middle camera plates that no data could be obtained from the short camera exposures. A summary of the experimental data for the plates used in the structure determination is found in Table 11.

All the usable plates from both experiments were scanned along a diametrical line on a modified (Gundersen and Hedberg, 1969) Joyce-Loebl microdensitometer while being rotated about the center of the diffraction rings. Digitalized data, punched on a paper tape, were collected at intervals of 0.3514 mm on the plate. During the acquisition of each datum, the plate was rotated two revolutions and translated 0.1171 mm on the plate, thus, each measurement reflected an integration over a path on the plate several centimeters long. The curves were read from the paper tape into the computer and stored on file for use by the "data reduction" program.

The data were reduced [for a fuller account of the data reduction procedure see Hedberg and Iwasaki (1962)] by a program written by Lise Hedberg. The program (1) converts the counts per second to density units, (2) finds the precise center of the rings by minimum sum of squares of deviations of each of the two branches of the trace, (3) calculates the s value corresponding to each measured point and interpolates the densities at each s value, (4) applies the geometrical

corrections given by equation (1), (5) multiplies the intensity curves $I_t(s)$ by s^4 , and (6) averages the two branches of the scan.

STRUCTURAL DETERMINATION

2, 3-Dichlorobutadiene

The results of data reduction of each dichlorobutadiene plate were plotted and a smooth background (B_t) was drawn through each curve. The difference of each curve from its corresponding background was multiplied by s . The result has the form of equation (4); these curves are shown in Figure 2. The ranges of the data from the 75- and 30 cm. camera distances were $1.25 \leq s \leq 12.25$ and $7.00 \leq s \leq 31.00$, respectively, and the data interval was $\Delta s = 0.25$.

A preliminary experimental radial distribution curve was calculated according to equation (5) using $B = 0.0018$ and omitting data in the unobserved region $0 < s \leq 1.25$. The "constant coefficient" intensity curve was calculated, as mentioned earlier, by multiplying the composite intensity curve by the factor $Z_C Z_{Cl} / A_C A_{Cl}$.

A theoretical intensity curve was calculated according to equation (4) using approximate values for r_{ij} and l_{ij} obtained from the preliminary experimental $D(r)$ curve. Comparison of the theoretical and experimental intensity curves suggested small background corrections. After their insertion, a new experimental $D(r)$ curve was calculated using theoretical intensity data in the range $0 < s \leq 1.25$ for the composite curve. Improved values of r_{ij} and l_{ij} resulted and

were used to calculate another theoretical intensity curve which suggested further background corrections. This cyclic process was repeated (three or four times) until most of the background errors were eliminated. Final, minor background corrections were made from comparisons based on the theoretical intensity curve calculated from a least squares refinement.

The principal peaks of the final experimental radial distribution curve (Figure 3) are due to the carbon-hydrogen (1.1 Å), carbon-carbon (1.35 Å), and carbon-chlorine (1.25 Å) bonded distances and the carbon-chlorine (2.67 and 3.20 Å) and chlorine-chlorine (4.32 Å) non bonded distances. These peak positions revealed that the molecule was essentially trans-coplanar. A cis isomer would have produced a chlorine-chlorine peak of about 3.22 Å no trace of which was found in the experimental radial distribution curve. Two of the three carbon-chlorine nonbonded distances are not resolved and are important for the structure determination since they determine the C-C-Cl and C-C=C angles.

Refinements of the structure were carried out by the method of least squares applied both to the individual and composite intensity curves, weighting all observations equally. The refinements were designed to explore the overall geometry of the molecule, as well as the twist about the carbon-carbon bond. Experience has shown that a pair of geometrically nonequivalent distances that differ only by a

small amount (0.01 to 0.1 Å) are so highly correlated with one another and with the corresponding amplitudes of vibration that the refinement often fails to converge. Experience has shown that in such cases (applicable to 2,3-dichlorobutadiene) convenient geometrical parameters would be a weighted carbon-carbon distance ($C-C_{ave}$), and a difference ($\Delta C-C$), together with the C-H and C-Cl distances, the C-C-Cl, C-C=C and C=C-H angles, and a twist about the conjugated single bond. The amplitudes of vibration of the C=C and C-Cl bonds as well as the C_3Cl_6 and Cl...Cl distances were also refinable parameters. The C-H and C-C amplitudes were held constant after preliminary refinements and other measurements established their approximate values. The other parameters that could not be simultaneously and independently refined were the C_2Cl_5 and C_3Cl_5 (see Figure 1 for the numbering scheme) amplitudes of vibration; these were refined under the condition $l_{C_2Cl_5} = l_{C_3Cl_5}$.

The refinable molecular parameters for various typical least squares refinements are listed in Table 8, with the final structure reported in Table 9. The theoretical and experimental intensity and radial distribution curves are shown in Figures 2 and 3, respectively.

The error estimates in Table 8 and 9 are calculated from following formulas

$$2\sigma_r = 2[2\sigma_{LS}^2 + (0.0005r)^2]^{1/2} \quad (8)$$

$$2\sigma_{\ell} = 2[2\ell_{LS}^2 + (0.02\ell)^2]^{1/2} \quad (9)$$

$$2\sigma_{\text{angle}} = 2\sqrt{2\sigma_{LS}} \quad (10)$$

where the quantities σ_{LS} were obtained from the diagonal terms of the least squares error matrix and reflect random errors including possible correlation among observations. The correlation matrix is shown in Table 10. The factors 0.0005 and 0.02 take into account errors in wavelength, camera distance, sector calibration, and errors in the conversion of the photographic density to scattered intensity.

The assumed value of 0.048 Å for the C-C amplitude shown in Table 8 was determined by least squares refinements not shown in the table. Various least squares refinements similar to #1 (Table 8) were carried out in which the assumed C-C amplitude of vibration was held constant at selected values in the range 0.045 to 0.052 Å. The refined C=C amplitude always attained a value about 0.003-0.01 Å less than that of the fixed C-C amplitude such as is shown in Table 8.

The final structure includes an assumed C=C-H angle of 120°, a value well within the range (119.5 ± 2.6°) obtained when the angle was refined. The assumption seemed justified by the fact that the C---H distance at 2.12 Å which primarily determines the angle is not well resolved in the radial distribution curve and is not one of the principal geometric factors determining the overall structure of

the molecule. In the final model, the deviation from coplanarity (torsional angle $\sim 7^\circ$) does not appear to be statistically significant. This conclusion is based on the fact that the electron diffraction experiment measures only molecular distances, not molecular geometry. Since the chlorine atoms account for approximately one-half the scattering power of the molecule, the chlorine-chlorine distance is well determined by the electron diffraction experiment. However, since this distance depends on the C-C and C-Cl distances, and the C-C-Cl and the torsion angles, the least squares process can fit the theoretical model to the observed Cl...Cl distance with several combinations of the geometrical parameters. The torsional angle is particularly affected by small changes in the other parameters as seen in Table 8 models 3 and 4. A shrinkage effect (Almennigen *et al.*, 1968; Morino, Nakamura, and Moore, 1962) in the carbon-chlorine bond or an oscillation of about 10° about the C-C bond, also, can not be excluded as plausible explanations for the observed twist.

2, 3-Dibromobutadiene

The reduction of the data from the 2, 3-dibromobutadiene plates included an extra correction (called the "blackness correction") that took into account the non-linear response of the photographic emulsion to scattered electron intensity. A description of the blackness correction is found in Appendix A. The correction was employed

because the density of the long camera plates ranged from 0.66 to 2.14 D (absolute density units) and the blackness correction was of appreciable magnitude for densities greater than 1.1 D. The differences between the resulting intensity data and the corresponding backgrounds were obtained, as outlined on pages 16 and 17. The difference curves were multiplied by s , which put them in the form of equation (4). The resulting individual intensity curves are shown in Figure 4. The ranges of the data from the 75- and 30-cm camera distances were $2.00 \leq s \leq 12.00$ and $7.00 \leq s \leq 30.50$, respectively, and the data interval was $\Delta s = 0.25$.

The method of deducing a trial structure was similar to that described for the dichlorobutadiene and will therefore be only briefly outlined. A composite intensity curve was made, from which the "constant coefficient" intensity curve was calculated by multiplication with factor $Z_C Z_{Br} / A_C A_{Br}$. A preliminary experimental radial distribution curve was calculated with $B = 0.002$ and methods of calculating theoretical intensity curves and background corrections described for 2,3-dichlorobutadiene were performed. The final experimental radial distribution curve, Figure 6, was very similar to the dichlorobutadiene $D(r)$ curve, but when the planar model (Figure 1) was assumed, the two twist dependent distances, $Br_5 Br_6$ and $C_3 Br_6 (C_4 Br_5)$, could not be simultaneously fit to the experimental radial distribution curve. The absence of a peak in the

experimental $D(r)$ curve at 3.36 Å corresponding to a bromine-bromine distance for a cis isomer and the existence of a strong peak at 4.62 Å that could only be due to a Br...Br interaction showed only the trans isomer was present.

As before, the final structure refinements were carried out by the method of least squares applied to the intensity curves, weighting all the observations equally. An average carbon-carbon bond distance and difference were used as refinable parameters for the reasons discussed for the dichlorobutadiene determination. The C_2Br_5 and C_3Br_5 (see Figure 1 for numbering scheme) amplitudes of vibration were again refined equal to one another and the C-C amplitude of vibration was assumed to be 0.006 Å smaller than the C=C amplitude. The value of 0.006 Å was determined from preliminary least squares refinements in which the C-C amplitude of vibration was held constant and for other refinements in which the amplitude difference was varied. Table 20 shows the significant least squares refinements that were designed to explore the question of the bromine orientation and the twist about the carbon-carbon single bond. The "twisted" model may be visualized as comprising two coplanar $Br-C=CH_2$ groups joined by the conjugated single bond but rotated about the bond such that they are not mutually coplanar. The "bent" model may be visualized as a coplanar carbon chain with the bromine atoms bent out of the carbon-carbon plane such that they

find themselves on the same side of that plane. The final structure results for both the twisted and bent models are shown in Table 21, and the corresponding intensity and radial distribution curves are shown in Figures 6 and 7, respectively, together with the differences between the theoretical and experimental curves.

Both final models include assumed values of 120° for the C=C-H angle. The refined amplitude of vibration for the carbon-hydrogen bond seems high compared to the results of other work (2,3-dimethyl-2,4-dimethyl butadiene: Aten, Hedberg, and Hedberg, 1968; butadiene: Haugen and Traetteberg, 1966), but the large errors for both this distance and its associated amplitude disclose that the values are not reliably determined compared to the heavy atom parameters. This result is expected since the contribution of the carbon-hydrogen bond distance to the overall structure is very small compared to the contribution from the carbon-bromine or bromine-bromine distances.

The twisted and bent molecular models exhibit a trans, non-planar geometry. The arguments for the trans isomer were given in a discussion of the experimental radial distribution curve. The differences between the two nonplanar and coplanar models are striking in terms of the appearance of the theoretical radial distribution curves. The two twist or bend dependent distances, Br_5Br_6 and $\text{C}_3\text{Br}_6(\text{C}_4\text{Br}_5)$, are not resolved by the coplanar model, but are resolved particularly well by the two nonplanar molecular models.

The two nonplanar models themselves are very similar, the major difference being the coplanar carbon chain for the bent model. The important similarity is the spacial orientation of the bromine atoms, i. e., they are displaced out of a coplanar formation in such a manner as to decrease the bromine-bromine distance. This displacement of the bromine atoms from the coplanar structure simultaneously increases the other twist or bend dependent distance (C_3Br_6) which was too short for the coplanar model compared to that experimentally observed.

The interdependence of the molecular parameters (twist or bend angle, C-C-Br angle, C-C=C angle, C-Br and C-C bond lengths) that involve the twist or bend dependent distances are complex, therefore attention must be given to the correlation matrices (Tables 22 and 23) for the full interdependent interpretation and correlation of the uncertainties accompanying the dependencies. In addition to showing the correlation of the C_3Br_6 and Br_5Br_6 distances, respectively, with an increase in the twist (bend) angle, Tables 22 and 23 show that the C-C-Br angle increases and the C-C bond distance decreases with an increase in the twist (bend) angle. These correlations are very important since the geometry of the molecule is determined, to a large extent, by the C-Br bond distance and the bromine-bromine distance. The correlations must be considered in

discussions concerning any conclusions about the carbon-carbon single bond and the reality of the twist (bend) angle.

DISCUSSION

The structure of 2, 3-dichlorobutadiene is not unusual. It is essentially trans with a coplanar skeleton and with a possible torsional oscillation about the carbon-carbon single bond of about 10° . As shown in Table 24, the carbon-carbon bond lengths of 2, 3-dichlorobutadiene compare favorably with those of butadiene; the small differences are well within the errors of the experiment.

The structure of 2, 3 dibromobutadiene, on the other hand, is very interesting if not a little puzzling. The molecule is trans, but not planar. The C=C bond distance is in good agreement with that in 2, 3-dichlorobutadiene and in butadiene itself, but the C-C bond distance in 2, 3-dibromobutadiene is about 0.014 \AA shorter than in 2, 3-dichlorobutadiene and in butadiene. Since the difference is about the same as the error for the C-C distance in dibromobutadiene, the statistical significance may be questionable, but it is interesting to consider the difference in regard to the theories of conjugation and π -electron delocalization. The short C-C bond might rule out resonance stabilization as a major factor in the bonding of butadiene, since with the rotation of the $p(\pi)$ -orbitals by 17° in 2, 3-dibromobutadiene a decrease in the π overlap would occur resulting in a more localized system. This should lead to a longer C-C bond in dibromobutadiene, not a shorter bond as observed.

The high correlation of the C-C bond with the C-C-Br and twist angles has already been pointed out. These correlations raise complex questions about the cause of the short C-C bond. The short C-C bond can be related to the twist or bend in the molecule, or to the influence of the halogen substitution, or to both the substitution and molecular deformation. The deviation from the coplanar structure would reduce nonbonded interactions, thus, qualitatively accounting for the observed difference when the dichlorobutadiene and dibromobutadiene compounds are compared. However, this argument is lost on butadiene itself due to the presence of only hydrogens. The presence of the halogen certainly influences the C-C bond, but, as pointed out by Bastiansen and Traetteberg (1962), the influence of negative groups on the carbon-carbon environment is not systematic. The effect of 1, 2-dichloro and 1, 2-dibromo substituted ethylene (Davis and Hansen, 1965; Davis, Kappler and Cowan, 1964) shows an increase in the C=C bond length compared to ethylene itself of about 0.017 Å, which is an opposite effect from that observed for the halogen substituted butadienes.

PART II

METHYLDIAZENE, $\text{CH}_3\text{N}=\text{ND}$

INTRODUCTION

The equilibrium internuclear distance, r_e , has been the ideal measurement in the determination of molecular structures, but it is not obtained directly by any experimental method. The principal methods of measurement, spectroscopy, X-ray, and electron diffraction, yield bond distances that are averages of the vibrational motion of the nuclei, and the nature of this averaging is not the same for the methods. For example, the $r_a (=r_g(1))$ derived from the electron diffraction experiment (Bartell, 1955) reflects the center of gravity of peaks in the radial distribution function of equation (5) and corresponds to a time average \bar{r} internuclear distance. On the other hand the measurement from microwave or infrared spectroscopy, the "effective" r_o bond distance, is obtained from the rotational constants in the ground vibrational state, that is, from an average of $1/r_o^2$.

In recent years, appropriate transformation methods have been developed that convert electron diffraction and microwave structures to a common basis called the zero-point average structure, r_α or $r_\alpha^o = r_z$ (Herschbach and Laurie, 1962; Morino, Kuchitsu, and Oka, 1962). Since the average structures determined in this

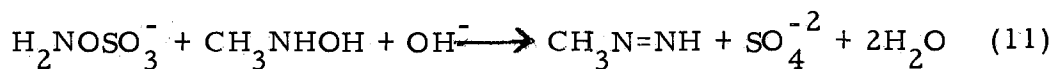
manner are well defined and equivalent to one another, Kuchitsu and coworkers have successfully combined the results of the above different experimental methods to make consistent structure analysis on a variety of compounds (for example see, Fukuyama and Kuchitsu, 1969, and the references therein).

For many molecules, however, the complete harmonic vibrational analyses required for the rigorous transformation of the electron diffraction and spectroscopic data to the zero-point basis are not known or are incomplete. Therefore, Bartell and coworkers (1970) have studied the problem of combining the electron diffraction and microwave data at a much lower level of approximation than that used by Kuchitsu. In their study of XeOF_4 , the simplifying assumption was made that the same value (0.003 Å) for the shrinkage parameter was used to relate each r_g (for bonds) to its corresponding r_{MW} value.

The present study of methyldiazene (methyldiimide) is partially concerned with the problem of using a crude approximation for the transformation of data from the two different experimental methods to a common basis. Even though least squares refinements using a combination of the electron diffraction and microwave data were not contemplated for this study, approximations are proposed and the potential benefits associated with simultaneous use of both types of data are considered.

The molecular structure of methyldiazene is interesting since it is a relatively stable, simple, monosubstituted derivative of diazene (N_2H_2), the chemical stability of which is important for a better understanding of the physical and chemical properties of nitrogen-nitrogen and nitrogen-hydrogen bonds. Diazene itself decomposes so rapidly that few detailed studies of its structure have been made. Rosengen and Pimentel (1965) produced diazene by photolyzing hydrozoic acid in solid nitrogen at 20°K , and studied the infrared spectra of diazene and various isotopic substituents. They reported the presence of both cis and trans conformations. Trombetti (1968) produced diazene by streaming hydrazine through a low-power microwave discharge and studied the gas phase infrared and ultraviolet spectra. They reported that the ground state structure has a planar-trans conformation with $r(\text{N}=\text{N}) = 1.238 \pm 0.007 \text{ \AA}$ and $\angle\text{NNH} = 109.5 \pm 1.5^\circ$, subject to the assumption that $r(\text{N}-\text{H})$ has a value between 1.05 and 1.08 \AA .

The existence of methyldiazene was first reported by Ackermann et al. (Ackermann, Ellenson, and Robinson, 1968), who prepared the compound according to the reaction

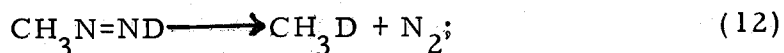


The infrared spectra of methyldiazene and the more stable N-deutero isomer were also reported. Consideration of the high-resolution

scans of the 844- and 662- cm^{-1} bands and moments of inertia calculations supported a trans configuration for both methyldiazene and the N-deutero isomer. A microwave study of the N-deutero isomer of methyldiazene was carried out by Steinmetz (1970). No consistent results were obtained for the hydrogen species due to its instability. The following rotational constants for the N-deutero isomer were obtained from the microwave data: $A_0 = 58,590 \pm 800 \text{ MHz}$, $B_0 = 10254 \pm 0.2 \text{ MHz}$, and $C_0 = 9,239.13 \pm 0.2 \text{ MHz}$. A more accurate value of A_0 ($=59,400 \pm 300 \text{ MHz}$) was obtained from the rotational structure of the infrared band assigned to the out-of-plane vibration. Since only two rotational constants were known to microwave accuracy, only an assumed molecular structure was proposed. The structural values are shown in Table 25.

EXPERIMENTAL AND DATA REDUCTION

The method of preparation of the methyldiazene (N-d) for this study was essentially that proposed by Ackermann et al. (1968): A closed reaction system was used which consisted of a three-necked flask equipped with a magnetic stirrer, a dropping funnel, a sample collection trap, and a trapped water aspirator that facilitated separation of the gaseous sample from the reaction vessel. A solution (D_2O) of 1.1304 grams of hydroxylamine-O-sulfonic acid (H_2NOSO_3H) was added to a basic solution comprising 1.200 grams of NaOH and 0.8352 grams of N-methyl-hydroxylamine-hydrochloride ($CH_3NHOH \cdot HCl$). The total volume of the solutions was 100 ml. which produced final concentrations of all the reactants of about 0.1 M. The evolved gas was first distilled through a Glas Wol packed U-tube cooled to $-45^\circ C$ to remove the water vapor, then collected in the sample trap which was cooled to $-196^\circ C$. Trace impurities of ammonia were removed by vacuum distillation while the sample was cooled to $-89^\circ C$, and the isolated sample was stored as a yellow solid at liquid nitrogen temperature ($-196^\circ C$). Upon warming, the sample decomposed to methane- d_1 and nitrogen according to the following reaction



therefore, decomposition products had to be continually removed during the experiments.

