AN INVESTIGATION OF THE DIPOLE
MOMENTS OF SEVERAL SERIES OF
UNSATURATED COMPOUNDS
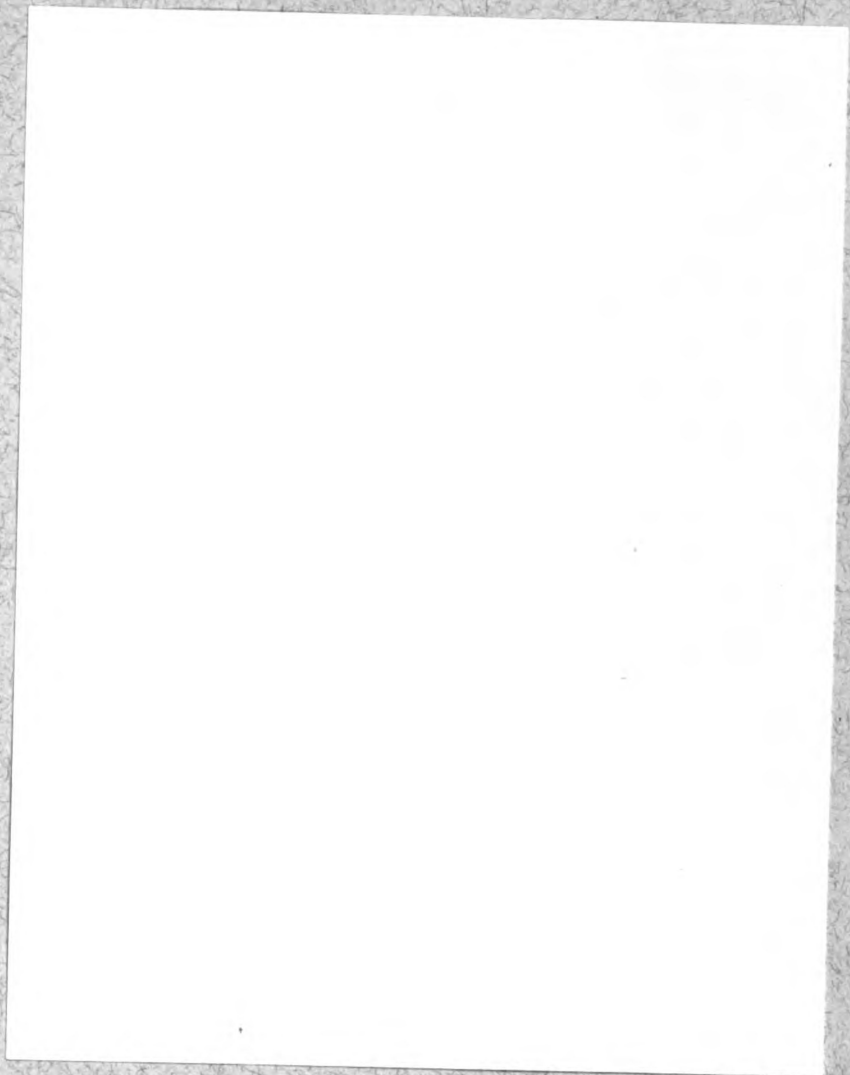
Thesis for the Degree of M. S.
MICHIGAN STATE COLLEGE
Morton B. Panish
1952

AN INVESTIGATION OF THE DIPOLE MOMENTS OF SEVERAL
SERIES OF UNSATURATED COMPOUNDS

By

Morton B. Panish

A THESIS

Submitted to the School of Graduate Studies of Michigan
State College of Agriculture and Applied Science
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

1952

AN INVESTIGATION OF THE DIPOLE MOMENTS OF SEVERAL SERIES OF UNSATURATED COMPOUNDS

AN ABSTRACT

Despite the great theoretical importance of the electric dipole moment in the interpretation of the properties of many molecules, very little work of this kind has been done with aliphatic compounds containing triple bonds. The purpose of the work described here is to measure this property in several series of substituted alkynes and related alkenes, and to present a theoretical interpretation of the results of these measurements. The series measured included some of the allyl and propargyl type halides, ethers, and alcohols, and a few other closely related compounds.

A brief outline of the procedure which was used in this work is as follows:

1) Preparation and purification of the compounds.

2) Determination of the refractive indices of the pure liquids at 25°C with an Abbé refractometer.

3) Preparation of a series of dilute solutions of the compound in benzene and the determination of the densities of these solutions.

4) Measurement of the dielectric constant of the solutions by the heterodyne-beat method.[1]

5) Calculation of the dipole moments of the compounds by the method suggested by Halverstadt and Kumler.[2]

The dipole moments of the propargyl and allyl halides were found to be appreciably lower than the moments of the corresponding saturated compounds.[3] It was also found that there is an appreciable increase in the dipole moments along the series

$$HC \equiv C - CH_2Br \qquad HC \equiv C - \underset{H}{\overset{CH_3}{C}} Br \qquad HC \equiv C - \underset{CH_3}{\overset{CH_3}{C}} Br,$$
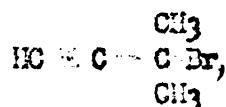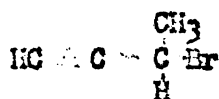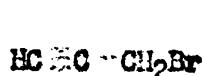
which is greater than can be accounted for by polarization of the
CH_3- groups by the C-Br bond.

In consideration of this evidence the following hyperconjugation
structure was proposed as one of the contributing structures for this
type of compound:

$$HC \equiv C - \overset{H}{\underset{H}{C}} - X \quad \longleftrightarrow \quad \overset{\ominus}{HC} \equiv C \equiv \overset{H}{\underset{H_{(+)}}{C}} - X$$
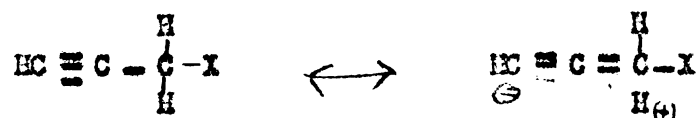
A similar structure was proposed for the allyl compounds. This type of
structure has been mentioned previously for methyl acetylene.[4]

The dipole moments found for the propargyl type halides might also
be interpreted as being partially due to the greater electronegativity
of the carbon atoms in the acetylenic group. However the evidence
presented is insufficient to permit the drawing of definite conclusions
regarding this.