Gas phase and matrix isolated (argon) infrared spectra were obtained. The gas phase spectrum displayed the same bands reported by Ackermann. The complete infrared results on methyldiazene will be published elsewhere.

In order to obtain the electron diffraction photographs, more than one sample had to be prepared since the methyldiazene decomposed slowly even at -196°C , preventing prolonged storage. A total of seven different samples were prepared in order to complete the electron diffraction and infrared spectroscopy experiments; gas phase infrared spectra were taken intermittently to check the purity of each sample. In order to reduce the presence of decomposition products during exposure, the sample bulb was opened to the diffraction apparatus before each exposure, thus, the more volatile decomposition products were distilled away from the less volatile methyldiazene by the pumping system of the diffraction apparatus. The electron diffraction photographs were prepared using an r^3 sector and Kodak process plates. The sample bulb was cooled to -63°C in order to provide the proper sample vapor pressure. The nozzle was cooled to about 0°C to reduce the possibility of decomposition while the sample was in the nozzle tube. The ambient pressure in the diffraction apparatus during exposure of the plates was 5.0×10^{-6} - 2.0×10^{-5} Torr. The exposure times were 1-12 minutes with beam currents of 0.42-0.5 μa . The average electron

wavelength was 0.05742 \AA as determined by calibration against CO_2 in separate experiments. From the total of 22 plates exposed eight of the best plates were selected for analysis: of these 3 came from the long (75 cm), 3 from the middle (30 cm), and 2 from the short (12 cm) camera distances. A summary of the experimental data for the plates used for structure analysis is shown in Table 26.

The method and procedure of obtaining the scattered molecular intensity were described in Part I, and no further detail will be given here. No blackness correction was applied to the measured densities since that part of the data reduction program had not been implemented at the time the methyldiazene plates were data reduced. Even though one long camera plate had densities in the range that warranted a correction, successive least squares refinements, including and excluding the data from the particular plate, showed that the molecular parameters differed by less than one-half of the reported errors (2σ) for the successive refinements. The final background corrected curves, sI_m , which are in the form of equation (4), are shown in Figure 8. The ranges of the data for the long, middle, and short camera distances were $1.00 \leq s \leq 12.25$, $7.00 \leq s \leq 28.50$, and $23.00 \leq s \leq 42.50$, respectively, and the data interval was $\Delta s = 0.25$.

STRUCTURE DETERMINATION

The composite curve obtained by combining the data from the different camera distances was multiplied by $Z_C Z_N / A_C A_N$ to convert it to a constant coefficient curve, I'_m , suitable for calculation of the radial distribution curve (equation (5)). A preliminary experimental radial distribution curve was calculated using $B = 0.0013$, and the theoretical intensity and radial distribution curves were calculated from the approximate molecular parameters obtained from the experimental $D(r)$ curve. The usual method of background correction, computed using the theoretical model, was not used since the orientation of the methyl group was not known. Instead, the background corrections were computed employing the condition that the radial distribution function be greater than or equal to zero for all $r \geq 0.0$. (The peaks of a $D(r)$ curve can exhibit negative contributions if the atom pair of the corresponding distance vary greatly in atomic number from the atom pair used for the constant coefficient factor, $Z_I Z_J / A_I A_J$. This was not a problem in the methyldiazene case, however.) Negative contributions of the experimental radial distribution curve were therefore transformed back into s space and the resulting intensity curve used as a guide for smooth background corrections. The calculated theoretical intensity curve provided the missing intensity data in the range $0.00 \leq s \leq 2.00$.

The corrected experimental radial distribution curve, Figure 10, shows three main peaks at about 1.25, 1.47, and 2.25 Å which are due to the N=N, N-C, and C--N₁ distances, respectively. The shoulder at 1.10 Å is due to the non-resolved C-H and N-D distances. The interesting feature of the D(r) curve is the broad, but nonetheless distinct peak at about 3.0 Å that is primarily due to the H---N₁ distances (see Figure 7 for the numbering scheme) which are dependent upon the orientation of the methyl group. If the methyl group is freely rotating, the H---N₁ distances would encompass a wide range of distances (2.31 to 3.20 Å) resulting in a very broad unresolved peak. The relatively well defined nature of the peak at 3.0 Å suggests some type of restricted methyl orientation. The relative areas of the peaks in the experimental D(r) curve also shows little or nothing (less than 5%) of the decomposition products N₂ and CH₃D [$r(\text{N}\equiv\text{N}) = 1.094\text{Å}$; $r(\text{C-H}) = 1.093\text{Å}$].

Further refinement of the structure was carried out by the method of least squares based upon the intensity functions. Refinements were carried out in which either the eight individual intensity curves corresponding to the long, middle, and short camera distances of Figure 8 or the composite intensity curve alone were used to refine a single theoretical intensity curve. Each point of each intensity curve was weighted equally (unit weight matrix).

The convenient geometrical parameters used to describe the

structure of methyldiazene were the N-D, N=N, C-N, and C-H bond distances, the NND, CNN, and HCN angles, as well as a rotation angle for the methyl group around the C-N bond. The rotation angle was defined equal to 0.0° when H_5 was in the C-N=N plane, and the methyl group was assumed to have C_{3v} symmetry. The deuterium atom was also assumed coplanar with the C-N=N group. The amplitudes of vibration of the N=N, N-C, and C-H bonds, as well as the N_2C_4 distance were also refined in most of the least squares refinements. The refinement problems for methyldiazene concerned the methyl group orientation and the N-D bond distance and its associated amplitude of vibration. The N-D distance is nearly equal to the C-H distance and therefore the differences between the C-H and N-D distances and their corresponding amplitudes of vibration are highly correlated. Such high correlations usually cause such an oscillation of the corresponding parameters that the refinements fail to converge. It was very surprising that the refinements converged when all the parameters except the N-D amplitude and the methyl rotation were simultaneously refined. In order to circumvent the problem of the refinement of the N-D distance, the initial least squares refinements were calculated with the N-D distance fixed at 1.004 \AA . Models were tested in which the torsional angle of the methyl group was fixed at various positions in the range $0^\circ - 60^\circ$. Other models representing free rotation of the methyl group were also tested.

For these, rotation of the methyl group was simulated by introducing six "one-half" hydrogen atoms, or nine "one-third" hydrogen atoms, on the circle of rotation at equal intervals in place of the three hydrogens of the ordinary methyl group. Both cis and trans molecular models were refined even though Ackermann et al. (1968) reported only the trans structure. The cis model which fit the experimental data the best ($R=0.16435$) had the methyl group in such an orientation (rotation of 0.0°) that the $H_5\cdots D$ distance was 1.178 \AA . Since the Van der Waal radii are about 1.2 \AA (Pauling, 1960), the cis models were considered unrealistic due to the probable steric repulsion in the one case and the relatively poor fit of the other cases. Results of least squares refinements obtained in the process of the structure analysis are summarized in Table 36.

Examination of the R values of Table 36 reveals that a static model with a rotation of the methyl group of greater than or equal to 30° does not fit the experimental data as well as a static model with a rotation of 0.0 or 15° . Comparison of the theoretical radial distribution curves, Figure 10, yields the same conclusion, but some form of restricted rotation of the methyl group can not be completely excluded. The R values, in this case, may be misleading since the radial distribution curve for the free rotation model compares to the experimental $D(r)$ curve just about as well as the 0° or 15° static models. The free-rotation model does not produce enough

area in the $D(r)$ curve at 3.0 Å., but a potential function for restricted rotation of the methyl group with a minimum at about 0° could easily weight the proper H---N₁ distances to fit the experimental data by weighting the 0° to 20° configurations much higher than the 30 - 60° configurations. The actual orientation of the methyl group is difficult to resolve since the distances (H---N₁) which determine the proper orientation contribute such a small amount to the total molecular scattering. If the molecule exhibited the cis conformer or if the methyl group had heavier atoms substituted for the hydrogens, the methyl orientation could be resolved with reasonable confidence.

Consideration of the above arguments and of the probable small significance of the small differences between models 6 and 7 suggest that the best model for methyldiazene lies somewhere close to model 6, for which the final results are shown in Table 37. The errors for the individual distances, amplitudes, and angles are calculated from equations (8), (9), and (10), and take into account possible correlations among the measured intensities and estimates of possible systematic errors. The final experimental and theoretical intensity curves are shown in Figure 9, along with the corresponding difference curve.

CONSIDERATION OF ROTATIONAL CONSTANTS

Although the microwave data alone was not sufficient to derive the precise structure of methyldiazene, it was hoped they would be effective as complementary information for determining the methyl orientation, the N=N-D angle, and the N-D bond distance to a greater accuracy than that determined by the electron diffraction method alone. These parameters were difficult to refine by the electron diffraction data since their relative contribution to the total molecular scattering was small compared to the heavier atom distances. This difficulty was evidenced by the relatively high errors for the corresponding parameters. Utilization of the rotational constants with the electron diffraction results required a transformation of the r_a electron diffraction distances to r_o or conversion of both to the zero-point average basis, r_α or $r_\alpha^0 = r_z$. No direct utilization of the combined data by the method of least squares was attempted in this study.

Initially the rotational constants, A, B, C, were calculated from the molecular parameters of electron diffraction model 6 assuming no correction of the r_a values. The following rotational constants were obtained: $A_a = 1.98 \pm 0.014 \text{ cm}^{-1}$, $B_a = 0.3424 \pm 0.0012 \text{ cm}^{-1}$, and $C_a = 0.3096 \pm 0.0012 \text{ cm}^{-1}$ (A_a , B_a , C_a refer to rotation constants determined from r_a distances). These

values compared surprisingly well with the observed values, Table 39, $A_0 = 1.981 \pm 0.01 \text{ cm}^{-1}$ (I.R. determined), $B_0 = 0.34205 \pm 0.00001 \text{ cm}^{-1}$, $C_0 = 0.30818 \pm 0.00001 \text{ cm}^{-1}$. The errors for the calculated rotational constants were estimated from equations similar to

$$\sigma_A^2 = 1/n \sum_1^n \left[\left(\frac{\delta A}{\delta r_1} \right)^2 (\Delta r_1)^2 + \dots \left(\frac{\delta A}{\delta r_4} \right)^2 (\Delta r_4)^2 + \left(\frac{\delta A}{\delta \theta_1} \right)^2 (\Delta \theta_1)^2 + \dots \left(\frac{\delta A}{\delta \theta_3} \right)^2 (\Delta \theta_3)^2 \right] \quad (13)$$

in which the sum of the cross terms, $\frac{\delta A}{\delta q_i} \frac{\delta A}{\delta q_j} \Delta q_i \Delta q_j$ ($i \neq j$), were assumed to be equal to zero or much smaller than the sum of squares of the diagonal terms. The values of Δr_i and $\Delta \theta_i$ were taken as the $2\sigma_i$ values from the least squares results, Table 37, and the $\delta A / \delta q_i$ terms were approximated from differences. A naive approximation for the distance transformation was introduced that considered an overall shift of the molecular parameters (r_a and θ_a) by a constant factor of their corresponding errors (2σ). The factor was determined from a set of equations similar to

$$\Delta A = \frac{\delta A}{\delta r_1} dr_1 + \dots \frac{\delta A}{\delta r_4} dr_4 + \frac{\delta A}{\delta \theta_1} d\theta_1 + \dots \frac{\delta A}{\delta \theta_3} d\theta_3 \quad (14)$$

where $d_{qi} = k\sigma_{iT}$ ($\sigma_T = 2\sigma$). A shift of $0.12 \sigma_T$ applied to the molecular parameters of Table 37 resulted in the following calculated rotational constants: $A = 1.98 \text{ cm}^{-1}$, $B = 0.3416 \text{ cm}^{-1}$, and $C = 0.3089$

cm^{-1} . This approximate transformation for the r_a distances was a little too simple and was difficult to justify since in all reported studies r_a is greater than r_0 , a relationship in the opposite direction from that calculated here. This approximation also shifted the r_a values and the angles in the same direction whereas in other studies r_a is greater than r_0 , but θ_a is less than θ_0 (see for example, Fukuyama and Kuchitsu, 1970, Laurie and Herschbach, 1962).

The second approximate transformation of r_a to r_0 was a simple estimate of the $r_a - r_0$ and $\theta_a - \theta_0$ differences for the molecular parameters of methyldiazene. Plausible values of the differences based on differences calculated for other molecules were 0.002 \AA for $\text{N}=\text{N}$, 0.003 \AA for $\text{C}-\text{N}$, 0.006 \AA for $\text{C}-\text{H}$, and 0.005 \AA for $\text{N}-\text{D}$, -0.25° for $\angle\text{C}-\text{N}=\text{N}$, -0.50° for $\angle\text{N}=\text{N}-\text{D}$, and -0.50° for $\angle\text{H}-\text{C}-\text{N}$. These differences were all less than or equal to the errors associated with the r_a electron diffraction measurements. When the estimated differences were applied to the electron diffraction model #5, Table 36, the following rotational constants were calculated: $A_0(\text{calc}) = 1.98 \pm 0.01 \text{ cm}^{-1}$, $B_0(\text{calc}) = 0.343 \pm 0.001 \text{ cm}^{-1}$, and $C_0(\text{calc}) = 0.309 \pm 0.001 \text{ cm}^{-1}$. (The error for the $\text{N}-\text{D}$ distance was assumed to be 0.014 \AA .) An overall scale factor change was then calculated using the approximation described for the first transformation which resulted in a shift of $0.07 \sigma_T$ for all the molecular parameters. The corrected molecular parameters for methyldiazene were

$r_a(\text{N}=\text{N}) = 1.2455 \text{ \AA}$, $r_a(\text{N}-\text{C}) = 1.4708 \text{ \AA}$, $r_a(\text{C}-\text{H}) = 1.1033 \text{ \AA}$,
 $r_a(\text{N}-\text{D}) = 1.0062 \text{ \AA}$, $\theta_a(\text{NNC}) = 112.030^\circ$, $\theta_a(\text{NND}) = 109.845^\circ$,
 $\theta_a(\text{HCN}) = 108.853^\circ$, and the rotation of the methyl was a constant
 15° . The calculated rotational constants (corrected to r_0) were
 $A_0(\text{calc}) = 1.986 \pm 0.01 \text{ cm}^{-1}$, $B_0(\text{calc}) = 0.3416 \pm 0.001 \text{ cm}^{-1}$, and
 $C_0(\text{calc}) = 0.3088 \pm 0.001 \text{ cm}^{-1}$.

These calculations increase one's confidence of the results for
 methyldiazene ($\text{CH}_3\text{N}=\text{ND}$), but they do not improve the accuracy of
 the structure determination. Since the changes in the rotational
 constants with respect to changes in the N-D distance and the $\angle\text{N}=\text{N}-\text{D}$
 are a factor of 5-10 times smaller than the changes in the rotational
 constants with respect to, say, the N=N or C-N distances or $\angle\text{C}-\text{N}=\text{N}$,
 a least squares refinement of the microwave results or a combina-
 tion of the microwave and the electron diffraction data probably would
 not resolve the N-D bond distance of the $\angle\text{N}-\text{N}-\text{D}$ much better than
 the electron diffraction determination. The low accuracy of $A_0(\text{obs})$
 (either the microwave or spectroscopic determination) also reduces
 the possible benefits of such refinements, especially since the $\delta A/\delta q_i$
 terms are a factor of five or greater than the corresponding $\delta B/\delta q_i$
 or $\delta C/\delta q_i$ terms. In other words, the N-D distance and the $\angle\text{N}=\text{N}-\text{D}$
 would not be as sensitive to a refinement procedure as the other mole-
 cular parameters, as was the case for the electron diffraction deter-
 mination.

DISCUSSION

Although the utilization of the microwave data did not yield an improvement in the accuracy of the structure determination, it did provide a check on the electron diffraction structure determination. It would be remiss to dismiss the possibilities of such combinations of electron diffraction and spectroscopic data for the purpose of more accurate structure determinations based on the results of this one compound. It is very probable that the results of a more complete and accurate spectroscopic investigation of methyldiazene could be utilized with a more extensive electron diffraction study (analysis at various temperatures would add information about the rotation of the methyl group) to yield a more accurate structure determination. This statement is partially justified by the overall agreement of the structure determination of this study which adopted very rough approximations in order to utilize the rotational constants.

The N=N distance in methyldiazene ($\text{CH}_3\text{N}=\text{ND}$) of 1.245 Å agrees well with the N=N distance in similar compounds: 1.247 ± 0.003 Å in $\text{CH}_3\text{N}=\text{NCH}_3$ (Almennigen, Anfinson, and Haaland, 1970), 1.247 ± 0.003 Å in azobenzene (Brown, 1966), and 1.240 ± 0.003 Å in $\text{HN}=\text{NN}$ (Amble and Dailey, 1950). The N=N bond distance in methyldiazene is 0.007 Å longer than that reported for diazene (H_2N_2), but the errors for the diazene measurement can easily account for the difference.

The C-N bond distance in $\text{CH}_3\text{N}=\text{ND}$ of 1.469 \AA might resolve the differences between the estimates for the C-N distance in the two independent electron diffraction studies of azomethane ($\text{CH}_3\text{N}=\text{NCH}_3$). Almennigen et al. report a distance of $1.482 \pm 0.002 \text{ \AA}$, while Chang, Porter and Bauer (1969) report a value of $1.474 \pm 0.002 \text{ \AA}$; a large difference compared to the estimated errors. The estimated C-N distance in methyldiazene also agrees well with the C-N distance in methylamine, $1.474 \pm 0.005 \text{ \AA}$ (Nishikawa, 1957), and with the calculated value of the sum of the Schomaker-Stevenson single bond radii corrected for electronegativity differences, 1.465 \AA (Schomaker and Stevenson, 1951). An inductive effect in $\text{CH}_3\text{N}=\text{NCH}_3$ which would increase the electron density on the nitrogen atoms might qualitatively account for the estimate of a larger bond by Almennigen et al., but the decrease in covalent radii of the nitrogens going from sp^3 to sp^2 (methylamine to azomethane) must also be considered.

The C-N=N valence angle is significantly different from 120° in methyldiazene, but the smallness of this angle appears to be a characteristic feature for a number of molecules containing the C-N=N grouping: $112.3 \pm 0.3^\circ$ in $\text{CH}_3\text{N}=\text{NCH}_3$ ($111.9 \pm 0.5^\circ$ estimated by Chang et al.), $113.6 \pm 0.3^\circ$ in azobenzene, and in CH_3NO the C-N=O angle is $112.6 \pm 1.0^\circ$ (Coffey, Britt, and Boggs, 1968). The simplest explanation for the small angle may be the lone pair: bond pair repulsion of the non-bonding electrons of the nitrogen atoms.

Table 1. Data for electron diffraction photographs used for the structure determination of 2,3-dichlorobutadiene.

Plate I. D.	Plate ^a size (in.)	Acceler- ating Voltage (Volts)	Wavelength ^b (Å)	Expo- sure time (min.)	Beam Current (μa)	Nozzle Temp. (°C)	Bath Temp. (°C)	Ambient Pressure (Torr)	Nozzle-to- Plate distance (cm.)	s range
1-272-4	8x10	44097	0.057181	0.5	0.199	30	-3	5.0x10 ⁻⁶	74.918	1.00-12.25
1-272-5	8x10	44097	0.057181	1	0.199	30	-3	5.0x10 ⁻⁶	74.918	1.00-12.25
1-269-4	8x10	44080	0.057192	3.5	0.160	17	3	6.0x10 ⁻⁶	11.954	7.00-31.50
1-269-9	8x10	44050	0.057213	1.3	0.200	20	2	6.0x10 ⁻⁶	11.954	7.00-31.25
1-269-10	8x10	44050	0.057213	2	0.190	20	2	5.6x10 ⁻⁶	11.954	7.00-30.00

^a Kodak process plates.

^b Wavelengths were determined from the accelerating voltage which was calibrated against diffraction patterns of gaseous CO₂.

Table 2. Experimental intensity curve (sI_m) for 2,3-dichlorobutadiene. Data from long camera plate 1-272-4.

Δs s	0.0000	0.2500	0.5000	0.7500
1.00	1.3127	2.7568	-4.4189	-11.9083
2.00	-18.8261	-21.3183	-16.9004	.5961
3.00	13.5171	.3614	-58.5335	-133.5140
4.00	-169.6927	-113.4735	18.4141	153.0053
5.00	221.0626	204.5106	124.9056	32.8505
6.00	-51.9073	-121.8951	-157.5584	-144.5637
7.00	-58.8580	71.6277	170.7515	180.7024
8.00	95.0005	-16.2786	-90.8877	-98.2005
9.00	-77.5420	-64.4085	-74.8840	-75.7670
10.00	-20.3882	60.3521	115.9586	92.6154
11.00	19.6169	-58.1497	-62.5582	-5.9408
12.00	24.2642	-13.4074		

Table 3. Experimental intensity curve (sI_m) for 2,3-dichlorobutadiene. Data from long camera plate 1-272-5.

Δs s	0.0000	0.2500	0.5000	0.7500
1.00	1.7560	2.3296	-4.2974	-11.7665
2.00	-17.0177	-19.8897	-13.7945	3.8808
3.00	14.6114	.6518	-57.0277	-133.6029
4.00	-168.7356	-111.7805	15.6980	140.3045
5.00	201.0250	188.2559	130.9485	48.1660
6.00	-28.6310	-99.8802	-145.3017	-145.7374
7.00	-59.8155	73.5828	173.0275	188.0918
8.00	101.6743	-20.0210	-97.7150	-109.2832
9.00	-84.3591	-77.7417	-99.7097	-97.7067
10.00	-35.7110	63.8560	114.9434	92.2491
11.00	-0.8065	-65.8044	-16.0842	107.5481
12.00	251.4615	294.4682		

Table 4. Experimental intensity curve (sl_m) for 2,3-dichlorobutadiene. Data from middle camera plate 1-269-4.

Δs s	0.0000	0.2500	0.5000	0.7500
7.00	-37.1705	91.9526	161.2740	156.6631
8.00	82.9574	-22.4966	-89.7507	-102.1710
9.00	-75.7674	-63.6866	-75.8338	-57.7752
10.00	-9.5585	76.9863	121.7262	58.4903
11.00	-32.4586	-98.1286	-62.5071	69.0528
12.00	187.3558	184.4720	102.5246	-30.3933
13.00	-148.6691	-200.4586	-227.3182	-224.6416
14.00	-166.3993	-20.9117	178.2058	357.0253
15.00	363.3279	238.4311	44.1850	-114.3131
16.00	-119.0786	-80.6932	-47.9393	-62.9503
17.00	-113.0352	-150.9764	-130.6019	-136.5573
18.00	-96.7990	-70.1090	17.3611	183.7704
19.00	334.7283	366.8532	250.6327	45.3880
20.00	-124.4045	-216.1653	-187.8826	-116.2425
21.00	-96.8132	-74.8002	-33.4021	12.0652
22.00	76.7497	59.8363	37.5736	-30.4443
23.00	-29.9568	27.8426	98.7424	69.8596
24.00	-0.1474	-74.1909	-127.4247	-112.6890
25.00	-21.8487	20.4126	60.7534	92.6713
26.00	118.8256	123.6233	79.6523	33.2948
27.00	-88.9295	-195.9337	-214.4460	-188.0427
28.00	-83.1923	-23.9444	8.0698	55.7642
29.00	108.4340	179.9560	95.6280	39.9037
30.00	33.9293	-22.8537	13.1936	-7.6875
31.00	-144.9895	-277.7949	-385.6675	

Table 5. Experimental intensity curve (sI_m) for 2,3-dichlorobutadiene. Data from middle camera plate 1-259-9.

Δs s	0.0000	0.2500	0.5000	0.7500
7.00	-12.9883	26.8661	53.2649	50.6057
8.00	23.2350	-8.9329	-24.5531	-24.6535
9.00	-18.9687	-17.2974	-22.5970	-20.2178
10.00	-7.9767	15.9846	35.1256	13.7639
11.00	-13.7594	-27.4323	-13.1769	18.8138
12.00	48.3725	59.1680	31.1434	-8.3223
13.00	-41.4291	-56.3051	-61.7667	-61.2464
14.00	-44.5575	-7.7198	44.6582	85.8046
15.00	92.7884	57.6213	11.0838	-25.0756
16.00	-35.3791	-22.5917	-8.7364	-21.0068
17.00	-29.9154	-41.7191	-34.5749	-30.9631
18.00	-28.0133	-16.0683	8.2342	50.0123
19.00	85.8244	94.8964	64.9967	14.7144
20.00	-36.4652	-50.7001	-45.1736	-30.5054
21.00	-26.0560	-13.2559	-6.3929	9.4317
22.00	20.1444	18.5162	1.6009	-3.6402
23.00	-3.6928	6.0692	28.1088	21.8998
24.00	-1.7494	-20.8176	-35.2332	-24.0911
25.00	-15.7348	7.3233	10.6245	25.3537
26.00	25.4494	29.6032	23.0776	9.2336
27.00	-19.5717	-51.6410	-49.1083	-28.5443
28.00	-20.8875	-8.6423	.0694	6.3412
29.00	27.9766	31.5787	32.1901	26.0478
30.00	12.1541	-0.5572	1.5311	2.1073
31.00	-0.4057	-6.3091		

Table 6. Experimental intensity curve (sI_m) for 2,3-dichlorobutadiene. Data from middle camera plate 1-269-10.

Δs s	0.0000	0.2500	0.5000	0.7500
7.00	-14.4556	25.9522	54.8428	51.4095
8.00	25.0368	-6.6944	-26.5030	-29.7299
9.00	-18.0520	-17.4012	-25.4541	-20.0363
10.00	-2.3338	23.5547	35.8676	21.2387
11.00	-11.8641	-34.0402	-15.2516	27.8572
12.00	57.7567	63.4185	32.8136	-9.8413
13.00	-42.9332	-57.0075	-69.6057	-59.7352
14.00	-47.3554	-9.6943	50.0823	109.7920
15.00	121.0650	75.0514	4.5086	-24.9876
16.00	-36.4894	-27.5320	-14.8068	-24.9512
17.00	-34.3086	-36.7423	-33.3827	-31.7628
18.00	-30.7768	-15.7717	20.4104	53.3065
19.00	93.1461	100.9004	72.2322	20.8371
20.00	-35.0662	-66.0674	-59.3805	-33.8754
21.00	-13.9898	-9.2314	-6.2848	1.8320
22.00	28.6066	24.2594	13.3774	-5.4110
23.00	-6.8913	16.5403	22.0336	31.6289
24.00	-4.6258	-19.3005	-33.1928	-34.9280
25.00	-6.9232	11.1937	19.0058	24.4642
26.00	33.3542	38.1556	29.6381	3.0817
27.00	-27.0971	-21.6631	-46.2466	-40.8905
28.00	-15.3933	-7.8445	9.3784	14.8201
29.00	26.9954	44.9572	28.4564	14.0436
30.00	8.0797			

Table 7. Experimental intensity curve (sI_m) for 2,3-dichlorobutadiene. Composite curve of long and middle camera data.

Δs s	0.0000	0.2500	0.5000	0.7500
1.00	-	2.3781	-4.0755	-11.0699
2.00	-16.7589	-19.2674	-14.3505	2.0954
3.00	13.1531	.4739	-54.0338	-124.8999
4.00	-158.2434	-105.3243	15.9486	137.1393
5.00	197.3492	183.6415	119.6373	37.8917
6.00	-37.6439	-103.6849	-141.6052	-135.7412
7.00	-55.4906	67.8995	160.7473	172.3539
8.00	91.9663	-20.9099	-89.0906	-97.4190
9.00	-72.3232	-64.3031	-81.7128	-73.9554
10.00	-21.0022	64.9098	116.1088	60.2661
11.00	-41.2087	-104.7760	-54.1743	77.4713
12.00	186.9513	205.8583	109.5126	-31.4503
13.00	-148.9340	-200.3889	-230.1614	-217.6109
14.00	-163.6437	-27.4016	170.7091	347.9593
15.00	371.3785	234.7061	33.5144	-97.0590
16.00	-124.3901	-85.6883	-43.3009	-74.9653
17.00	-113.1092	-143.1507	-123.7173	-119.3447
18.00	-101.4243	-60.8899	38.8334	182.8589
19.00	322.0507	352.6839	244.8374	56.6864
20.00	-125.9217	-208.6519	-184.9249	-114.4242
21.00	-80.2411	-51.6120	026.0544	17.8558
22.00	82.5165	70.0418	29.3353	-20.6506
23.00	-22.2076	35.2581	92.4287	85.8172
24.00	-7.4049	-72.1317	-123.2826	-106.3809
25.00	-34.6715	28.4128	54.5835	89.6820
26.00	108.3534	120.5046	88.3045	26.0077
27.00	-84.1331	-153.6042	-183.9697	-143.4868
28.00	-70.8297	-27.4953	13.2156	42.8938
29.00	100.9981	149.1622	103.6874	61.5107
30.00	35.4575			

Table 8. Refined molecular parameters for 2,3 dichlorobutadiene.^a

Structural feature	1		2		3		4	
	r_a, l_a	2σ	r_a, l_a	2σ	r_a, l_a	2σ	r_a, l_a	2σ
C=C	1.346	0.003	1.347	0.003	1.346	0.004	1.346	0.003
C-C	1.465	0.005	1.466	0.008	1.463	0.008	1.465	0.005
C-H	(1.094)		1.106	0.014	1.105	0.013	1.100	0.010
C-Cl	1.747	0.002	1.747	0.003	1.747	0.003	1.747	0.002
\angle C-C-Cl	114.7	0.28	114.7	0.36	114.9	0.45	114.7	0.28
\angle C-C=C	126.8	0.24	126.8	0.30	126.7	0.35	126.9	0.24
\angle C=C-H	(120.0)		119.5	2.69	119.8	2.58	(120.0)	
twist	(0.0)		(0.0)		7.2	1.85	(0.0)	
l (C=C)	0.0397	0.004	0.0411	0.004	0.0419	0.004	0.0386	0.004
l (C-C)	(0.048)		(0.0480)		(0.0480)		(0.0480)	
l (C-H)	0.0698	0.010	(0.0698)		(0.0698)		(0.0698)	
l (C-Cl)	0.0398	0.002	0.0402	0.003	0.0404	0.003	0.0385	0.003
l (C ₂ Cl ₅)	0.0564	0.003	0.0574	0.004	0.0573	0.004	0.0554	0.003
l (C ₃ Cl ₆)	0.0794	0.006	0.0772	0.006	0.0770	0.006	0.0780	0.005
l (Cl ₅ Cl ₆)	0.0604	0.004	0.0608	0.005	0.0608	0.005	0.0597	0.004

The parenthesized values were assumed.

^a Distances of (r_a) and root-mean-square amplitudes (l_a) in angstroms, angles in deg. The 2σ values include estimates of systematic as well as random error.

Table 9. Final structural results for 2,3 dichlorobutadiene.^a

Distance or angle	r	2 σ	Amp.	2 σ
C=C	1.346	.003	.0386	.004
C-C	1.465	.005	(.0480)	
C-H	1.100	.010	(.0698)	
C-Cl	1.747	.002	.0385	.003
C ₂ Cl ₅	2.708	.004	.0554*	.003
C ₂ C ₃	2.515	.007	(.0650)	
C ₁ H ₇	2.122	.009	(.0100)	
Cl ₅ Cl ₆	4.316	.005	.0597	.004
Cl ₅ H ₇	3.694	.011	(.1400)	
C ₃ Cl ₅	2.666	.004	.0554*	
C ₃ Cl ₆	3.045	.006	.0780	.005
Cl ₅ H ₉	2.791	.007	(.1200)	
C ₃ C ₄	3.758	.009	(.0750)	
Cl ₆ H ₉	4.144	.012	(.1200)	
Cl ₆ H ₇	2.618	.007	(.1200)	
C ₂ H ₇	2.784	.009	(.1200)	
C ₂ H ₉	3.495	.012	(.1200)	
C ₄ H ₇	4.127	.011	(.1200)	
C ₄ H ₉	4.638	.013	(.1200)	
\angle C-C-Cl	114.7	.28		
\angle C-C=C	126.9	.24		
\angle C=C-H	(120.0)			

*Set equil.

^a Distances (r_a) and root-mean-square amplitudes (ℓ_a) in angstroms, angles in deg.The 2 σ values include estimates of systematic as well as random error.

The parenthesized values were assumed.

Table 10. Correlation Matrix for 2,3-dichlorobutadiene.^a

$l_{C=C}$	l_{C-Cl}	$l_{C_2Cl_5}$	l_{Cl-Cl}	$l_{C_3Cl_6}$	$r_{C=C}$	r_{C-C}	r_{C-H}	r_{CCl}	$r_{C_2Cl_5}$	$r_{C_2C_3}$	$r_{C_1H_7}$	$r_{C_3Cl_5}$	$r_{Cl_5H_7}$
1.00	.25	.22	.07	.03	-.16	-.28	-.18	.23	-.15	-.27	-.21	.08	-.19
	1.00	.30	.20	.13	-.32	.06	-.01	-.08	-.09	-.13	-.09	-.04	-.04
		1.00	.18	.13	.03	-.16	-.07	.25	-.39	-.12	-.06	-.27	-.03
			1.00	.07	-.08	-.02	.05	-.03	.03	-.04	.03	.01	.04
				1.00	-.06	.05	.04	-.06	.08	-.03	.03	.04	.05
					1.00	.07	-.02	.04	-.18	.48	.22	-.24	.14
						1.00	.14	-.33	.40	.83	.16	-.24	.22
							1.00	-.09	.11	.10	.97	.01	.96
								1.00	-.47	-.03	-.08	.04	.02
									1.00	.07	.07	.74	-.01
										1.00	.21	-.41	.23
											1.00	-.05	.97
												1.00	-.13
													1.00

^a Distances and amplitudes in angstroms, angles in degrees.

$r_{C_3Cl_5}$	$r_{C_3Cl_6}$	$r_{Cl_5H_9}$	$r_{C_3C_4}$	$r_{Cl_6H_9}$	$r_{Cl_6H_7}$	$r_{C_2H_7}$	$r_{C_2H_9}$	$r_{C_4H_7}$	$r_{C_4H_9}$	$\angle C-C-Cl$	$\angle C-C=C$	$\angle C=C-Cl$
-.07	-.19	-.18	-.25	-.23	-.11	-.27	-.29	-.27	-.30	.11	-.05	-.08
-.08	-.17	-.01	-.22	-.08	-.21	-.16	-.06	-.22	-.14	-.03	-.18	+.16
.35	-.44	.24	-.08	-.24	-.34	-.11	-.12	-.09	-.11	-.18	-.04	.29
.01	-.07	.05	-.06	.01	-.10	-.03	.02	-.04	-.00	.01	-.01	.01
.03	-.06	.07	-.05	.01	-.11	-.03	.03	-.04	.00	.02	-.12	.10
.50	.33	.30	.69	.12	.42	.44	.21	.61	.42	-.20	.30	-.08
.36	.37	.47	.65	.28	.24	.61	.58	.54	.57	-.63	.26	.53
-.01	.09	.52	.07	.91	-.23	.56	.86	.50	.76	-.04	.01	.04
.03	-.10	-.00	.05	-.12	.06	.08	-.14	.07	-.08	-.29	.47	-.15
-.37	.51	-.17	-.06	.30	.21	-.04	.17	-.08	-.08	.41	-.39	-.11
.46	.57	.42	.96	.32	.57	.85	.60	.84	.70	-.77	.68	.24
.11	.16	.58	.23	.92	-.13	.65	.88	.63	.84	-.09	.08	.02
-.52	.33	-.46	-.42	.14	.13	-.36	-.19	-.37	-.26	.72	-.41	-.48
.27	.00	.72	.22	.84	-.28	.64	.89	.61	.83	-.23	.07	.22
1.00	-.34	.82	.50	-.15	-.26	.33	.23	.40	.33	-.69	.13	.74
	1.00	-.31	.58	.49	.91	.54	.35	.55	.43	.00	.51	-.51
		1.00	.39	.33	-.44	.51	.66	.52	.65	-.58	-.01	.77
			1.00	.30	.63	.84	.54	.89	.69	-.71	.72	.12
				1.00	.17	.71	.89	.66	.85	-.04	.22	-.20
					1.00	.44	.07	.47	.22	-.12	.68	-.60
						1.00	.87	.98	.94	-.66	.71	.07
							1.00	.82	.97	-.42	.31	.20
								1.00	.92	-.62	.69	.35
									1.00	-.49	.43	.15
										1.00	-.67	-.55
											1.00	-.26
												1.00

Table 11. Data for electron diffraction photographs used for the structure determination of 2,3-dibromobutadiene.

Plate I. D.	Plate ^a size	Acceler- ating Voltage (Volts)	Wavelength ^b (Å)	Expo- sure time (min.)	Beam Current (μa)	Nozzle Temp. (°C)	Bath Temp. (°C)	Ambient Pressure (Torr)	Nozzle-to- Plate distance (cm.)	s range
1-279-7	5x7	44109	0.057173	1.5	0.48	55	55	3.1×10^{-6}	74.980	1.00-7.00
1-279-8	8x10	44067	0.057201	1	0.48	55	55	3.1×10^{-6}	74.980	1.00-12.25
1-279-9	8x10	44108	0.057173	.75	0.48	55	55	3.1×10^{-6}	74.980	1.00-12.00
1-275-8	8x10	44049	0.057213	3	0.22	53	55	4.2×10^{-6}	29.911	7.00-30.50
1-276-4	8x10	44070	0.057199	3.5	0.22	50	57	4.3×10^{-6}	29.907	7.00-30.50
1-282-2	5x7	44043	0.057217	1.5	0.39	55	60	5.0×10^{-6}	29.950	7.00-17.75
1-282-3	8x10	44049	0.057213	2	0.36	55	60	4.0×10^{-6}	29.953	7.00-30.50

^a Kodak process plates.

^b Wavelengths were determined from the accelerating voltage which was calibrated against diffraction patterns of gaseous CO₂.

Table 12. Experimental intensity curve (sI_m) for 2,3-dibromobutadiene. Data from long camera plate 1-279-7.

Δs s	0.0000	0.2500	0.5000	0.7500
1.00	.9333	-0.6821	-2.2843	-4.7551
2.00	-9.8770	-11.5968	-2.3418	18.7597
3.00	24.5963	-8.9786	-76.5648	-122.3344
4.00	-91.8132	9.7126	99.9618	123.8875
5.00	76.5034	14.9470	-15.1249	-50.9159
6.00	-102.4746	-130.8355	-69.4515	96.3823
7.00	261.2000			

Table 13. Experimental intensity curve (sI_m) for 2,3-dibromobutadiene. Data from long camera plate 1-279-8.

Δs s	0.0000	0.2500	0.5000	0.7500
1.00	.8362	-0.5719	-1.8977	-3.7933
2.00	-7.9833	-9.2911	-3.4733	13.3443
3.00	17.6940	-7.1525	-55.3929	-88.5955
4.00	-66.9095	5.4726	79.5630	91.3866
5.00	56.5350	10.7758	-10.3753	-36.3994
6.00	-75.5864	-103.7052	-57.2377	62.6706
7.00	187.9527	202.5622	91.9850	-39.3033
8.00	-110.5894	-85.2854	-51.4548	-86.5461
9.00	-142.5150	-112.9502	.2755	109.0510
10.00	143.9585	57.7892	-17.8410	21.9938
11.00	110.4172	147.9278	79.1027	-55.2481
12.00	-142.1177	-116.8901	-124.2028	

Table 14. Experimental intensity curve (sI_m) for 2,3-dibromobutadiene. Data from long camera plate 1-279-9.