An attempt was made to calculate the dipole moments of propargyl
ethyl ether and the alcohols corresponding to the bromides mentioned
above by assuming hyperconjugation structures similar to that already
proposed , and by also assuming that the magnitude of the contribution
of this structure is the same as the magnitude of the moment of
methylacetylene. The results of these calculations were inconclusive
in the case of the ether, but were in good agreement with the moments
determined for the alcohols.

REFERENCES

1) J. Chien, J. Chem. Educ., **24**, 494(1947).

2) L. F. Halverstadt and W. D. Kumler, J. Am. Chem. Soc., **64** 2988(1942).

3) Appendix on Dipole Moments, Trans. Faraday Soc., **39**(1943).

4) Y. K. Syrkin and M. E. Dyatkina, The Structure of Molecules, Inter-science Publishers Inc., New York, N.Y., 1950, page 212.

ACKNOWLEDGMENT

****
****
*****
****
**
*

TABLE OF CONTENTS

TABLES AND GRAPHS

GRAPHS

Compound	Graph (ϵ Vs X_2)	Graph (1/d Vs X_2)
Allyl Amine	III	VII
Allyl Bromide	II	XII
Allyl Cyanide	II	XI
Allyl Ethyl Ether	III	X
Allyl Iodide	II	XI
Benzyl Amine	IV	VIII
2 Bromo-3-butyne	III	VII
3 Butyn-1-ol	VI	XII
3 Butyn-2-ol	V	VII
1 Chloro-4-octyne	IV	VIII
1 Diethylamino-2-propyne	IV	VIII
2 Methyl-2-bromo-3-butyne	III	X
2 Methyl-3-butyn-2-ol	VI	X
3 Octyn-1-ol	IV	VIII
Propargyl Alcohol	V	XI
Propargyl Bromide	I	IX
Propargyl Ethyl Ether	I	IX
Propargyl Iodide	I	IX

INTRODUCTION

I INTRODUCTION

Despite the great theoretical importance of the electric dipole moment and the large number of measurements which have been made, very little work has been done with aliphatic compounds containing triple bonds. The purpose of this work is to measure this property in a series of substituted alkynes and the related alkenes, and to present a theoretical interpretation of the results of these measurements.

THEORY

II THEORY[1-5]

For this discussion we may consider a molecule as a system of atoms
in which the electrons act as if they were located in certain definite
positions. If the centers of action of the positive and negative charges
do not coincide the molecule is said to be polar and it tends to orient
itself in an electric field as would any object containing separated
electric charges. The dipole moment is a quantitative measure of the
polarity of a molecule of a substance and is defined by

$$\mu = Er,$$

where μ represents the magnitude of the dipole moment, E the total
magnitude of one of the charges (either positive or negative) and r
represents the distance between the centers of action of the charges.
This definition assumes that the molecule is electrically neutral.
Since this discussion is concerned only with neutral molecules and not
with ions the assumption is valid.

It is obvious from the definition that the dipole moment is a vector
quantity possessing all the usual attributes and being subject to all
the usual manipulations which may be applied to such a quantity. Thus
the total dipole moment of any molecule may be considered to be the
vector sum of the moments of all the individual bonds in the molecule.
Since the charges on a molecule are of the order of 10^{-10} esu and the
intramolecular distances are of the order of one angstrom unit, the

magnitude of the dipole moment is of the order of 10^{-18} esu, or one Debye (D).

Most of the common methods of measuring the dipole moment of a substance depend upon a measurement of dielectric constant. The electrons and nuclei of a molecule are displaced from their mean positions in an electric field so that both polar and non-polar molecules will become polarized. This polarization will correspond to individual moments m_E and m_A where m_E is the moment induced by the displacement of the electrons and m_A is the moment induced by the displacement of the nuclei by an electric field. If a unit field induces the moments m_E' and m_A' in a non-polar molecule, and if F is the field strength

$$\bar{m} = (m_E' + m_A')\, F$$

where $\bar{m}$ is the moment due to polarization.

If the molecules in the field also have a permanent dipole moment they will orient themselves in such a way that a slight excess of them will be directed against the field at any time. The magnitude of this effect varies inversely with temperature. These molecules produce a further moment $\bar{m}_O$, which is the orientation polarization. This was evaluated by Debye[8],[10] as

$$\bar{m}_O = \frac{\mu^2 F}{3kT} \, ,$$

where k is the Boltzman constant and T is the absolute temperature.

Thus, $\qquad \bar{m}_{total} = (m_E' + m_A' + \frac{\mu^2}{3kT})\, F.$

To obtain μ we must have another expression for m_t/F. This can be obtained[11] by a consideration of the definition of the dielectric constant and the force acting upon a unit charge in a spherical cavity in a dielectric which has been placed in an electric field.

$$\frac{\bar{m}_t}{F} = \frac{M}{Nd} \cdot \frac{3}{4} \cdot \frac{\epsilon - 1}{\epsilon + 2} ,$$

where ϵ is the dielectric constant, M is the molecular weight, d is the density and N is Avogadros number.

Combining the last two equations it now follows that

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4 \pi N}{3} (m_E^! + m_A^! + \frac{\mu_s}{3KT}) .$$

The left hand equation is the total molecular polarization (P_t) of the substance and is the sum of three terms which are the electronic, atomic and orientation polarizations: P_E, P_A, and P_o. It should be pointed out that in the above derivation the assumption is made that the electric charge is in a vacuum and thus these calculations apply best to a gaseous dielectric.

It is obvious that if instead of using a steady field in these calculations an alternating field is used, as the frequency is increased it will reach a point at which the inertia of the molecules prevents them from rotating with the field. Thus the term for $\bar{m}_o$ will eventually disappear. Similarly, the moment due to atomic polarization will also disappear. Using Maxwells relation $\epsilon = n^2$, where n is the refractive index at infinite wavelength.

$$P = \frac{n^2 - 1}{n^2 + 2} \frac{M}{d} = \text{The molar refraction (MR).}$$

In actual practice when the refractivity method is used it is usually assumed that

$$P_E + P_A = MR_D.$$

MR_D is the molar refraction measured at the frequency of the sodium "D" line. The error introduced by the inclusion of P_A in this equation tends to cancel that introduced by the failure to extrapolate n to infinite wavelength. P is obtained from dielectric constant measurements made at lower frequencies. It follows that:

$$P_0 = P - MR_D = \frac{4\pi N \mu^2}{9kT}$$

At 25°C:-
$$\mu = .0128 \sqrt{298.16 \ (P_T - MR_D)}$$

As an approximation the above formulas can be applied to dilute solutions of polar solutes in nonpolar solvents. When this is done the polarization of the solute at a particular concentration is obtained as follows:

$$P_2 f_2 = \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \frac{M_1 f_1 + M_2 f_2}{d_{12}} - P_1 f_1.$$

Where 1 refers to the solvent, 2 to the solute, 12 to the solution and f is the mole fraction. P_1 is the total polarization term for the nonpolar solvent. When a series of P_2 values are obtained at various concentrations they can be extrapolated to infinite dilution (P_0). Using this value μ is calculated as indicated previously.

In dipole moments obtained from measurements of this type an error
is introduced by the assumptions in the derivation of the equations which
is usually assumed to have a maximum value of a few tenths of a Debye
unit[6] although in some cases it is appreciably higher, especially if the
compound whose moment is being determined forms solutions which are
slightly conducting.

The precision of this method is 0.1D or less. The difference between
the value of the moment determined by measurements in the gas phase and
those made by measurements in dilute solutions of nonpolar solvents is
usually not greater than 0.2D,[12] the gas phase moment ordinarily being
higher. It is obvious that comparisons of dipole moments which have
been determined by the same method are much more valid than comparisons
of moments which have been determined by different methods. In this work
it has been necessary to refer to many dipole moments determined previously.
Wherever possible values were selected which were determined in benzene
solution at 25°C.

CALCULATIONS

III CALCULATIONS

For the purposes of this work the calculations were modified slightly according to the method suggested by Halverstadt and Kumler[18] who have shown that plots of ϵ and $1/d$ versus the mole fraction of solute are essentially straight lines in dilute solutions and have suggested that the value of P_{too} calculated from these extrapolated values will be essentially free of error due to small amounts of impurity in the solvent. The actual equation used is determined as follows:

$$P_{12} = \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \cdot \frac{1}{d} . $$

P_{12} is the specific solute polarization at a specific concentration. This equation follows immediately from those presented previously.

The equations

$$\epsilon_{12} = \epsilon' + \alpha \omega_2$$

and

$$v_{12} = v' + \beta \omega_2$$

follow from the straight line relationships mentioned above. ϵ' and v' are the dielectric constant and specific volume at infinite dilution. The slopes of the straight lines are α' and β', and ω is the weight fraction of solute.

Solving and eliminating ϵ_{12} and v_{12}, then

$$P_{too} = \frac{3 \alpha' v'}{(\epsilon' + 2)^2} + (v' + \beta') \frac{\epsilon' - 1}{\epsilon' + 2} .$$

Or, in terms of mole fraction

$$P_{too} = \frac{3 \, \alpha \, v}{(\epsilon + 2)^2} \, M_1 + (M_2 V + M_1 \beta) \, \frac{\epsilon - 1}{\epsilon + 2} \, ,$$

where ϵ , v , α , β have the same significance as the primed values in the previous equation. This equation is the one which is used in the calculations in this work.

A brief outline of the actual procedure in calculation is as follows:

1) The molar refraction is calculated from the measured values of the refractive index and density for the pure solute by the equation indicated previously.

2) The cell constant, relative to benzene as standard, is determined by measuring the capacity of the cell at $25^{\circ}C$ with air, then benzene, as the dielectric.

$$\text{Cell constant} = \frac{C_{air} - C}{\epsilon_{\beta z} - 1}$$

The value 2.2725 for the dielectric constant of benzene is used throughout.

3) The values of ϵ_{12} at various concentrations are determined by measuring the capacity of the cell with air and then the solution as the dielectric at $25^{\circ}C$.

$$\epsilon_{12} = \frac{(C_{air} - C_{solu}) + \text{cell const.}}{\text{cell const.}}$$

4) The density of the solutions is determined at $25^{\circ}C$.

5) The values obtained for ϵ_{12} and V_{12} are plotted against the mole fraction of solute (X_2) and the slopes α and β are determined. These graphs are shown at the end of the experimental section.

6) P_{too} is calculated by the use of the equation indicated above.

7) The dipole moment is calculated from:-

$$\mu_{25} = .0128 \sqrt{298.16 (P_{too} - MR_D)}$$

EXPERIMENTAL

IV EXPERIMENTAL

Refractive Indices

The refractive indices of the pure liquids were determined at 25°C with an Abbé refractometer.

Densities

Densities were determined with a modified Ostwald pycnometer at 25°C.[28]
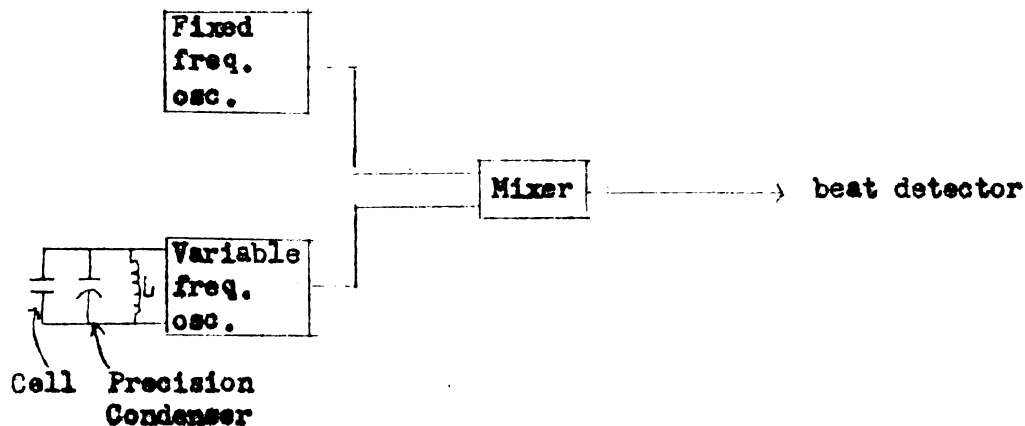
Dielectric Constants

The dielectric constant measurements were made by the heterodyne-beat method. In this method two radio frequency signals are combined by impressing them across two of the grids of a mixer tube (6SA7). This introduces a frequency, which is equal to the difference between the frequencies of the two oscillators, into the output of the mixer tube. When the frequencies of the oscillators are nearly equal the output of the mixer tube is in the audio range and can be heard if the signal is amplified and put through a loudspeaker. The pitch becomes lower as the frequencies of the oscillators become more nearly alike and finally ceases when the frequencies are equal. In this work the null point from the mixer was observed roughly as above, and a fine adjustment made by impressing the amplified mixer signal on the grid of a 6E5 "Magic Eye" indicator tube.