Δs s	0.0000	0.2500	0.5000	0.7500
1.00	.7694	-0.1303	-1.5701	-2.9505
2.00	-4.9551	-5.2541	-1.4863	9.8054
3.00	11.9435	-4.3380	-35.8498	-56.9498
4.00	-43.6257	-10.3605	50.5433	61.3593
5.00	39.6332	13.1192	-4.8731	-23.4073
6.00	-53.3215	-70.9487	-44.1240	36.1065
7.00	120.4082	132.0700	57.7992	-30.8130
8.00	-79.5162	-68.7311	-50.8903	-61.9291
9.00	-98.8037	-78.8681	-5.9221	79.8146
10.00	94.4775	40.6767	-21.0400	4.4415
11.00	70.4876	103.6786	30.2142	-49.1673
12.00	-120.7319			

Table 15. Experimental intensity curve (sI_m) for 2,3-dibromobutadiene. Data from middle camera plate 1-282-2.

Δs s	0.0000	0.2500	0.5000	0.7500
7.00	80.4300	121.1327	62.2885	-24.8508
8.00	-64.0680	-42.3619	-13.9433	-34.5471
9.00	-68.9750	-62.9106	.3443	75.9211
10.00	83.4356	31.7073	-9.9253	-1.0250
11.00	74.9736	105.8473	57.8426	-38.1226
12.00	-91.1980	-73.6182	-59.2830	-80.6674
13.00	-125.7084	-92.0252	26.4139	151.7568
14.00	190.3535	121.7870	-7.2576	-66.5292
15.00	-38.8595	-17.5172	-9.5999	-33.7960
16.00	-40.3000	2.8280	63.1567	40.5761
17.00	-26.1772	-92.9257	-70.1279	23.9431

Table 16. Experimental intensity curve (sI_m) for 2,3-dibromobutadiene. Data from middle camera plate 1-275-8.

Δs	0.0000	0.2500	0.5000	0.7500
s				
7.00	72.8329	87.0351	43.2091	-17.3145
8.00	-47.3304	-39.2596	-19.3061	-31.3362
9.00	-49.6520	-37.7595	1.4461	46.4323
10.00	55.1715	23.4461	-6.5622	.7687
11.00	46.7252	69.9496	36.5826	-12.3104
12.00	-66.0080	-46.2773	-33.5460	-53.8540
13.00	-80.3268	-56.8355	17.4432	98.7766
14.00	128.5744	86.6222	-2.0935	-46.3124
15.00	-36.7988	-10.2687	-4.6451	-30.9400
16.00	-27.7875	3.8261	42.5584	26.1219
17.00	-17.2734	-56.9750	-34.5989	23.9431
18.00	57.0459	47.7300	-4.2439	-39.7881
19.00	-39.5231	-11.7852	-4.3656	-8.0026
20.00	2.4901	33.6551	64.3102	74.0672
21.00	18.2351	-25.2267	-59.6017	-49.8508
22.00	-22.3453	-1.0562	-33.5351	-33.7951
23.00	-5.2595	29.7961	34.8171	18.8291
24.00	-6.7611	-6.8595	17.8476	37.7311
25.00	5.2872	-23.3290	-14.0581	-10.0366
26.00	22.6349	-2.6588	-8.4172	-10.2312
27.00	-12.7798	8.0446	28.6845	-12.1885
28.00	6.5310	-19.0923	-0.3715	16.5351
29.00	-13.3054	6.9220	11.6698	0.0000
30.00	13.5273	30.5708	3.0495	

Table 17. Experimental intensity curve (sI_m) for 2,3-dibromobutadiene. Data from middle camera plate 1-276-4.

Δs	0.0000	0.2500	0.5000	0.7500
s				
7.00	36.6039	105.8330	60.4703	-28.6666
8.00	-62.8544	-51.5082	-22.3545	-30.5632
9.00	-50.5900	-44.0637	1.1018	80.3192
10.00	79.0641	28.4815	-9.1051	18.7908
11.00	68.5777	95.4194	60.1410	-31.9674
12.00	-95.6191	-75.1075	-49.0542	-78.9632
13.00	-107.5323	-77.7558	19.3121	145.7276
14.00	188.9015	105.0871	6.8389	-76.9961
15.00	-51.3711	-14.9501	-7.2773	-56.6441
16.00	-40.7875	-4.4915	46.3036	59.0356
17.00	-24.2183	-85.7355	-61.0131	30.7840
18.00	76.8374	58.6228	-0.4042	-68.6499
19.00	-68.9552	-28.9273	.4366	-10.2255
20.00	-9.5076	33.8856	93.6488	64.7491
21.00	21.1528	-44.7650	-109.3956	-53.4299
22.00	-19.4872	-23.2357	-76.9966	-100.8402
23.00	-0.2768	51.1594	61.3580	25.7814
24.00	-5.2913	13.1224	33.2752	21.7797
25.00	17.7275	-6.6204	-44.4110	-25.2533
26.00	7.5450	10.9676	9.4272	-21.1445
27.00	-36.2671	15.7394	5.6661	-17.5658
28.00	11.6106	-12.1163	-1.8574	25.5542
29.00	22.0490	43.0700	-36.1763	-49.5734
30.00	5.3711	28.9618	32.9347	

Table 18. Experimental intensity curve (sI_m) for 2,3-dibromobutadiene. Data from middle camera plate 1-282-3.

Δs s	0.0000	0.2500	0.5000	0.7500
7.00	62.0787	82.5042	40.6054	-25.5662
8.00	-58.9102	-51.7756	-32.1769	-40.7905
9.00	-56.7909	-50.0396	-0.7575	41.3853
10.00	52.2321	14.7128	-8.3668	-1.5374
11.00	39.7964	65.6124	42.3285	-18.4657
12.00	-54.3898	-46.7028	-32.3362	-54.5357
13.00	-75.0498	-60.4633	13.9545	112.5027
14.00	132.6667	86.6222	2.6518	-46.4558
15.00	-30.1750	-21.8965	-8.9805	-21.4200
16.00	-24.5375	1.4972	26.3862	20.2010
17.00	-8.5476	-47.8736	-36.4591	3.6105
18.00	54.1354	41.5905	9.4983	-40.4066
19.00	-26.2787	-8.3568	-10.9140	-9.3363
20.00	11.3186	28.8143	64.0755	75.0229
21.00	29.4194	-34.3776	-80.4749	-48.5726
22.00	-15.8496	-6.0730	-38.6324	-21.2582
23.00	-9.6885	43.5698	30.5363	28.9678
24.00	20.5774	-9.8418	14.5201	7.3622
25.00	13.0624	-13.5560	-35.1454	-4.2089
26.00	5.2487	6.6470	14.8142	-13.6416
27.00	-6.9080	12.5915	7.0826	8.6037
28.00	-11.9734	-10.6477	-10.7728	-4.5096
29.00	9.1237	31.1488	5.4459	-24.7867
30.00	8.1562	-1.4079	.6099	

Table 19. Experimental intensity curve (sI_m) for 2,3-dibromobutadiene. Composite curve of long and middle camera data.

Δs s	0.0000	0.2500	0.5000	0.7500
1.00	.5892	-0.2780	-1.3052	-2.5766
2.00	-4.9835	-5.6453	-1.6313	9.1986
3.00	11.7997	-4.4518	-36.3565	-57.9994
4.00	-43.9153	-0.6975	50.2978	60.3293
5.00	37.8578	9.1294	-6.3216	-23.9373
6.00	-50.7567	-67.3365	-38.3772	41.2142
7.00	123.1758	132.5360	59.0982	-28.3097
8.00	-76.0645	-62.3647	-42.3377	-59.3776
9.00	-96.1894	-76.5155	-2.8706	75.2794
10.00	89.2242	34.8776	-13.5557	6.9776
11.00	71.2135	102.6581	51.2185	-36.4834
12.00	-95.3741	-74.8384	-53.7313	-83.5945
13.00	-120.8805	-89.6088	24.0284	159.3506
14.00	200.0550	126.0635	.2048	-73.4426
15.00	-49.5069	-20.8888	-9.6634	-44.0270
16.00	-41.4173	1.5468	55.1230	44.1150
17.00	-23.1461	-87.2008	-61.7422	24.9819
18.00	84.4274	66.6962	2.5787	-65.6710
19.00	-58.3914	-20.6929	-7.6625	-12.5389
20.00	3.6506	44.0816	99.2745	99.4354
21.00	31.9810	-46.5814	-110.9801	-69.4870
22.00	-26.4979	-12.0257	-64.5941	-64.3940
23.00	-7.7437	55.9241	55.4529	33.7180
24.00	5.2303	-3.8070	28.5004	30.7720
25.00	15.7773	-21.1837	-41.1812	-16.3520
26.00	16.8985	6.0157	6.7330	-19.8144
27.00	-23.0979	16.2184	20.2330	-8.0946
28.00	1.3481	-19.5205	-6.3898	15.2805
29.00	5.8777	35.0249	-4.3153	-30.5885
30.00	12.9873	25.2227	13.7259	0

Table 20. Refined molecular parameters for 2,3 dibromobutadiene.

Structural feature	1 ^b		2 ^{b*}		3 ^b		4 ^b		5 ^b		6 ^b	
	r _a , l _a	2σ	r _a , l _a	2σ	r _a , l _a	2σ	r _a , l _a	2σ	r _a , l _a	2σ	r _a , l _a	2σ
C=C	1.344	0.0068	1.339	0.0057*	1.342	0.0065	1.342	0.0066	1.344	0.0070	1.342	0.0058
C-C	1.457	0.0118	1.458	0.0057*	1.451	0.0112	1.451	0.0113	1.456	0.0118	1.457	0.0100
C-H	1.111	0.0296	1.092	0.0431	1.098	0.0265	1.098	0.0272	1.098	0.0452	1.102	0.0258
C-Br	1.909	0.0039	1.910	0.0047	1.909	0.0036	1.909	0.0037	1.911	0.0046	1.910	0.0037
∠C-C-Br	114.62	0.54	115.95	0.72	116.20	0.65	116.19	0.68	117.05	0.905	116.90	0.77
∠C-C=C	127.41	0.48	126.24	0.88	126.07	0.60	126.12	0.79	125.47	0.96	125.58	0.86
∠C=C-H	(120.00)		(120.00)		(120.00)		120.41	3.46	(120.00)		121.02	3.29
twist/bend	(0.0)		17.02	1.53	16.74	1.18	16.70	1.23	11.30	1.75	10.91	1.56
ℓ (C=C)	0.0416	0.0140	0.0402	0.0135	0.0426	0.0126	0.0423	0.0127	0.0416	0.0140	0.0398	0.0127
ℓ (C-H)	0.0946	0.0291	0.0905	0.0353	0.0945	0.0258	0.0951	0.0263	0.0990	0.0380	0.0948	0.0255
ℓ (C-Br)	0.0429	0.0065	0.0404	0.0080	0.0421	0.0061	0.0416	0.0062	0.0408	0.0077	0.0429	0.0060
ℓ (C ₂ Br ₅) =]												
ℓ (C ₃ Br ₅)	0.0680	0.0055	0.0662	0.0082	0.0672	0.0057	0.0671	0.0059	0.0528	0.0032	0.0561	0.0086
ℓ (Br ₅ Br ₆)	0.0714	0.0044	0.0702	0.0050	0.0705	0.0042	0.0702	0.0042	0.0701	0.0048	0.0710	0.0042
ℓ (C ₃ Br ₆)	0.1067	0.0119	0.0850	0.0134	0.0912	0.0100	0.0908	0.0100	0.0855	0.0130	0.0906	0.0100

^a Distances (r_a) and root-mean-square amplitudes (ℓ_a) in angstroms, angles in deg.

^b Model #1 assumes a coplanar structural model, #2-4 a twist about the carbon-carbon single bond; #5-6 the bromine atoms bend out of the carbon-carbon plane.

* Model #2 assumes a Δ(C-C) value of 0.119 angstroms.

Parenthesized values were assumed.

Table 21. Final structural results for 2,3 dibromobutadiene.^a

Distance or angle	Twisted Model				Bent Model			
	r_a	2σ	ℓ_a	2σ	r_a	2σ	ℓ_a	2σ
C=C	1.342	.0065	.0426*	.0126	1.344	.0070	.0416*	.0140
C-C	1.451	.0112	.0486*		1.456	.0118	.0476*	
C-H	1.098	.0265	.0945	.0258	1.098	.0452	.0990	.0380
C-Br	1.909	.0036	.0421	.0061	1.911	.0046	.0408	.0077
C ₂ Br ₅	2.863	.0073	.0672**	.0057	2.811	.0120	.0528**	.0132
C ₂ C ₃	2.490	.0130	(.0600)		2.489	.0163	(.0600)	
Br ₅ Br ₆	4.619	.0055	.0705	.0042	4.619	.0061	.0702	.0048
C ₁ H ₇	2.117	.024	(.1100)		2.118	.0384	(.1100)	
Br ₅ H ₇	3.834	.027	(.1300)		3.816	.044	(.1300)	
C ₃ Br ₅	2.798	.0066	.0672**		2.784	.0090	.0528**	
C ₃ Br ₆	3.173	.011	.0912	.0100	3.175	.0132	.0855	.0130
Br ₅ H ₉	2.876	.012	(.1300)		2.861	.017	(.1300)	
C ₃ C ₄	3.714	.019	(.0750)		3.726	.021	(.0750)	
Br ₆ H ₉	4.259	.029	(.1300)		4.266	.048	(.1300)	
Br ₆ H ₇	2.722	.018	(.1300)		2.704	.021	(.1300)	
C ₂ H ₇	2.755	.022	(.1200)		2.748	.031	(.1200)	
C ₂ H ₉	3.472	.030	(.1200)		3.473	.045	(.1200)	
C ₄ H ₇	4.070	.029	(.1200)		4.088	.033	(.1200)	
C ₄ H ₉	4.570	.032	(.1200)		4.607	.044	(.1200)	
∠C-C-Br	116.20	0.65			117.05	0.91		
∠C-C=C	126.07	0.60			125.47	0.95		
∠C=C-H	(120.00)				(120.00)			
twist/ bend	16.74	1.18			11.30	1.75		

^aDistances (r_a) and root-mean-square amplitudes (ℓ_a) in angstroms, angles in degrees.
 Parenthesized values were assumed.

*assumed $\ell(\text{C-C}) = \ell(\text{C=C}) + 0.006$.

**Set equil.

Table 22. Correlation Matrix for 2,3-dibromobutadiene, twisted model.^a

$l_{C=C}$	l_{C-H}	l_{CBr}	$l_{C_2Br_5}$	$l_{Br_5Br_6}$	$l_{C_3Br_6}$	$r_{C=C}$	r_{C-C}	r_{CH}	r_{CBr}	$r_{C_2Br_5}$	$r_{C_2C_3}$	$r_{Br_5Br_6}$	$r_{C_1H_7}$	$r_{Br_5H_7}$
1.00	.20	.19	.29	.15	.02	.52	-.61	-.15	-.03	-.20	-.36	.00	-.01	-.11
	1.00	-.05	.00	-.04	-.00	.31	-.13	-.04	-.09	-.07	0.00	-.14	.04	.00
		1.00	.40	.36	-.03	.07	-.10	.03	-.06	.07	-.12	.01	.04	.02
			1.00	.31	-.02	.27	-.20	.07	.16	-.07	-.03	-.12	.13	.11
				1.00	-.02	.01	-.04	-.00	-.03	.06	-.06	-.00	.00	-.01
					1.00	-.03	-.12	-.03	.08	-.32	.00	.00	-.04	-.05
						1.00	-.49	.13	-.10	-.35	.06	-.03	.36	.22
							1.00	.09	-.15	.32	.74	-.01	-.03	.08
								1.00	.14	-.13	.27	.02	.97	.98
									1.00	-.28	.05	-.01	.11	.22
										1.00	-.21	.20	-.20	-.19
											1.00	-.03	.27	.30
												1.00	.02	-.02
													1.00	.98
														1.00

^a Distances and amplitudes in angstroms, angles in degrees.

$r_{C_3Br_5}$	$r_{C_3Br_6}$	$r_{Br_5H_9}$	$r_{C_3C_4}$	$r_{Br_6H_9}$	$r_{Br_6H_7}$	$r_{C_2H_7}$	$r_{C_2H_9}$	$r_{C_4H_7}$	$r_{C_4H_9}$	C-C-Br	C-C=C	twist	C=C-Br
.09	-.03	-.12	-.18	-.15	.09	-.25	-.28	-.09	-.17	.42	-.22	.07	-.39
.16	-.02	.08	.11	-.03	.01	-.00	-.03	.07	.03	.09	-.06	-.04	-.07
-.02	.06	-.00	-.09	-.04	.06	-.07	-.02	-.07	-.03	.16	-.14	.10	-.06
.17	.10	.10	.06	.09	.12	.05	.03	.07	.07	.08	.00	.11	-.15
-.03	.06	-.03	-.06	.01	.06	-.05	-.03	-.05	-.03	-.08	-.07	.07	-.03
-.10	-.24	-.13	.08	-.10	-.19	.05	-.05	.10	-.00	-.13	.22	-.26	-.13
.46	-.01	.28	.44	.13	-.01	.19	.10	.41	.31	.23	-.01	-.16	-.40
.03	.12	.23	.37	.14	-.04	.42	.40	.25	.30	-.64	.34	-.17	.59
.11	.04	.65	.29	.94	-.31	.74	.92	.64	.87	-.21	.28	-.15	-.07
.33	-.01	.17	.05	.12	.04	.21	.11	.13	.10	-.34	.41	.07	-.06
-.32	.74	-.22	-.52	.10	.67	-.38	-.14	-.56	-.32	.48	-.60	.77	.13
.25	-.01	.37	.89	.30	-.16	.82	.61	.78	.67	-.83	.78	-.55	.20
-.23	.07	-.18	-.00	.07	-.03	-.01	.01	.03	.01	.15	-.02	-.16	-.23
.22	.03	.68	.38	.92	-.29	.74	.89	.70	.89	-.14	.26	-.18	-.17
.30	-.03	.77	.36	.90	-.35	.76	.92	.68	.87	-.26	.29	-.17	.00
1.00	-.40	.79	.38	-.03	-.35	.23	.19	.32	.28	-.33	.05	-.17	.51
	1.00	-.31	-.19	.36	.92	-.04	.04	-.21	-.05	.41	-.19	.72	-.41
		1.00	.40	.49	-.52	.56	.69	.55	.69	-.40	.12	-.22	.52
			1.00	.26	-.30	.82	.56	.91	.73	-.70	.79	-.73	-.03
				1.00	.01	.71	.89	.58	.82	-.10	.24	.05	-.23
					1.00	-.31	-.31	-.43	-.36	.48	-.26	.77	-.43
						1.00	.91	.95	.96	-.70	.79	-.54	-.04
							1.00	.80	.96	-.49	.49	-.31	.06
								1.00	.92	-.65	.78	-.70	-.11
									1.00	-.52	.60	-.46	-.04
										1.00	-.83	.66	-.42
											1.00	-.68	-.15
												1.00	-.06
													1.00

Table 23. Correlation Matrix for 2,3-dibromobutadiene, bent model.^a

$l_{C=C}$	l_{C-H}	l_{C-Br}	$l_{C_2Br_5}$	l_{Br}	l_{Br}	C_3Br_6	$r_{C=C}$	r_{C-C}	r_{C-H}	r_{C-Br}	$r_{C_2Br_5}$	$r_{C_2C_3}$	$r_{Br_5Br_6}$	$r_{C_1H_7}$	$r_{Br_5H_7}$
1.00	.01	.26	.23	.18	.04	.40	-.46	-.19	-.05	-.14	-.21	-.00	-.12	-.17	
	1.00	-.00	.06	-.04	-.03	.31	-.07	-.04	-.07	-.03	.08	-.02	.01	-.02	
		1.00	.32	.43	.02	.14	-.10	.07	-.03	-.03	-.05	.01	.09	.08	
			1.00	.30	.01	.30	-.06	.06	.14	-.65	.39	-.02	.10	.19	
				1.00	.00	.04	.02	.05	-.01	-.00	.01	-.01	.06	.06	
					1.00	-.07	-.13	.01	-.01	-.03	.01	-.01	.00	.02	
						1.00	-.34	.00	-.16	-.14	.16	-.05	.16	.07	
							1.00	.03	-.17	.25	.64	-.03	-.02	.04	
								1.00	.13	-.02	.10	-.02	.99	.98	
									1.00	-.12	.03	.00	.10	.17	
										1.00	-.39	.02	-.04	-.15	
											1.00	-.03	.12	.18	
												1.00	-.03	-.01	
													1.00	.98	
														1.00	

^a Distances and amplitudes in angstroms, angles in degrees.