In this equipment, which is similar to that described by Chien,[19] the fixed frequency oscillator is crystal controlled by use of a 200

kilocycle quartz crystal. A General Radio precision condenser, type
722D, is in parallel with the dielectric constant cell in the L-C circuit
of the variable frequency oscillator. Since the frequency of the
variable frequency oscillator is given approximately by

$$f = 1/2 \pi \sqrt{LC},$$

it is obvious that any change in the capacity of the cell must be cor-
rected for by a corresponding change in the precision condenser in order
to keep the frequencies of the two oscillators equal.

```
 ┌────────┐
 │ Fixed  │
 │ freq.  │──────┐
 │ osc.   │      │
 └────────┘      │       ┌───────┐
                 ├───────│ Mixer │───────────⟶  beat detector
 ┌──┬──┬───┌─────│       └───────┘
 │  │  │   │Variable│
 ═╪═ ╤ ⌇L  │freq.  │──┘
 │  │  │   │osc.   │
 └──┴──┴───└───────┘
  Cell  Precision
         Condenser
```

A diagram of the cell may be found at the end of this section.

Preparation of Compounds

Preparation of the compounds whose dipole moments were measured.
The final purification of most of the following compounds was accomplished
by distillation through a 60 cm. helix packed column until successive one
ml. portions showed a constant refractive index.

Allylamine -- Eastman White Label compound was dried and redistilled, b.p. 53°C (745mm.), $n_D^{25} = 1.4225$, $d_4^{25} = 0.7597$.

Allyl Bromide -- The compound obtained commercially was dried over calcium chloride and distilled, b.p. 71°C (740mm.), $n_D^{25} = 1.4660$, $d_4^{25} = 1.4201$.

Allyl Cyanide -- This compound was prepared by the action of cuprous cyanide upon allyl bromide by the procedure given in Organic Syntheses,[20] b.p. 116°C (745mm.), $n_D^{25} = 1.4039$, $d_4^{25} = 0.8267$.

Allyl Ethyl Ether -- Eastman White Label compound was dried and re-distilled, b.p. 67°C (740mm.), $n_D^{25} = 1.3892$, $d_4^{25} = 0.7596$.

Allyl Iodide -- This compound was prepared from allyl bromide by refluxing the pure allyl bromide with methyl alcohol and sodium iodide. The reaction mixture was decanted from the solid residue and fractionally distilled through a 60 cm helix packed column under reduced pressure. The distillate was redistilled as described above, b.p. 102°C (745mm.), $n_D^{25} = 1.5482$, $d_4^{25} = 1.7955$.

Since allyl iodide is extremely sensitive to light[21] the distillations were performed in the dark as were determinations of the dielectric con-stants and densities of the solutions. When it was necessary to have light a small red "pencil light" was used since the decomposition has been shown to be slower in light of longer wavelengths. It was noted that after a four hour storage in complete darkness the refractive index remained constant but began to change soon after exposure to white light.

Benzylamine -- The Eastman White Label compound was distilled as described above, b.p. 183°C (740mm.), $n_D^{25} = 1.5407$, $d_4^{25} = 0.9798$.

2-Bromo-3-butyne -- This compound was prepared in low yield by the addition of phosphorus tribromide to a slight excess of 3-butyn-2-ol at -15°C in the presence of 0.1 mole of pyridine. The reaction was very vigorous and HBr was given off. When the addition was complete the mixture was washed with water and the organic layer was removed and dried over calcium chloride. The organic layer was then distilled through a 60 cm helix packed column at reduced pressure and then redistilled as described above, b. p. 28-30°C (84mm.), $n_D^{25} = 1.4766$, $d_4^{25} = 1.3815$. It is believed that the major products of this reaction are the esters of phosphorous acid.

3-Butyn-1-ol -- This compound was obtained from the Farchan Research Laboratories. The compound was dried over sodium sulfate and then calcium sulfate and distilled as above, b.p. 128°C (745mm.), $n_D^{25} = 1.4393$, $d_4^{25} = 0.9198$.

3-Butyn-2-ol -- This compound was obtained and purified in the same manner as 3-butyn-1-ol, b. p. 107°C (741mm.), $n_D^{25} = 1.4238$, $d_4^{25} = 0.8890$.

1-Chloro-4-octyne -- This compound was obtained from the Farchan Research Laboratories, dried over calcium chloride and distilled as above, b.p. 99.5 (47mm.), 184 (741mm.), $n_D^{25} = 1.4551$, $d_4^{25} = 0.9429$.

1-Diethylamino-2-propyne -- This compound was obtained from the Farchan Research Laboratories and distilled as above, b.p. 119°C (746mm.), $n_D^{25} = 1.4291$, $d_4^{25} = 0.7982$.

2-Methyl-2-bromo-3-butyne -- Dry hydrogen bromide was passed through the pure alcohol (2-methyl-3-butyn-2-ol) at 0°C until the reaction mixture was saturated. The organic layer was then separated from the heavier

layer of hydrobromic acid. The organic layer was washed three times with water (the mixture was neutralized with K_2CO_3 in the first washing), separated and allowed to stand for twenty-four hours over dry K_2CO_3 at $0°C$. The reaction mixture was distilled from fresh K_2CO_3 under reduced pressure. Two fractions were obtained, the smaller high boiling one gave no reaction with alcoholic selair net rate and rapidly polymerized. It is thought to have been 1-bromo-3-methyl-butadiene-1,3 or a similar compound. This method is similar to that of Campbell and Eby,[22]

b.p.   , $n_D^{25} = 1.4631$, $d_4^{25} = 1.2657$.

2-Methyl-3-butyn-2-ol — This compound was obtained and purified in the same manner as 3-butyn-1-ol, b.p. $103°C$ ($745mm.$), $n_D^{25} = 1.4240$, $d_4^{25} = 0.8566$.

3-Octyn-1-ol — This compound was obtained and purified in the same manner as 3-butyn-1-ol, b.p. $108-109°C$ ($37mm.$), $n_D^{25} = 1.4542$, $d_4^{25} = 0.8767$.

Propargyl Alcohol — This compound was obtained and purified in the same manner as 3-butyn-1-ol, b.p. $114°C$ ($745mm.$), $n_D^{25} = 1.4393$, $d_4^{25} = 0.9436$.