$r_{C_3Br_5}$	$r_{C_3Br_6}$	$r_{Br_5H_9}$	$r_{C_3C_4}$	$r_{Br_6H_9}$	$r_{Br_6H_7}$	$r_{C_2H_7}$	$r_{C_2H_9}$	$r_{C_4H_7}$	$r_{C_4H_9}$	$\angle C-Br-C$	$\angle C-C=C$	Bend	$\angle C=C-Br$
.06	-.08	-.14	-.02	-.20	.08	-.20	-.26	-.10	-.19	.21	-.09	-.02	-.21
.10	.08	.02	.17	-.01	.12	.03	-.01	.09	.04	.04	.01	-.02	-.09
.09	-.05	.11	.00	.05	-.08	.01	.05	.05	.06	.06	-.06	-.01	.01
.61	-.38	.37	.49	-.03	-.20	.38	.15	.42	.24	-.56	.48	-.60	.08
.07	-.04	.10	.02	.04	-.07	.03	.05	.04	.06	-.01	-.02	-.01	.06
-.02	-.16	-.04	.02	-.02	-.08	.07	-.00	.05	.05	-.14	.18	-.23	-.10
.32	.20	.14	.48	.06	.26	.15	.04	.35	.21	.17	.02	-.06	-.33
.11	.25	.21	.36	.10	.12	.30	.27	.20	.22	-.44	.18	-.05	.44
.00	.09	.68	.09	.97	-.47	.71	.95	.69	.91	-.08	.11	.00	-.07
.18	.05	.09	.03	.14	.04	.19	.11	.15	.11	-.26	.30	.12	-.11
-.47	.56	-.20	-.49	.10	.24	-.44	-.09	-.44	-.18	-.72	-.75	.90	.13
.33	.25	.22	.93	.18	.32	.74	.39	.72	.48	-.79	.78	-.55	-.07
-.01	-.00	-.06	-.04	-.02	-.02	-.02	-.03	-.03	-.04	-.04	-.01	-.22	.10
.06	.12	.70	.17	.96	-.43	.72	.95	.73	.93	-.05	.11	-.01	-.17
.19	-.02	.79	.19	.92	-.05	.76	.96	.75	.93	-.20	.19	-.12	.01
1.00	-.58	.69	.39	-.14	-.44	.23	.10	.28	.17	-.53	.20	-.47	.58
	1.00	-.39	.25	.34	.78	.18	.17	.20	.20	.30	.02	.50	-.58
		1.00	.21	.54	-.73	.54	.71	.55	.69	-.34	.04	-.22	.54
			1.00	.18	.37	.73	.35	.80	.50	-.68	.77	-.57	-.25
				1.00	-.23	.73	.95	.72	.92	-.02	.14	.11	-.23
					1.00	-.08	-.35	-.03	-.26	.11	.22	.22	-.62
						1.00	.86	.98	.91	-.64	.73	-.48	-.23
							1.00	.83	.98	-.29	.30	-.13	-.05
								1.00	.91	-.56	.68	-.46	-.29
									1.00	-.34	.39	-.21	-.14
										1.00	-.86	.78	-.17
											1.00	-.75	-.37
												1.00	.01
													1.00

Table 24. Comparison of structures of 2,3-dichlorobutadiene and 2,3-dibromobutadiene and related molecules.^a

	2,3-dichlorobutadiene ^b		2,3-dibromobutadiene ^b		Butadiene ^c		2,3-dimethylbutadiene ^b	
	Value	Error	Value	Error	Value	Error	Value	Error
C=C	1.346	0.003	1.342	0.007	1.344	0.001	1.349	0.006
C-C	1.465	0.005	1.451	0.011	1.467	0.003	1.491	0.006
C=H ₂	1.100	0.010	1.098	0.027	1.094	0.003	1.093	0.007
ℓ (C=C)	0.0386	0.004	0.0426 ^d	0.013	0.0436	0.001	0.0407	0.006
ℓ (C-C)	(0.0480)		0.0486 ^d		0.0513	0.002	(0.0448)	
ℓ (C-H)	(0.0698)		0.0945	0.026	0.0821	0.002	0.0805	0.014
\angle C=C-C	126.9	0.24	126.1	0.60	122.9	0.50	122.0	1.04
\angle C=C-H	(120.0)		(120.0)		119.5	1.00	(120.4)	
\angle C-C-X	114.7	0.28	116.2	0.65			117.9	0.74
Method	Electron Diffraction		Electron Diffraction		Electron Diffraction ^e		Electron Diffraction ^f	

Parenthesized values were assumed.

^a Distances (r) and amplitudes (ℓ) in Å, angles in degrees.

^b Distances and amplitudes are r_a and ℓ_a ; errors are 2σ .

^c Distances and amplitudes are $r_g(1)$ and $\ell_g(1)$; errors are σ_{LS} .

^d C-C amplitude set equal to C=C amplitude plus 0.0060 Å.

^e Haugen and Traetteberg (1966).

^f Aten, Hedberg, and Hedberg (1968).

Table 25. Structure of trans-methyldiazene proposed from microwave data.

$r_{\text{(C-H)}} = 1.09 \text{ \AA} \text{ (assumed)}$	$\angle\text{HCH} = 109.5^\circ \text{ (assumed)}$
$r_{\text{(C-N)}} = 1.47 \text{ \AA} \text{ (assumed)}$	$\angle\text{CNN} = 112^\circ$
$r_{\text{(N=N)}} = 1.24 \text{ \AA} \text{ (assumed)}$	$\angle\text{NNH} = 110^\circ$
$r_{\text{(N-H)}} = 1.014 \text{ \AA} \text{ (assumed)}$	

Table 26. Data for electron diffraction photographs used for the structure determination of Methyldiazene.

Plate I. D.	Plate ^a size (in.)	Acceler- ating Voltage (Volts)	Wavelength ^b (Å)	Expo- sure Time (min.)	Beam current (μ a)	Nozzle Temp. (°C)	Bath Temp. (°C)	Ambient Pressure (Torr)	Nozzle-to- Plate distance (cm.)	s range
1-295-4	8x10	43727	0.057432	2	0.42	0	-63	6.0×10^{-6}	74.914	1.00-12.25
1-295-8	8x10	43736	0.057426	1	0.44	0	-63	2.0×10^{-5}	74.914	1.00-11.50
1-295-10	8x10	43750	0.057416	1	0.44	0	-63	8.0×10^{-5}	74.914	1.00-12.00
1-294-5	8x10	43722	0.057436	3	0.42	-5	-63	9.0×10^{-6}	29.942	7.00-28.50
1-294-6	8x10	43730	0.057430	2.5	0.42	-5	-63	8.0×10^{-6}	29.942	7.00-28.50
1-294-7	8x10	43730	0.057430	3.5	0.42	0	-63	8.0×10^{-6}	29.942	7.00-28.50
1-296-2	5x7	43778	0.057397	11	0.46	0	-63	8.0×10^{-6}	12.029	23.00-44.25
1-296-3	5x7	43750	0.057416	12	0.50	0	-63	7.0×10^{-6}	12.029	23.00-44.25

^a Kodak process plates.

^b Wavelengths were determined from the accelerating voltage which was calibrated against diffraction patterns of gaseous CO₂.

Table 27. Experimental intensity curve (sI_m) for N-deuterated Methyldiazene. Data from long camera plate 1-295-4.

Δs s	0.0000	0.2500	0.5000	0.7500
1.00	6.0259	6.4938	6.9776	6.8239
2.00	3.5882	-5.7904	-18.6248	-30.4699
3.00	-48.1255	-64.1831	-83.9538	-105.5388
4.00	-127.8417	-142.3343	-146.0340	-131.5646
5.00	-93.9753	-28.5845	53.9955	140.1462
6.00	216.7367	267.8245	285.0092	252.9512
7.00	177.9792	71.6515	-41.8151	-121.1335
8.00	-158.0539	-154.3174	-118.1623	-75.5554
9.00	-46.9012	-33.8616	-45.8066	-57.0985
10.00	-64.1378	-55.5305	-37.8102	-9.2595
11.00	25.9161	57.3377	91.0984	99.8512
12.00	94.4485	87.0559		

Table 28. Experimental intensity curve (sI_m) for N-deuterated Methyldiazene. Data from long camera plate 1-295-8.

Δs s	0.0000	0.2500	0.5000	0.7500
1.00	1.1752	2.3309	3.2803	2.4768
2.00	.6525	-2.6725	-7.5126	-12.2423
3.00	-19.0982	-25.7360	-31.8396	-36.2731
4.00	-40.5876	-44.0370	-42.9767	-39.3562
5.00	-26.2999	-6.7373	18.2357	46.4666
6.00	72.1572	87.7025	88.3745	2.6062
7.00	47.8209	16.6523	-11.1706	-30.7953
8.00	-39.8827	-38.2600	-35.5593	-28.2464
9.00	-23.4942	-18.7087	-22.4142	-24.3341
10.00	-22.6941	-19.9712	-13.1743	-3.7066
11.00	4.9613	16.3435	22.0929	

Table 29. Experimental intensity curve (sI_m) for N-deuterated Methyldiazene. Data from long camera plate 1-295-10.

Δs s	0.0000	0.2500	0.5000	0.7500
1.00	4.1828	8.0015	9.4067	8.8008
2.00	4.7525	-3.1592	-13.3626	-24.8457
3.00	-39.3064	-51.9607	-63.7771	-75.3965
4.00	-82.4876	-86.7011	-85.7345	-73.0927
5.00	-51.6285	-14.6064	36.1652	93.8367
6.00	150.1335	182.8986	188.9016	161.4640
7.00	105.2117	30.6048	-35.9658	-85.1068
8.00	-105.3121	-98.6701	-76.2912	-47.3985
9.00	-26.7250	-17.9155	-24.8550	-29.6055
10.00	-40.7168	-41.0901	-27.7590	-11.6980
11.00	13.2697	38.3816	55.0351	71.4449
12.00	69.0043			

Table 30. Experimental intensity curve (sI_m) for N-deuterated Methyldiazene. Data from middle camera plate 1-294-5.

Δs s	0.0000	0.2500	0.5000	0.7500
7.00	87.9756	9.1715	-46.4730	-97.4805
8.00	-113.3407	-94.1002	-66.6760	-44.5653
9.00	-30.9175	-21.0034	-22.6099	-35.5016
10.00	-50.8365	-50.0846	-33.3752	-17.9851
11.00	10.0498	43.3662	59.3618	69.5367
12.00	73.8446	61.6380	40.4614	7.5558
13.00	-21.8495	-37.0237	-29.0370	-15.4720
14.00	-3.8999	19.9748	24.9029	18.8613
15.00	-6.5476	-39.3770	-60.0415	-74.9804
16.00	-85.2898	-59.1657	-31.1736	15.2940
17.00	54.3658	73.9686	88.6552	70.5754
18.00	48.1657	1.5527	-41.3890	-72.8023
19.00	-89.0383	-98.1195	-86.1342	-60.0845
20.00	-30.8796	-5.6465	113.6196	27.9479
21.00	47.3200	57.4925	75.3257	94.8380
22.00	123.2418	105.9708	90.4866	72.6595
23.00	40.4154	-23.5797	-88.9119	-131.7630
24.00	-174.6869	-180.8229	-172.6261	-126.7873
25.00	-60.1138	5.7815	68.5152	103.9626
26.00	122.3509	140.1665	184.1359	147.2832
27.00	120.6294	72.3397	30.6984	-14.7769
28.00	-62.4991	-74.4479	-135.7541	

Table 31. Experimental intensity curve (sI_m) for N-deuterated Methyldiazene. Data from middle camera plate 1-294-6.

Δs s	0.0000	0.2500	0.500	0.7500
7.00	177.2328	228.4348	38.5189	-96.7407
8.00	-121.1870	-107.4473	-73.8421	-49.4107
9.00	-27.3056	-19.9456	-23.0247	-26.9637
10.00	-48.0119	-42.4858	-25.2209	-15.4727
11.00	18.8340	53.9349	71.6229	79.4096
12.00	79.0305	61.9653	35.3932	3.0406
13.00	-28.6002	-48.4164	-48.1305	-26.7443
14.00	-7.1411	14.4876	27.0306	27.0709
15.00	-3.3553	-32.2059	-66.0567	-92.8900
16.00	-78.5726	-41.3614	5.3371	52.4215
17.00	95.2697	132.1486	121.4251	108.2965
18.00	70.9393	8.0923	-47.6576	-99.7536
19.00	-132.4840	-135.9592	-132.4670	-86.7530
20.00	-53.5200	-9.6977	8.2009	28.6884
21.00	53.7461	81.6992	94.9060	114.0272
22.00	133.3803	133.6574	115.4784	67.2224
23.00	41.0236	-24.2643	-96.0099	-150.0274
24.00	-200.5557	-234.0806	-198.6977	-144.7321
25.00	-73.8774	1.5114	86.4010	161.3192
26.00	190.2442	194.4470	173.3810	136.7888
27.00	105.1264	41.9996	-10.1640	-53.3605
28.00	-78.0602	-168.8813	-217.9238	

Table 32. Experimental intensity curve (sI_m) for N-deuterated
Methyldiazene. Data from middle camera plate 1-294-7.

Δs	0.0000	0.2500	0.5000	0.7500
s				
7	320.2548	413.0716	-55.0198	-126.2812
8	-170.0500	-163.8255	-122.8970	-93.2868
9	-66.5313	-49.2101	-52.3392	-51.6455
10	-63.4254	-56.2973	-30.0399	.8155
11	35.1091	78.2264	103.1762	113.3695
12	114.1449	89.9748	57.1614	2.0194
13	-30.1210	-47.2486	-45.5746	-39.7200
14	-19.7979	7.2794	12.5892	11.0392
15	-3.7901	-49.1954	-89.1483	-107.8589
16	-93.1888	-63.8496	-15.2540	52.1833
17	120.5238	167.5995	175.1133	158.2948
18	104.4901	21.6202	-76.1827	-113.7411
19	-154.3293	-164.6306	-144.8727	-109.5252
20	-64.3846	-47.3128	-4.1551	18.2471
21	64.6532	88.0377	128.0779	163.7926
22	165.8862	156.9711	127.0188	119.8073
23	59.4915	-21.7353	-143.1616	-214.0062
24	-254.6069	-288.4966	-268.3987	-192.7611
25	-96.3818	-30.1271	76.7528	159.2276
26	219.1363	253.2163	235.8780	243.5888
27	160.6167	106.7903	38.6097	-56.5406
28	-58.1183	-146.5695	-184.7232	

Table 33. Experimental intensity curve (sI_m) for N-deuterated Methyldiazene. Data from short camera plate 1-296-2.

Δs	0.0000	0.2500	0.5000	0.7500
s				
23.00	36.1606	-55.7304	-128.6478	-226.8564
24.00	-300.6488	-317.9658	-265.5907	-186.2876
25.00	-96.8561	-2.1471	89.5273	158.1308
26.00	223.8299	254.7752	246.4255	217.3924
27.00	174.5398	101.1288	28.0641	-39.0359
28.00	-65.3893	-127.1639	-214.1647	-239.0934
29.00	-260.1659	-232.5401	-203.3769	-172.5228
30.00	-54.4926	42.6493	50.2604	85.3677
31.00	161.1730	168.1845	180.2116	161.9871
32.00	60.2458	-23.0795	-84.9695	-123.1865
33.00	-181.0837	-191.5900	-212.4777	0181.6795
34.00	-159.9702	-129.9911	-52.9840	3.5850
35.00	-12.8482	16.0557	95.8252	53.4684
36.00	77.3175	161.9659	148.4784	110.5254
37.00	32.5600	38.2027	32.8111	

Table 34. Experimental intensity curve (sI_m) for N-deuterated
Methyldiazene. Data from short camera plate 1-296-3.

Δs s	0.0000	0.2500	0.5000	0.7500
23.00	46.4891	046.0020	-156.8271	-242.5455
24.00	-278.4014	-324.6380	-301.1728	-224.0365
25.00	-134.7985	18.0866	80.5111	163.7906
26.00	247.1014	304.3231	284.2766	217.6058
27.00	180.8230	107.0324	3.2813	-49.7762
28.00	-96.6840	-143.5241	-183.0868	-239.8738
29.00	-259.5900	-201.0167	-155.4907	-183.1094
30.00	-89.2214	-23.4885	63.0162	153.4390
31.00	220.5950	240.7558	226.7793	250.0452
32.00	176.1396	72.8308	-49.4737	-56.4817
33.00	-110.8258	-201.1540	-242.7600	-224.6255
34.00	-214.2578	-133.9425	-87.0626	-67.7843
35.00	-12.1830	62.0612	139.3525	138.7139
36.00	161.2368	252.8724	291.2144	237.6218
37.00	184.7086	-21.4258	-10.4543	-41.7402
38.00	-64.8629	-95.3951	-48.3988	-85.9970
39.00	-118.0950	-190.8019	-116.7533	-121.4559
40.00	-85.2265	27.6548	49.6395	66.6823
41.00	122.5457	111.8095	59.4968	87.3311
42.00	120.6936	105.4920	72.0958	

Table 35. Experimental intensity curve (sI_m) for N-deuterated Methyldiazene. Composite curve of long, middle and short camera data.

Δs s	0.0000	0.2500	0.5000	0.7500
1.00	3.2298	5.2306	6.3644	5.6341
2.00	2.5847	-3.8286	-12.5998	-21.4951
3.00	-33.8176	-45.1302	-56.5830	-67.2671
4.00	-76.6329	-83.0117	-82.7730	-73.7117
5.00	-51.3139	-14.4644	33.4720	86.3143
6.00	135.2088	165.3403	171.0236	146.1626
7.00	98.1832	34.2687	-26.4657	-69.8307
8.00	-89.1695	-86.0571	-65.8630	-45.5671
9.00	-30.6833	-22.4142	-26.7708	-31.8006
10.00	-39.8433	-36.7390	-23.5338	-8.7038
11.00	13.2940	37.5737	55.6345	62.7407
12.00	64.2227	51.6864	32.3035	3.6191
13.00	-19.6204	-32.5587	-29.5282	-18.7559
14.00	-6.5714	11.4839	17.1274	14.8467
15.00	-3.6756	-29.7446	-52.0027	-66.8532
16.00	-64.1864	-41.1846	-11.8142	27.1711
17.00	62.8212	86.7337	90.3597	78.1360
18.00	51.9706	6.3458	-38.7493	-68.8477
19.00	-89.4703	-95.1816	-86.8105	-60.6914
20.00	-34.8111	-12.6863	5.7946	19.5556
21.00	40.3942	54.7626	71.0673	88.5995
22.00	103.1520	95.8715	80.9397	61.9638
23.00	34.0746	-22.5342	-77.3630	-122.1547
24.00	-154.0537	-170.4993	-152.6585	-110.7067
25.00	-58.4089	.4539	51.6505	94.3006
26.00	126.0901	144.2499	143.7416	121.2653
27.00	94.8434	54.5711	8.7573	-23.6687
28.00	-43.0278	-72.3704	-106.9864	-128.4534
29.00	-139.4125	-116.7301	-96.9288	-95.2350
30.00	-38.0551	6.0735	30.2019	63.0890
31.00	101.5550	108.6572	108.5017	109.2677
32.00	61.7640	11.9889	-36.5606	-49.1314
33.00	-79.2860	-105.2033	-121.6721	-108.3689
34.00	-99.6052	-70.7341	-37.0806	-16.2107
35.00	-6.7230	20.3019	62.4624	50.3412
36.00	62.7974	109.9801	115.9141	91.5815
37.00	56.1245	5.3421	6.6076	-21.2111
38.00	-32.9613	-48.4768	-75.4116	-43.7010
39.00	-60.0122	-96.9595	-59.3303	-61.7201
40.00	-43.3094	14.0533	25.2252	33.8858
41.00	62.2739	56.8181	30.2344	44.3789
42.00	61.3327	53.6077	36.6368	

Table 36. Refined molecular parameters for N-deuterated Methyldiazene.^a

Structural feature	1		2		3		4		5		6		7	
	r_a, ℓ_a	2σ	r_a, ℓ_a	2σ	r_a, ℓ_a	2σ	r_a, ℓ_a	2σ	r_a, ℓ_a	2σ	r_a, ℓ_a	2σ	r_a, ℓ_a	2σ
N=N	1.2455	0.0018	1.2453	0.0023	1.2453	0.0024	1.2453	0.0024	1.2453	0.0023	1.2449	0.0019	1.2449	0.0019
N-C	1.4695	0.0029	1.4705	0.0045	1.4704	0.0045	1.4705	0.0045	1.4705	0.0045	1.4687	0.0029	1.4686	0.0029
H-C	1.1009	0.0060	1.1027	0.0093	1.1023	0.0093	1.1031	0.0091	1.1026	0.0093	1.0972	0.0068	1.0967	0.0067
N-D	(1.004)		(1.004)		(1.004)		(1.004)		(1.004)		0.9888	0.0177	0.9870	0.0173
\angle N=N-C	112.20	0.361	112.00	0.651	111.98	0.668	112.01	0.668	111.99	0.656	112.33	0.372	112.30	0.374
\angle N=N-D	110.44	3.920	110.30	7.236	109.62	7.227	109.89	7.177	109.12	8.956	110.27	5.056	109.22	5.028
\angle N-C-H	(109.47)		(109.47)		(109.47)		(109.47)		108.56	3.704	108.45	1.946	108.10	2.049
CH ₃ rotation	(0)		(15)		(30)		Free rotation ^c		(15)		(0)		(15)	
ℓ (N=N)	0.0298	0.0026	0.0302	0.0035	0.0305	0.0035	0.0305	0.0035	0.0304	0.0036	0.0316	0.0029	0.0320	0.0029
ℓ (N-C)	0.0469	0.0032	0.0485	0.0046	0.0488	0.0047	0.0489	0.0046	0.0487	0.0047	0.0488	0.0034	0.0492	0.0034
ℓ (C-H)	0.0551	0.0051	0.0537	0.0073	0.0537	0.0073	0.0529	0.0072	0.0537	0.0073	0.0511	0.0055	0.0508	0.0052
ℓ (N-D)	(0.0573)		(0.0573)		(0.0573)		(0.0573)		(0.0573)		(0.0573)		(0.0573)	
ℓ (N ₂ C ₄)	0.0537	0.0044	0.0558	0.0067	0.0557	0.0067	0.0557	0.0067	0.0558	0.0067	0.0554	0.0046	0.0556	0.0046
Ratio ^b (C)	0.16168		0.16168		0.16508		0.16450		0.16149				0.15671	
Ratio (all)	0.16849										0.17080		0.16982	

^a Distances (r_a) and root-mean-square amplitudes (ℓ_a) in angstroms, angles in degrees. The 2σ values include estimates of systematic as well as random error. Parenthesized values not refined.