Propargyl Bromide — This compound was obtained and purified in the same manner as 1-chloro-4-octyn, b.p. $88°C$ ($740mm.$), $n_D^{25} = 1.4945$, $d_4^{25} = 1.5657$.
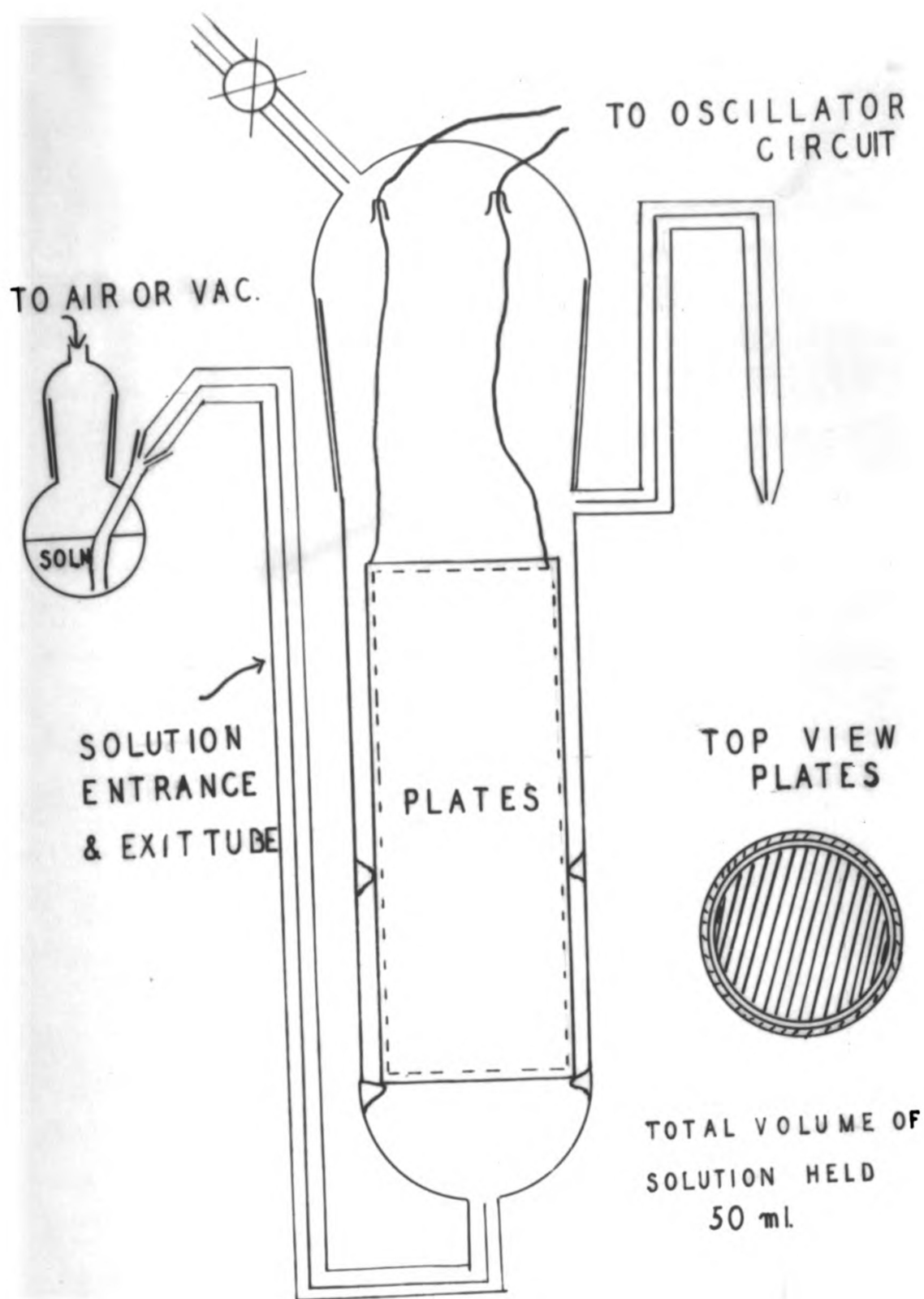
Propargyl Ethyl Ether — To one gram molecular weight of propargyl alcohol 0.2 gram atomic weight of sodium was added in small pieces. Each piece of sodium was added when the previous one had almost completely reacted. Care must be taken not to allow the reaction mixture to get too hot (above $70°C$) or to try to force more sodium to react by warming. When either of the above is done the reaction mixture decomposes violently.

When the sodium had reacted 0.2 gram molecular weights of ethyl iodide were added and the mixture was refluxed for two hours. The reaction mixture was then distilled through a 60 cm packed column. A small fraction of ethyl iodide came over first at $72^{\circ}C$. The desired product distilled at $80-81^{\circ}C$. The yield was approximately 50%. The excess alcohol remaining could have been recovered or used directly to prepare more ether.

The crude ether was redistilled as above, b.p. $80^{\circ}C$ (750mm.), $n_D^{25} = 1.4019$, $d_4^{25} = 0.8374$.

Propargyl Iodide -- This compound was prepared from the bromide in the same manner as allyl iodide. Decomposition in light did not seem to present a serious problem here, b.p. $114^{\circ}C$ (740mm.), $n_D^{25} = 1.5914$, $d_4^{25} = 2.0214$.

C E LL

TO OSCILLATOR CIRCUIT

TO AIR OR VAC.

SOLN

SOLUTION ENTRANCE & EXIT TUBE

PLATES

TOP VIEW PLATES

TOTAL VOLUME OF SOLUTION HELD 50 ml.