^b Ratio = $[\sum \omega_i \Delta_i^2 / \sum \omega_i I_i^2(\text{obs})]^{1/2}$ where $\Delta_i = I_i(\text{obs}) - I_i(\text{calc.})$. Ratio (C) pertains to composite curve ($I(\text{obs})$) refinements, Ratio (all) to refinements on all eight curves of Figure 9.

^c Nine "one-third" hydrogen located on the circle of rotation at equal intervals approximates free rotation.

Table 37. Final structural results for N-deuterated Methyldiazene.^a

Distance or angle	r_a	2σ	ℓ_a	2σ
N=N	1.2449	0.0019	0.0316	0.0029
N-C	1.4687	0.0029	0.0488	0.0034
C-H	1.0972	0.0068	0.0511	0.0055
N-D	0.9888	0.0177	(0.0573)	
N ₂ C ₄	2.2576	0.0048	0.0554	0.0046
N ₃ D ₁	1.8386	0.0551	(0.0900)	
N ₃ H ₅	2.0932	0.0257	(0.1000)	
N ₂ H ₆	2.9746	0.0227	(0.1200)	
N ₂ H ₇	2.9746	0.0227	(0.1200)	
N ₂ H ₅	2.2918	0.0376	(0.1200)	
C ₄ D ₁	3.1353	0.0362	(0.1200)	
H ₆ H ₇	1.8027	0.0230	(0.1200)	
∠C-N=N	112.33	0.372		
∠N=N-D	110.27	5.056		
∠H-C-N	108.45	1.946		

^a Distances (r_a) and rms amplitudes (ℓ_a) in angstroms, angles in degrees.
 Parenthesized values not refined. The 2σ values include estimates of
 systematic as well as random error.

Table 38. Correlation matrix for N-deuterated Methyldiazene.^a

ℓ N=N	ℓ N=C	ℓ N ₂ C ₄	ℓ C-H	r_{NN}	r_{NC}	$r_{N_2C_4}$	r_{DN_3}	r_{CH}	r_{ND}	$r_{N_3H_5}$	$r_{N_2H_6}$	$r_{N_2H_7}$	$r_{N_2H_5}$	r_{DC_4}	r_{H-H}	$\angle NNC$	$\angle NND$	$\angle HCN$	$\angle HCH$
1.00	.45	.41	-.20	-.25	-.21	-.01	-.21	-.60	-.47	-.32	-.32	-.32	-.20	-.30	-.11	.17	-.09	-.19	.19
	1.00	.31	-.19	-.15	-.26	-.06	-.18	-.31	-.37	-.25	-.25	-.25	-.19	-.26	.01	.07	-.09	-.18	.18
		1.00	-.21	-.12	-.04	-.04	-.16	-.28	-.28	-.17	-.18	-.18	-.13	-.22	-.03	.02	-.09	-.12	.12
			1.00	.51	-.02	.02	.07	.43	.59	.19	.21	.21	.11	.17	.11	-.10	-.09	.11	-.11
				1.00	-.09	.01	.02	.55	.39	.18	.21	.21	.07	.09	.19	-.19	-.10	.08	-.08
					1.00	-.01	.11	.15	.08	.08	.00	.00	-.05	.14	.11	-.43	.09	-.04	.04
						1.00	.16	.01	-.01	.17	.32	.32	.34	.23	-.15	.87	.16	.17	-.17
							1.00	.08	.13	.65	.64	.64	.65	.97	-.56	.09	.10	.65	-.65
								1.00	.64	.27	.29	.29	.09	.20	.42	-.20	-.10	.07	-.07
									1.00	.27	.28	.28	.15	.34	.18	-.13	-.13	.14	-.14
										1.00	.98	.98	.96	.68	-.76	.07	.58	.97	-.97
											1.00	1.00	.98	.68	-.73	.22	.57	.96	-.96
												1.00	.98	.68	-.73	.22	.57	.96	-.96
													1.00	.66	-.85	.30	.61	.99	-.99
														1.00	-.50	.11	.89	.65	-.65
															1.00	-.23	-.61	-.88	.88
																1.00	.12	.15	-.15
																	1.00	.62	-.62
																		1.00	1.00
																			1.00

^a Distances and amplitudes in angstroms, angles in degrees.

Table 39. Rotational constant calculations for Methyldiazene (N-d).^a

Method	A	error	B	error	C	error
Obs. Microwave)	1.954	0.026	0.34205	0.00001	0.30818	0.00001
Obs. (I R)	1.981	0.010				
E. D. calc. r_a^b	1.982	0.014	0.3424	0.0012	0.3096	0.0012
E. D. calc. $r_a^{c'}$	1.980	0.015	0.3416	0.001	0.3089	0.001
E. D. calc. r_o^d	1.980	0.010	0.343	0.001	0.309	0.001
E. D. calc. $r_o^{e'}$	1.986	0.010	0.3416	0.001	0.3088	0.001

^aRotational constants, A, B, C in cm^{-1} .

^b r_a values of least squares Model #6.

^c r_a of Model #6 with an increase of $0.12 \sigma_T$ made to all geometric parameters, where $\sigma_T = 2\sigma$.

^dassumes $r_a - r_o$ and $\theta_a - \theta_o$ values applied to model L. S. #5.

^e r_o values with an increase of $0.014 \sigma_T$, where σ_T are the 2σ values of L. S. #5.

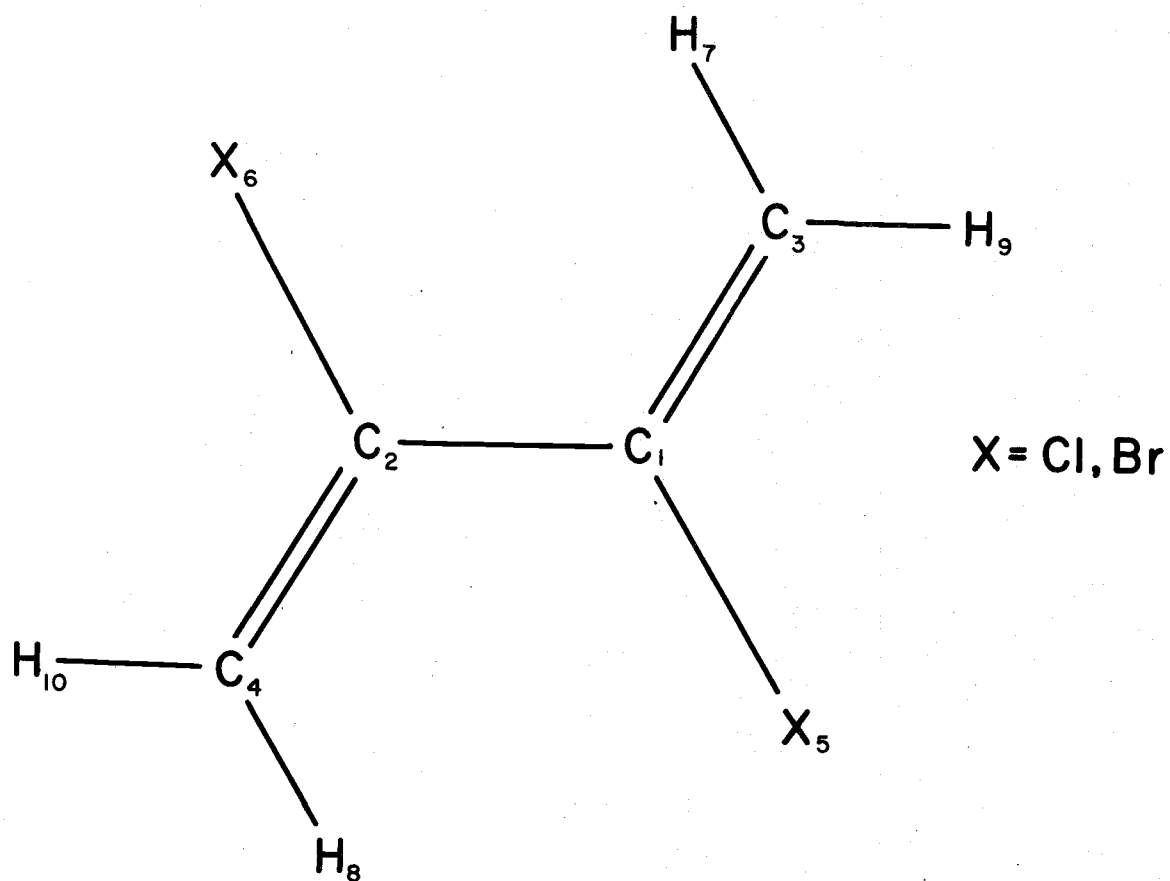


Figure 1. Configuration and atom numbering of 2,3-dichlorobutadiene and 2,3-dibromobutadiene.

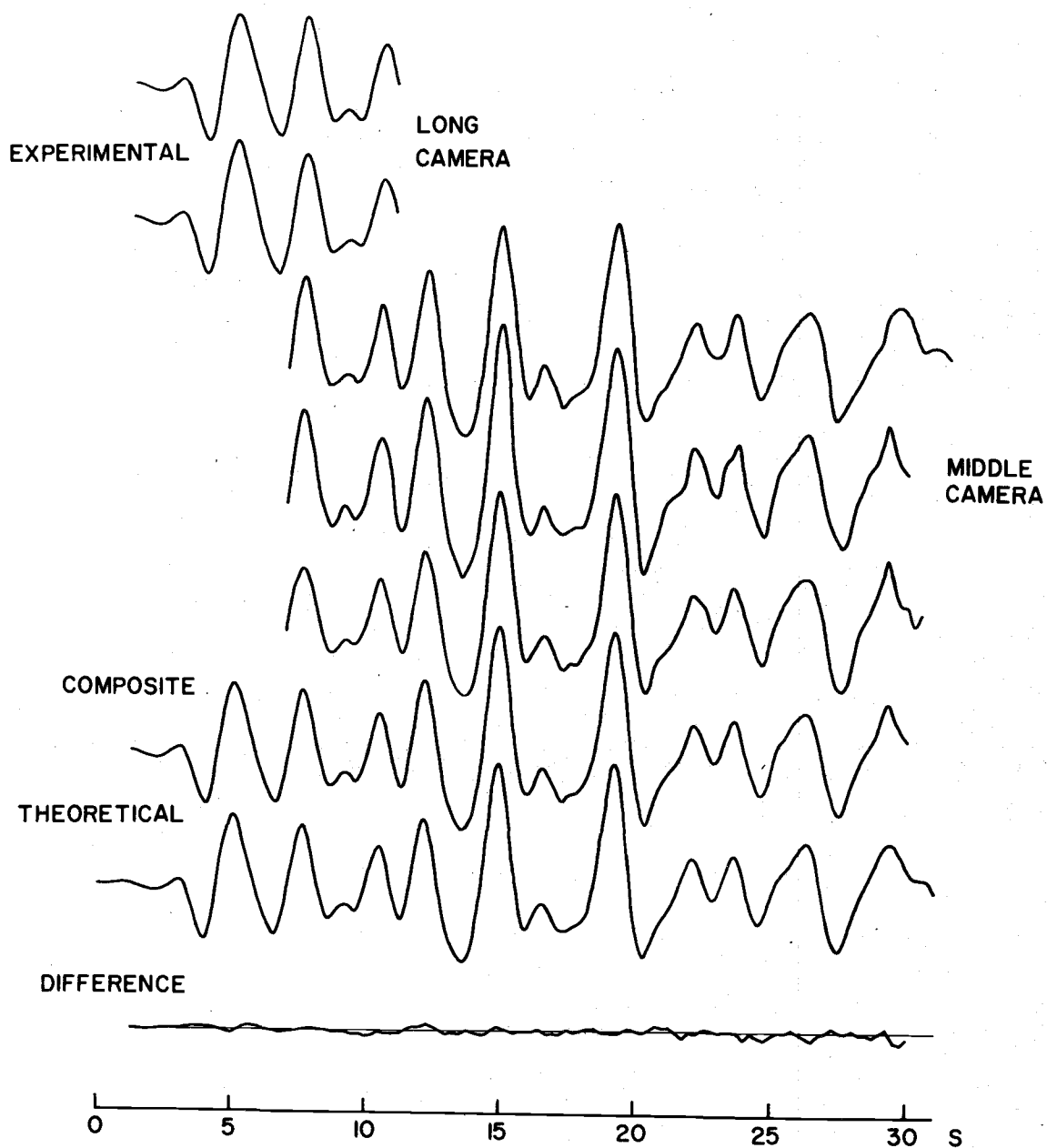


Figure 2. Intensity curves for 2,3-dichlorobutadiene. The theoretical curve corresponds to the parameter values of Table 9. The difference is the experimental minus the theoretical.

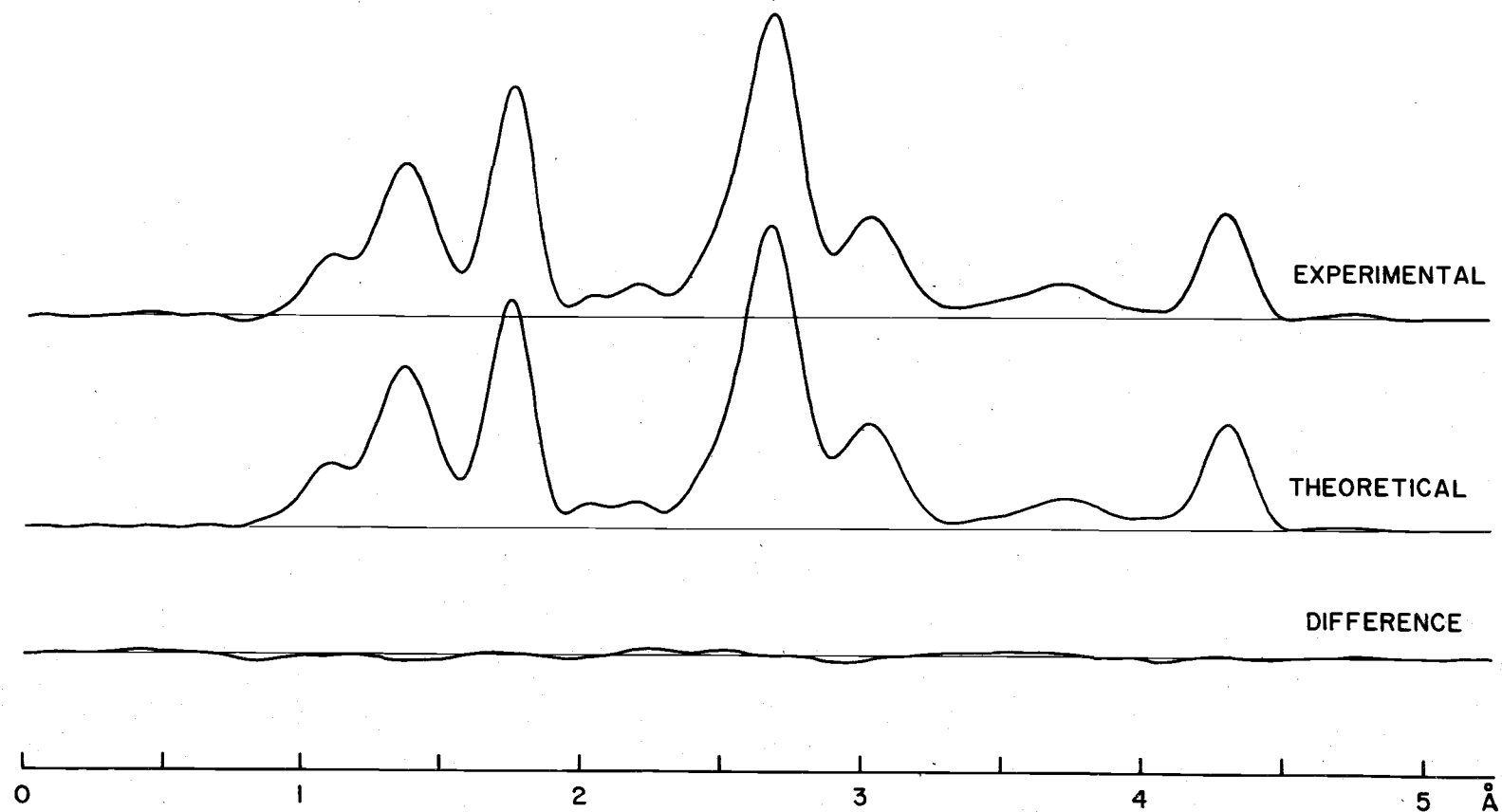


Figure 3. Radial distribution curves for 2,3-dichlorobutadiene. The curves were calculated from the composite and theoretical curves of Figure 2 using the theoretical curve data in the range $0 \leq s \leq 1.25$ for the composite curve. $B = 0.0018$.