RESULTS

V RESULTS

TABLE I

DIELECTRIC CONSTANTS AND SPECIFIC VOLUMES OF THE BENZENE SOLUTIONS AT 25°C

Allylamine			Allyl Bromide		
X_2	ϵ_{12}	V_{12}	X_2	ϵ_{12}	V_{12}
0.02849	2.3328	1.1492	0.09393	2.6885	1.0831
.01987	2.3147	1.1479	.06031	2.5285	1.0989
.01505	2.3045	1.1472	.03108	2.4055	1.1241
.01007	2.2939	1.1465	.01660	2.3449	1.1334
.00476	2.2818	1.1455	.01010	2.3142	1.1377
			.00420	2.2930	1.1418

Allyl Cyanide			Allylethyl Ether		
0.03378	2.8272	1.1461	0.02921	2.3377	1.1502
.02047	2.6059	1.1453	.02097	2.3202	1.1487
.01276	2.4786	1.1454	.01523	2.3068	1.1475
.00681	2.3841	1.1450	.00906	2.2926	1.1465
.00496	2.3561	1.1449	.00408	2.2822	1.1457
.00281	2.3174	1.1448	.00390	2.2811	1.1455

Allyl Iodide			Benzyl Amine		
0.05258	2.4644	1.0825	0.02573	2.3428	1.1406
.01790	2.3382	1.1226	.01809	2.3207	1.1418
.01426	2.3234	1.1270	.01070	2.3001	1.1430
.00996	2.3095	1.1323	.00552	2.2857	1.1439
.00345	2.2865	1.1402	.00285	2.2786	1.1443
.00130	2.2789	1.1433	.00126	2.2749	1.1449

2-Bromo-3-butyne			3-Butyn-1-ol		
0.02380	2.3745	1.1279	0.01869	2.3412	1.1443
.01726	2.3454	1.1326	.01297	2.3178	1.1442
.01240	2.3233	1.1362	.007935	2.3032	1.1445
.00678	2.3020	1.1396	.003302	2.2837	1.1446
.00465	2.2918	1.1416			
.00184	2.2817	1.1426			

TABLE I -- Continued

3-Butyn-2-ol			1-Chloro-4-octyne		
0.04764	2.4760	1.1458	0.01570	2.3489	1.1427
.03504	2.4055	1.1456	.01051	2.3235	1.1434
.01957	2.3427	1.1452	.00594	2.3021	1.1439
.00923	2.3039	1.1450	.00336	2.2890	1.1443
.00510	2.2903	1.1450	.00315	2.2579	1.1444
.00179	2.2775	1.1449	.00116	2.2786	1.1446

1-Diethylamino-2-propyne			2-Methyl-2-bromo-3-butyne		
0.01729	2.2801	1.1478	0.01473	2.3470	1.1350
.01308	2.2790	1.1471	.00910	2.3181	1.1386
.00957	2.2773	1.1465	.00416	2.2936	1.1418
.00597	2.2756	1.1458	.00305	2.2878	1.1426
.00190	2.2747	1.1454	.00183	2.2827	1.1434
.00110	2.2734	1.1449	.00108	2.2775	1.1440

2-Methyl-3-butyn-2-ol			3-Octyn-1-ol		
0.01876	2.3311	1.1461	0.01714	2.3430	1.1450
.01282	2.3126	1.1459	.01320	2.3260	1.1450
.00794	2.2965	1.1456	.00915	2.3095	1.1449
.00512	2.2878	1.1452	.00544	2.2937	1.1448
.00394	2.2850	1.1451	.00319	2.2852	1.1448
.00199	2.2787	1.1450	.00160	2.2791	1.1453

Propargyl Alcohol			Propargyl Bromide		
0.03259	2.4125	1.1433	0.02267	2.3417	1.1278
.01676	2.3406	1.1442	.01669	2.3245	1.1322
.00757	2.3038	1.1444	.00976	2.3023	1.1376
.00433	2.2928	1.1444	.00622	2.2902	1.1400
			.00312	2.2822	1.1422
			.00227	2.2800	1.1433

Propargyl Ethyl Ether			Propargyl Iodide		
0.01276	2.3049	1.1451	0.02253	2.3218	1.1145
.00845	2.2934	1.1454	.01745	2.3106	1.1213
.00547	2.2876	1.1452	.01167	2.2977	1.1288
.00390	2.2829	1.1452	.00607	2.2853	1.1364
.00272	2.2798	1.1450	.00474	2.2825	1.1387
.00069	2.2742	1.1449	.00190	2.2761	1.1421

TABLE II

DIPOLE MOMENTS, MOLAR POLARIZATIONS, MOLAR REFRACTIONS, SLOPES OF ϵ_{12} AND v_{12} vs X_2, DIELECTRIC CONSTANTS AND SPECIFIC VOLUME AT INFINITE DILUTION

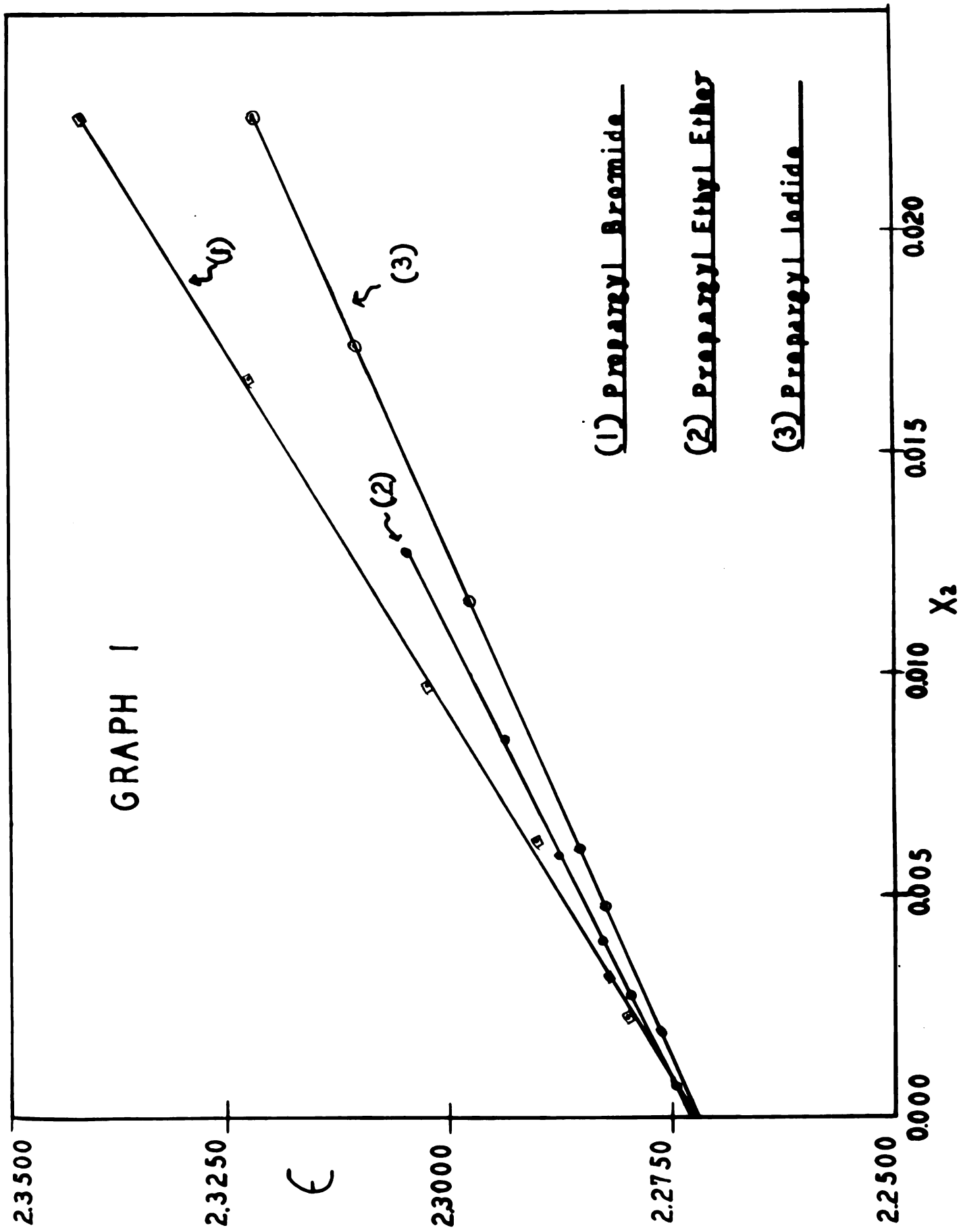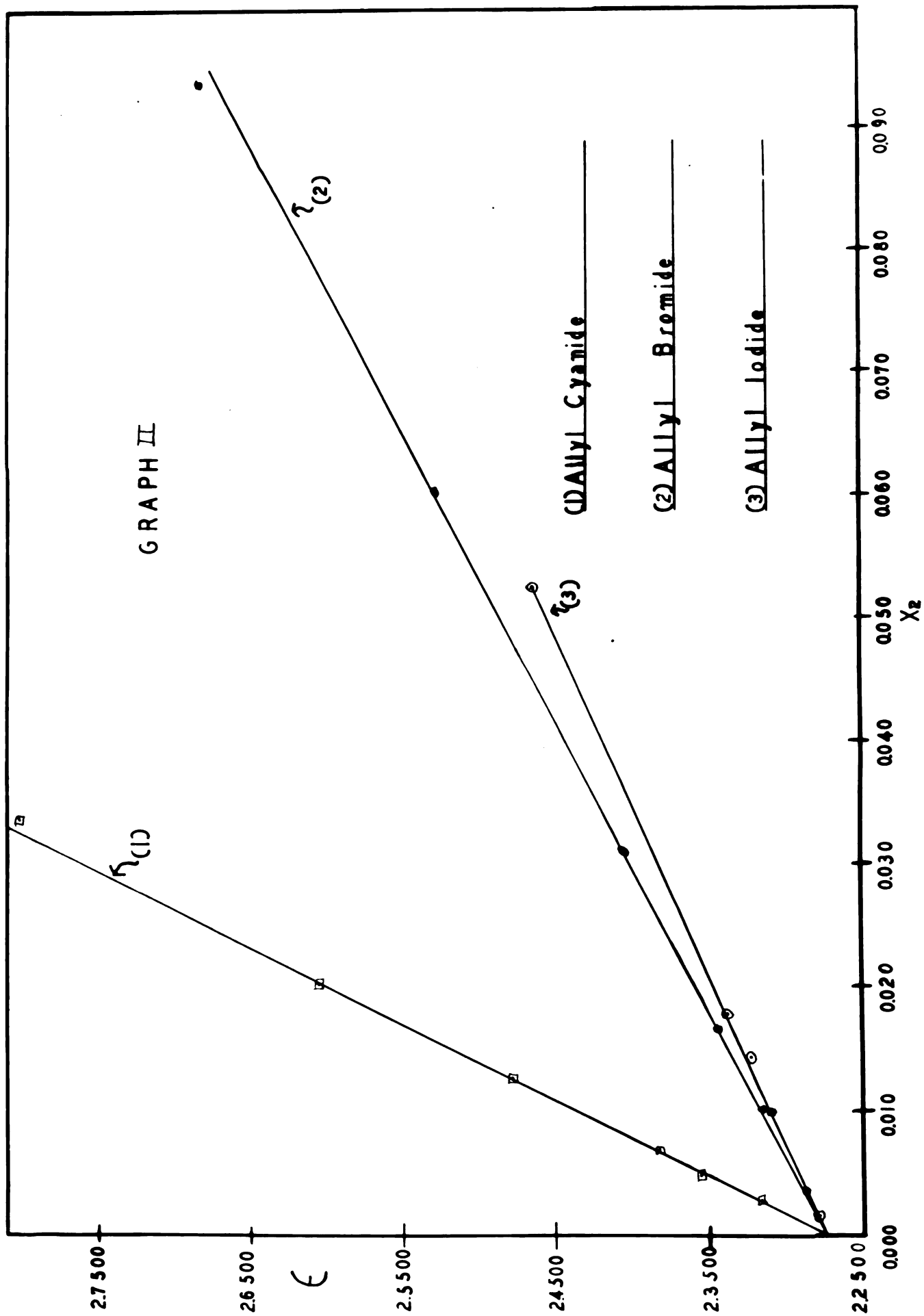| Compound	μ	P_{∞}	MR_D	Calc. MR_D	α	β	ϵ	v
Allylamine	1.31	54.42	19.17	19.09	2.14	0.15	2.2722	1.1449
Allyl Bromide	1.82	91.01	23.60	23.35	4.43	-0.656	2.2725	1.1446
Allyl Cyanide	3.44	262.0	19.84	19.95	16.13	0.09	2.2725	1.1447
Allyl Ethyl Ether	1.38	65.17	26.41	26.47	2.23	0.13	2.2727	1.1449
Allyl Iodide	1.62	83.36	29.73	28.37	3.70	-1.21	2.2725	1.1444
Benzylamine	1.38	73.23	34.35	34.25	2.75	-0.16	2.2710	1.1448
2-Bromo-3-butyne	1.77	90.97	27.18	26.44	4.22	-0.70	2.2730	1.1445
3-Butyn-1-ol	1.73	81.30	20.05	20.20	3.91	-0.01	2.2700	1.1445
3-Butyn-2-ol	1.69	78.20	20.11	20.20	3.66	0.02	2.2720	1.1449
1-Chloro-4-octyne	1.92	117.33	42.08	42.01	4.85	-0.14	2.2730	1.1448
1-Diethylamine-2-propyne	0.80	49.21	36.07	36.46	0.50	0.17	2.2725	1.1449
2-Methyl-2-bromo-3-butyne	1.94	109.0	32.00	31.05	5.02	-0.64	2.2724	1.1444
2-Methyl-3-butyn-2-ol	1.59	76.78	25.05	24.81	3.13	0.09	2.2722	1.1449
3-Octyn-1-ol	1.78	103.81	39.00	38.67	4.12	0.01	2.2720	1.1448
Propargyl Alcohol	1.78	80.54	15.35	15.58	4.25	-0.04	2.2725	1.1444
Propargyl Bromide	1.50	68.03	22.14	21.82	3.04	-0.74	2.2725	1.1447
Propargyl Ethyl Ether	1.46	67.87	24.45	24.93	2.54	0.08	2.2725	1.1448
Propargyl Iodide	1.21	57.86	27.76	26.85	2.20	-1.34	2.2720	1.1446