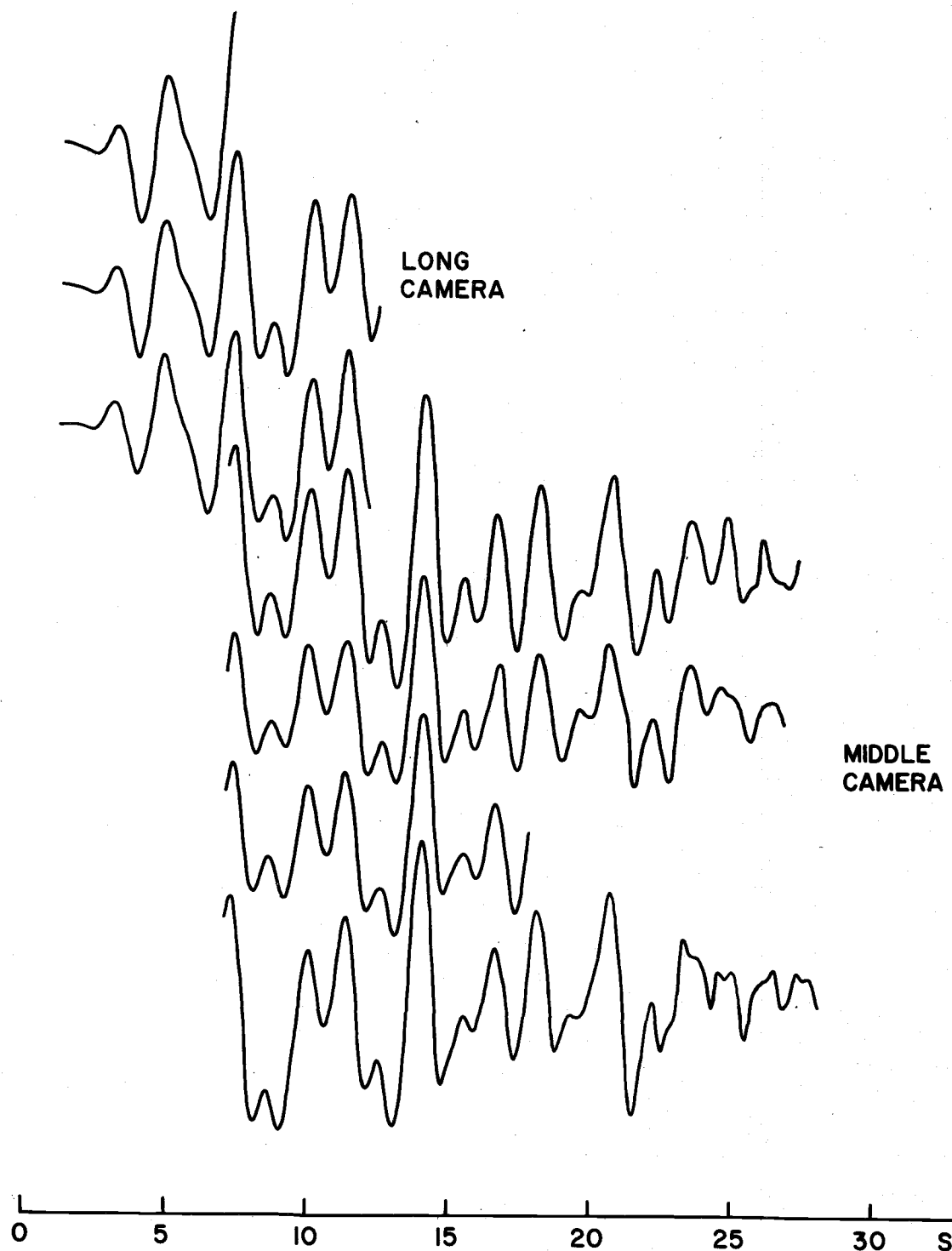


Figure 4. Experimental intensity curves for 2,3-dibromobutadiene.

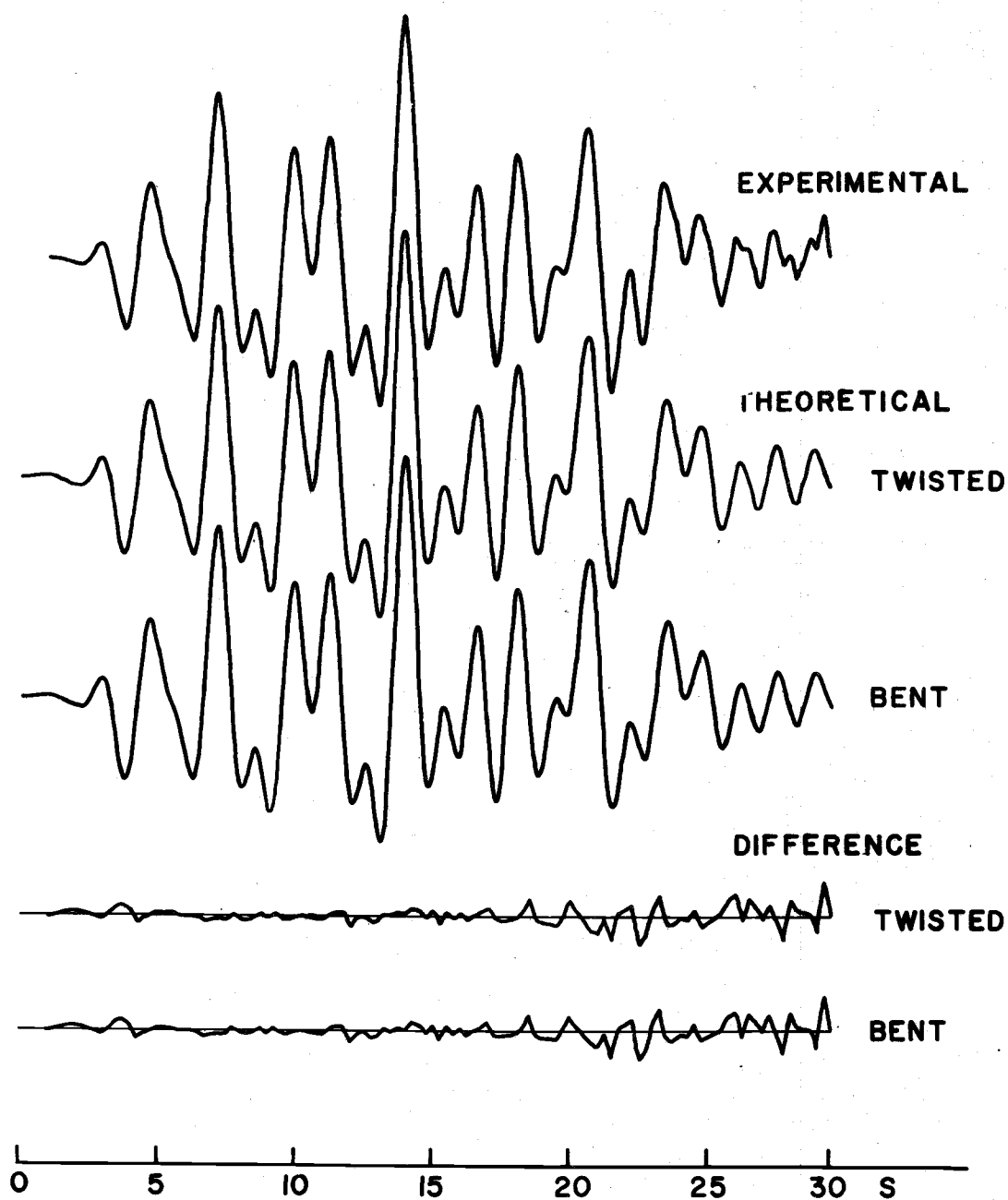


Figure 5. Intensity curves for 2,3-dibromobutadiene. The experimental curve is a composite from the long and middle camera data. The theoretical curves correspond to the models of Table 21. The difference curves are the experimental minus the theoretical.

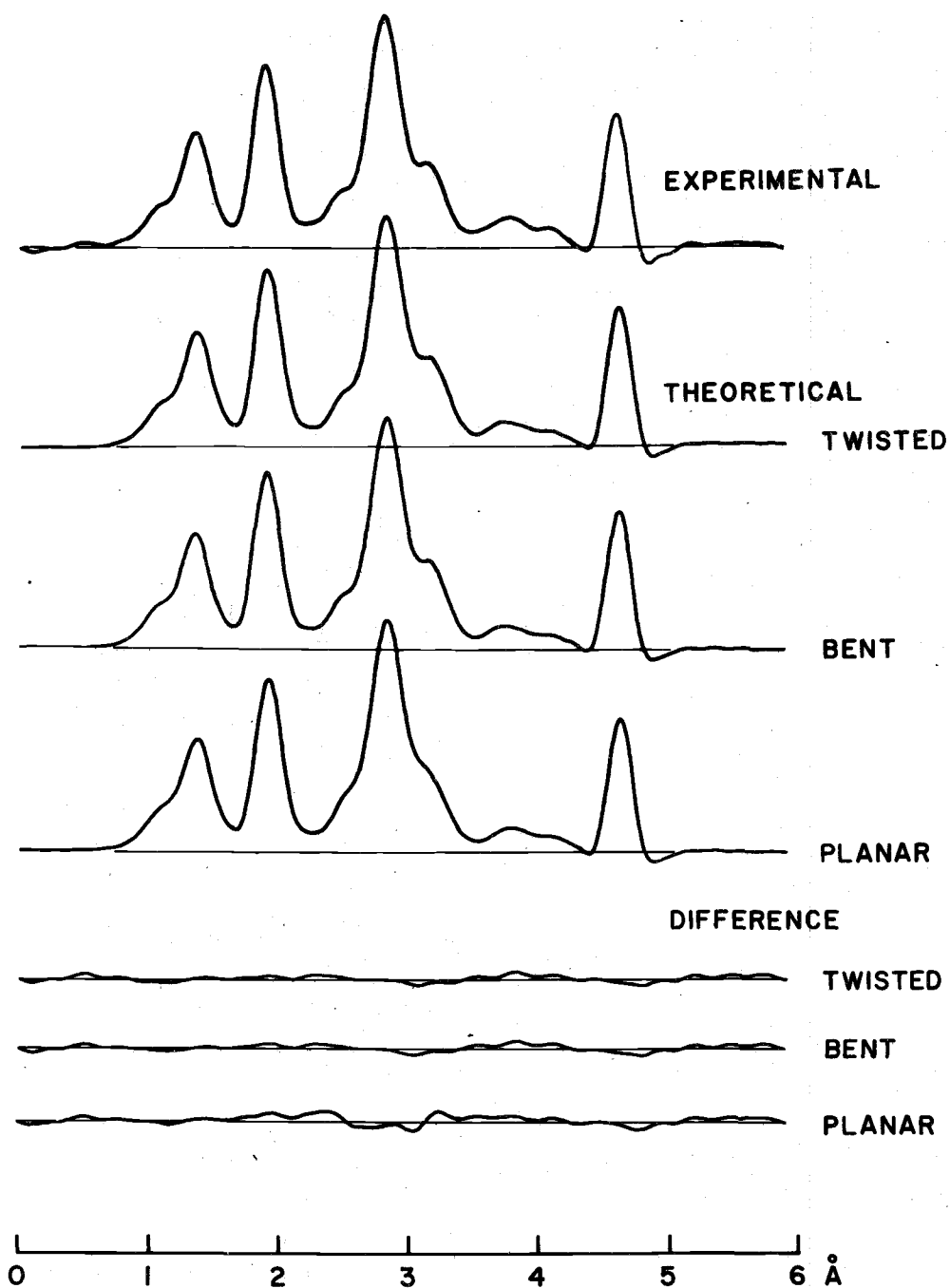


Figure 6. Radial distribution curves for 2,3-dibromobutadiene. The experimental curve was calculated from the composite curve of Figure 5 using the theoretical curve data in the range $0 < s \leq 1.50$. The theoretical curves were calculated from the intensity curves corresponding to models 1, 3, and 5 of Table 20. $B = 0.002$.

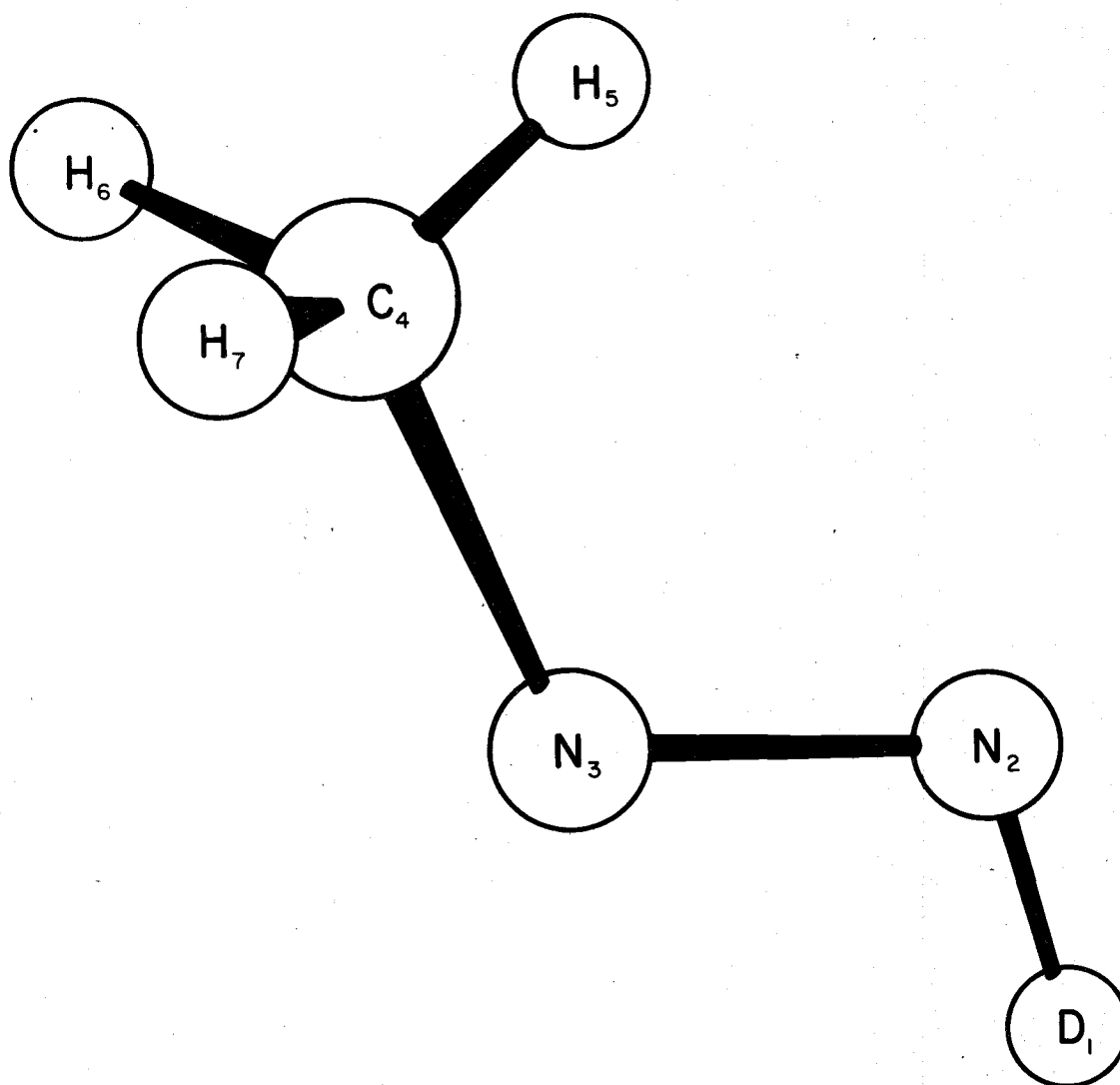


Figure 7. Configuration and atom numbering of methyldiazene.

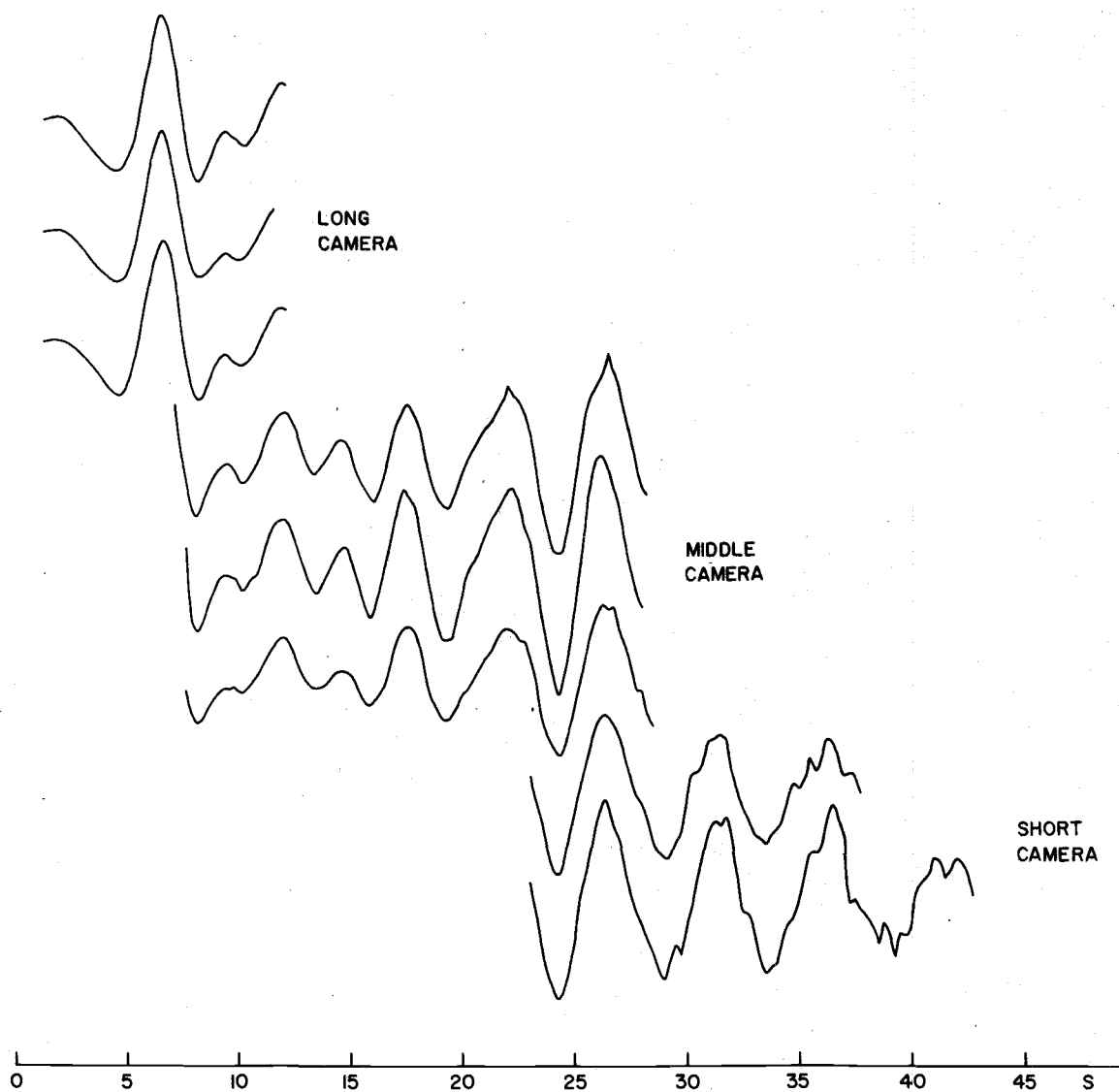


Figure 8. Experimental intensity curves for methyldiazenes.

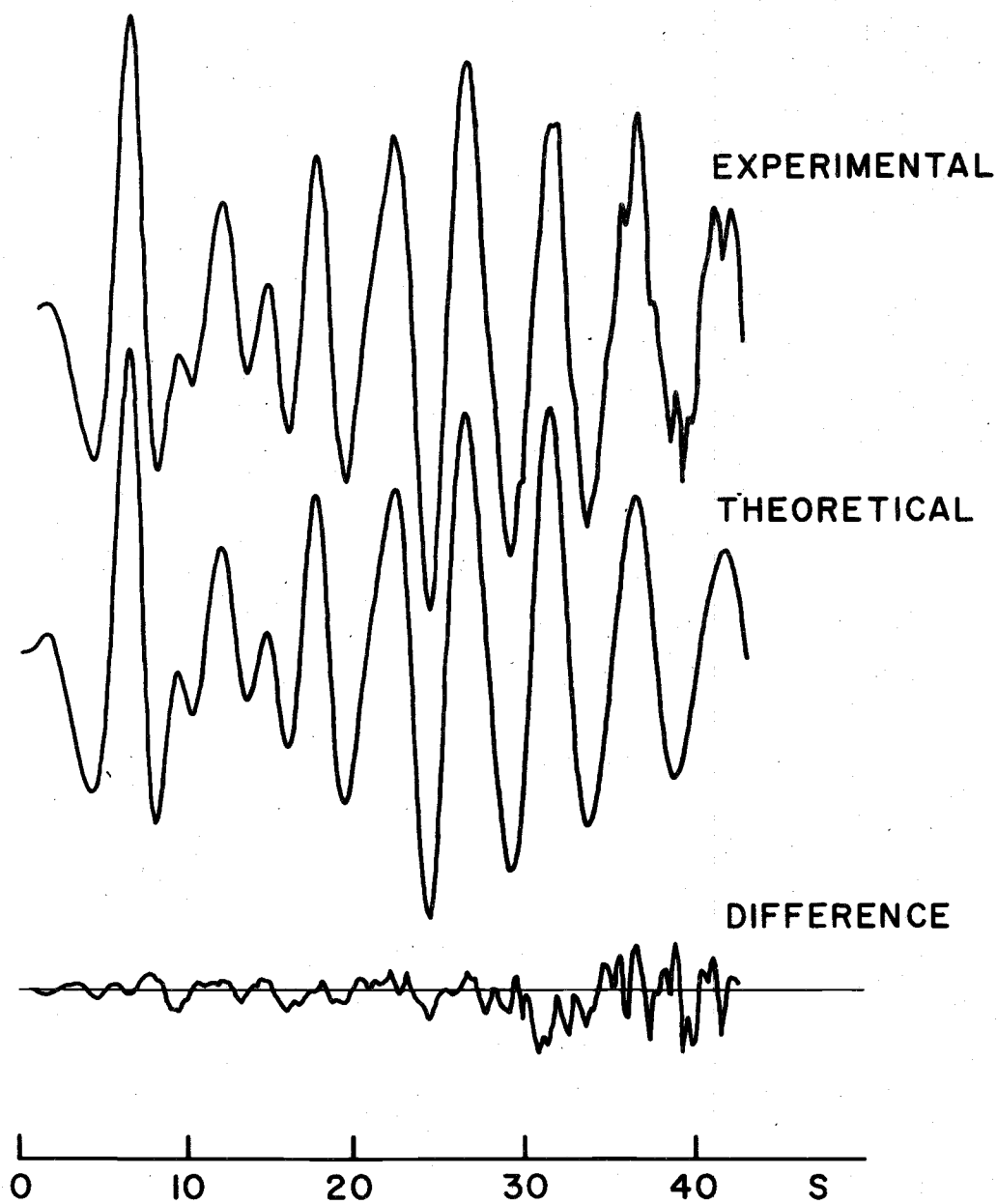


Figure 9. Intensity curves for methyldiazene. The experimental curve is a composite from the three camera distances, long, middle and short. The theoretical curve corresponds to the parameter values of Table 37. The difference curve is the experimental minus the theoretical.

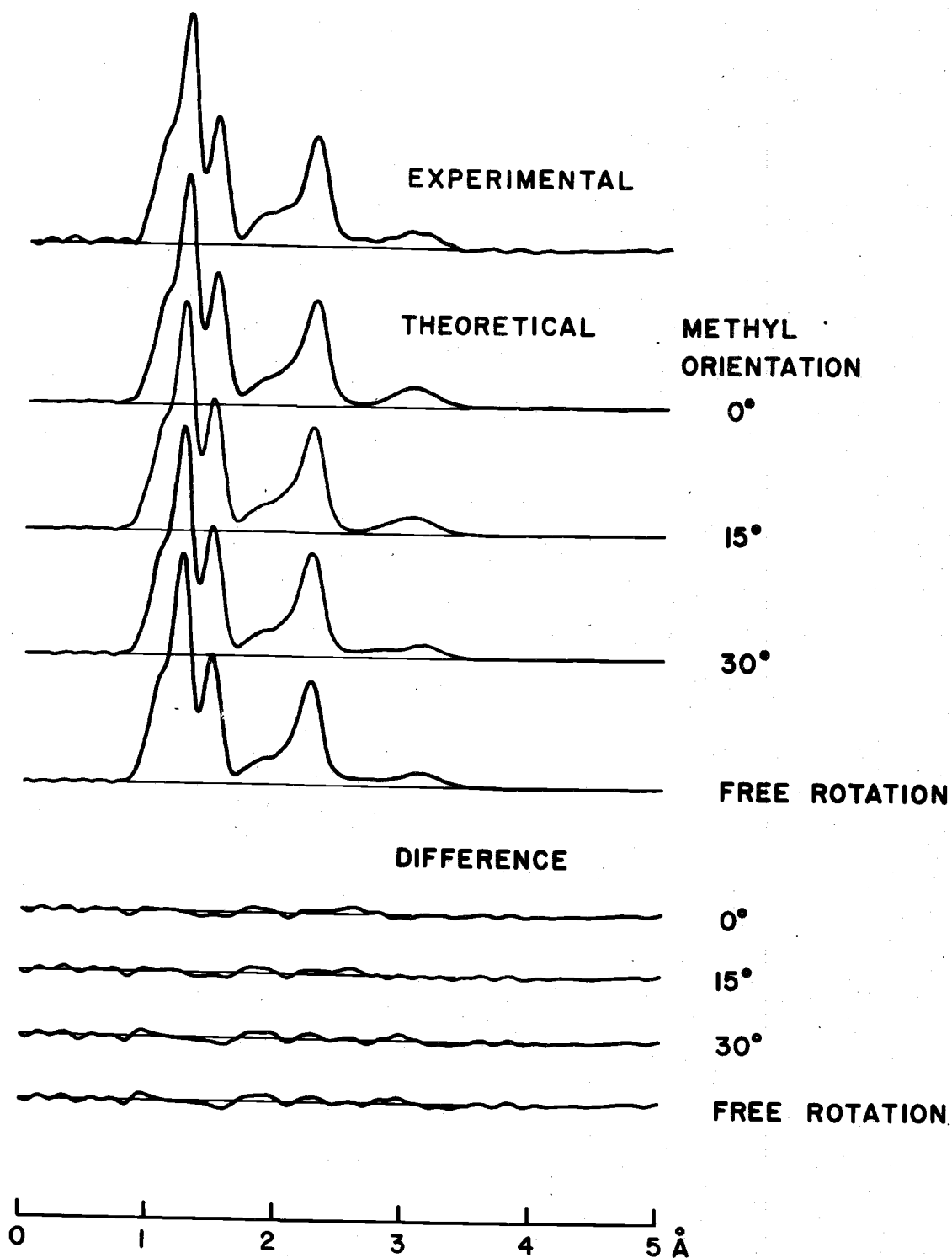


Figure 10. Radial distribution curves for methyldiazene. The experimental curve was calculated from the composite of Figure 9 using the theoretical curve data in the range $0 \leq s < 2.00$ for the composite curve. The theoretical curves were calculated from the intensity curves corresponding to models 6, 7, 3, and 4 of Table 36. $B = 0.0013$.

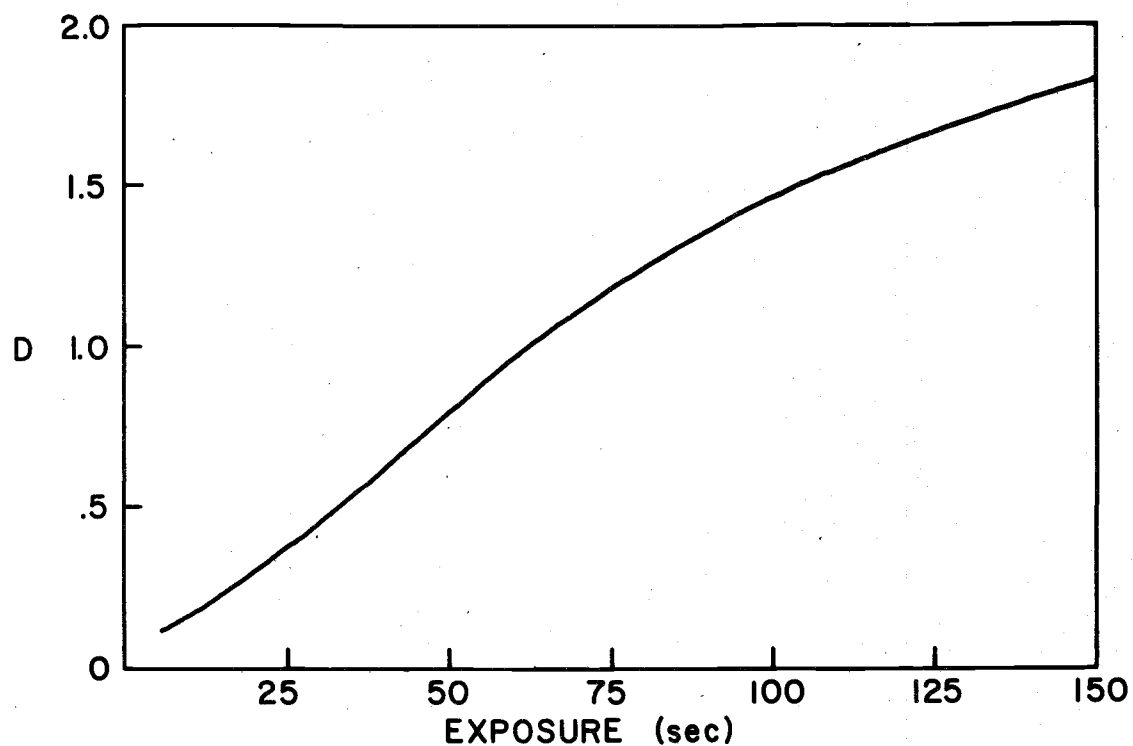


Figure 11. Typical observed density (D) vs. exposure plot.

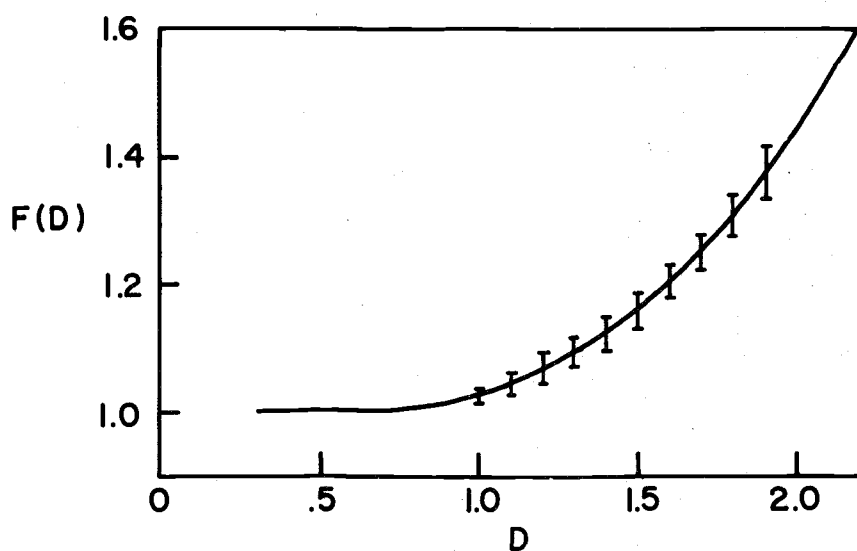


Figure 12. Average blackness calibration factor ($F(D)$), vs. density. The blackness corrected density $D_{\text{blackness}}$ is equal to D times $F(D)$.

BIBLIOGRAPHY

- M. N. Ackermann, J. L. Ellenson, and D. H. Robinson, *J. Am. Chem. Soc.*, 90, 7173 (1968).
- A. Almennigen, I. M. Anfinson, and A. Haaland, *Acta Chem. Scand.*, 24, 1230 (1970).
- A. Almennigen, O. Bastiansen, and T. Munthe-Kass, *Acta Chem. Scand.*, 10, 261 (1956).
- A. Almennigen, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand.*, 12, 1221 (1958).
- A. Almennigen et al., *Chem. Phys. Lett.*, 1, 569 (1968).
- E. Amble and B. P. Dailey, *J. Chem. Phys.*, 18, 1442 (1950).
- C. F. Aten, L. Hedberg, and K. Hedberg, *J. Am. Chem. Soc.*, 90, 2463 (1968).
- O. Bastiansen and M. Traetteberg, *Tetrahedron*, 17, 147 (1963).
- L. S. Bartell, *J. Chem. Phys.*, 23, 1219 (1955).
- L. S. Bartell, *Tetrahedron*, 17, 177 (1962).
- L. S. Bartell and L. O. Brockway, *J. Appl. Phys.*, 24, 656 (1953).
- L. S. Bartell, E. J. Jacob, and H. B. Thompson, private communication to Dr. Kenneth Hedberg, 1970.
- G. J. Berchel and W. H. Carothers, *J. Am. Chem. Soc.*, 55, 2004 (1933).
- L. O. Brockway, *Rev. Mod. Phys.*, 8, 231 (1936).
- C. J. Brown, *Acta Cryst.*, 21, 146 (1966).
- M. Brown, *Trans. Faraday Soc.*, 55, 694 (1959).

- C. H. Chang, R. F. Porter, and S. H. Bauer. Collected Abstracts, Eighth International Congress of Crystallography, Stone Brook, New York 1969.
- D. Coffey, Jr., C. O. Britt, and J. E. Boggs, J. Chem. Phys., 49, 491 (1968).
- C. C. Costain and B. P. Stoicheff, J. Chem. Phys., 30, 777 (1959).
- H. L. Cox, Jr. and R. A. Bonham, J. Chem. Phys., 47, 2599 (1967).
- M. I. Davis and H. P. Hansen, J. Phys. Chem., 69, 4091 (1965).
- M. I. Davis, H. A. Kappler, and D. J. Cowan, J. Phys. Chem., 68, 2005 (1964).
- M. J. S. Dewar and H. N. Schmeising, Tetrahedron, 5, 166 (1959).
- M. J. S. Dewar and H. N. Schmeising, Tetrahedron, 11, 96 (1960).
- T. Fukuyama and K. Kuchitsu, J. Mol. Structure, 5, 131 (1970).
- R. Glauber and V. Schomaker, Phys. Rev., 89, 667 (1953).
- G. Gundersen and K. Hedberg, J. Chem. Phys., 51, 2500 (1969).
- W. Haugen and M. Traetteberg, Acta Chem. Scand., 20, 1726 (1966).
- W. Haugen and M. Traetteberg, Selected Topics in Structure Chemistry, Universitetsforlaget, Oslo, 1967.
- K. Hedberg and M. Iwasaki, J. Chem. Phys., 36, 589 (1962).
- K. Hedberg and M. Iwasaki, Acta Cryst., 17, 529 (1964).
- D. R. Herschback and V. W. Laurie, J. Chem. Phys., 37, 1668 (1962).
- G. Herzberg and B. P. Stoicheff, Nature 175, 79 (1955).
- R. T. Hobgood, Jr. and J. H. Goldstein, J. Mol. Spectry., 12, 76 (1964).
- M. Iwasaki, F. N. Fritsch, and K. Hedberg, Acta Cryst., 17, 533 (1964).

- J. Karle and I. L. Karle, *J. Chem. Phys.*, 18, 957 (1950).
- K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Structure*, 1, 463 (1968).
- D. R. Lide, Jr., *Tetrahedron*, 17, 125 (1962).
- B. M. Mikhailov, *Tetrahedron*, 21, 1277 (1965).
- Y. Morino, K. Kuchitsu, and T. Oka, *J. Chem. Phys.*, 36, 1108 (1962).
- Y. Morino, J. Nakamura, and P. W. Moore, *J. Chem. Phys.*, 36, 1050 (1962).
- N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions*, 2nd ed., Oxford University Press, London, 1949.
- R. S. Mulliken, *Tetrahedron*, 5, 253 (1959).
- R. S. Mulliken, *Tetrahedron*, 6, 68 (1959).
- T. Nishikawa, *J. Phys. Soc. Japan*, 12, 668 (1957).
- L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, 1960.
- K. Rosengen and G. C. Pimentel, *J. Chem. Phys.*, 43, 507 (1965).
- V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.*, 63, 37 (1941).
- W. Steinmetz, *J. Chem. Phys.*, 52, 2788 (1970).
- B. P. Stoicheff, *Tetrahedron*, 17, 135 (1962).
- G. J. Szasz and N. Sheppard, *Trans. Faraday Soc.*, 49, 358 (1953).
- M. Traetteberg, Ph. D. Thesis. Trondheim, University of Trondheim, 1969.
- M. Traetteberg, G. Hagen and J. Cyvin, *Acta Chem. Scand.*, 23, 74 (1969).
- A. Trombetti, *Can. J. Phys.*, 46, 1005 (1968).
- J. Waser and V. Schomaker, *Rev. Mod. Phys.*, 25, 671 (1953).

APPENDIX

APPENDIX A

CALIBRATION OF PHOTOGRAPHIC DENSITY

Since electron diffraction patterns are collected on photographic plates, it is essential to know the precise response characteristics of the emulsion to exposure by high energy electrons. The emulsion response must be accurately known in order to obtain data for more reliable and more detailed structure determinations. It is necessary to have a simple procedure for routine calibration of the emulsion response to allow for fluctuations in photographic materials and other experimental parameters.

A calibration method has been devised by Karle and Karle (1950), and a related method devised by Bartell and Brockway (1953), for measuring the variation of photographic density as a function of the exposure of the incident electrons which relies upon the assumption that two diffraction plates exposed under identical conditions except for exposure time have radial intensity distributions of exactly the same shape. The Oregon State calibration does not depend upon any such assumption, but studies the deviation from the linearity of the optical density versus the exposure time. The main advantages of such a method are that it gives a positive calibration with no assumptions about the exposure conditions, easily recognized errors,

and an experiment that can be easily repeated to check the calibration.

The calibration procedure was as follows: Two metal plates were positioned immediately above the photographic plate inside the diffraction apparatus such that a small slit (1 cm wide) existed to allow only a small amount of the scattered electrons to expose the photographic plate. The photographic plates were moved beneath the slit about 1/2 inch after each exposure. The exposed plates thus showed a series of dark bands (one cm wide) about one-half inch apart on the plate. Air, the scattering material, was bled into the electron diffraction apparatus at a constant rate using a Nupro needle valve such that a constant ambient pressure of 3.00×10^{-4} Torr was maintained inside the apparatus during exposure of the plates. Since the beam intensity (beam current) was continually monitored during exposure of the plates, the only experimental variable was the exposure time. Successive exposures were taken for 5, 10, 20, 30, 40, 50, 60, 75, 90, 105, 120, 140, 160, 180, 200, 220 and 240 seconds with the nozzle set at the middle camera distance.

The plates were scanned along lines normal to the exposed bands with the Joyce-Loebl microdensitometer, and the data were converted from counts into density units using the data reduction program written by Lise Hedberg. The average density of each exposed band was computed, and the densities were plotted versus

their corresponding exposure times. Since the exposure is proportional to the product of exposure time and the beam intensity, an exposure time multiplied by a factor that normalized the beam intensity was a convenient ordinate. A typical density versus exposure (in seconds) plot is shown in Figure 11.

Figure 11 shows that the optical density was a linear function of the exposure in the range $D = 0.3$ to about 0.7 . The blackness correction or calibration, $F(D)$, was computed for the density range 0.7 to 2.5 by calculation the ratio of $D(\text{obs})$ to the corresponding extrapolated linear density. Blackness calibrations were determined for eight density versus exposure curves. The average calibration was determined and plotted versus the observed density, Figure 12. The separate calibrations differed from one another by about two percent. It was found that the calibration could be approximated accurately by $F(D) = a + b(D) + c(D^2)$ for densities greater than 0.6 . This calibration was compared with an independent calibration computed by Mr. Michael Gilbert using the method devised by Karle and Karle. Since the two calibrations agreed to within the projected errors of each determination (about two percent), the average of the two independent calibrations was used for the final blackness correction. The final values of a , b , and c were $a = 1.0976178$, $b = -0.29279183$, and $c = 0.22856468$. No calibration for densities less than 0.3 was determined since data in that density range is

not used.

The blackness correction was added to the data reduction computer program. The program converts each observed density that is greater than 0.6 to a blackness corrected density by multiplying them by blackness factor $F(D)$.

$$D_{\text{blackness}} = \begin{cases} D(\text{obs}) \cdot F(D(\text{obs})) & D \geq 0.6 \\ D(\text{obs}) & D < 0.6 \end{cases} \quad (15)$$