TABLE III[*]

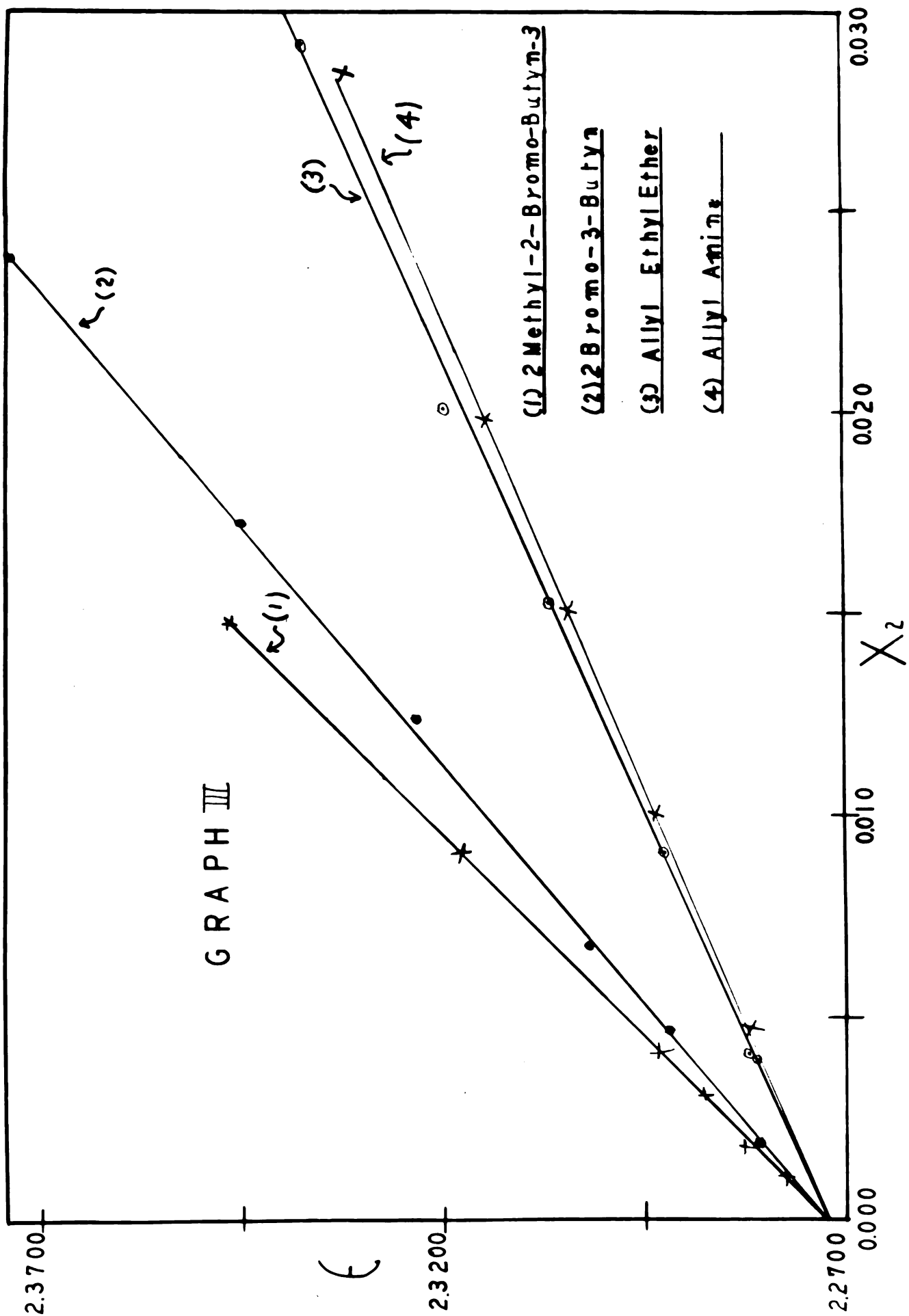### DIPOLE MOMENTS NOT DETERMINED HERE, BUT WHICH WILL AID IN THE EVALUATION OF THE RESULTS OF THIS WORK

Compound	μ (D)	Compound	μ (D)
Bromoacetylene[13]	0.0[**]	n-Propylamine	1.39[**]
2-Bromobutane	2.12 (20°C)	n-Propyl bromide	1.94 (20°C)
Chloroacetylene[13]	0.44[**]	n-Propyl chloride	1.94 (20°C)
Ethyl, n-propyl ether[24]	1.16	n-Propyl cyanide	3.57[25], 4.05[**17]
2-Hydroxy butane	1.79	Propylene[13]	0.35[**]
Methyl Acetylene[15]	0.77	n-Propyl iodide	1.85 (20°C)
2-Methyl-2-bromo butane	2.25 (20°C)	Vinyl bromide[13]	1.41[**]
2-Methyl-2-hydroxy butane	1.66	Vinyl chloride[13]	1.44[**]
1-Octanol	1.64	Vinyl iodide[13]	1.26[**]
n-Propyl alcohol	1.66 (22°C)		

[*] Unless otherwise stated these values are in benzene at 25°C and are from reference 23.

[**] Vapor phase measurements.

GRAPH I

(1) Propargyl Bromide
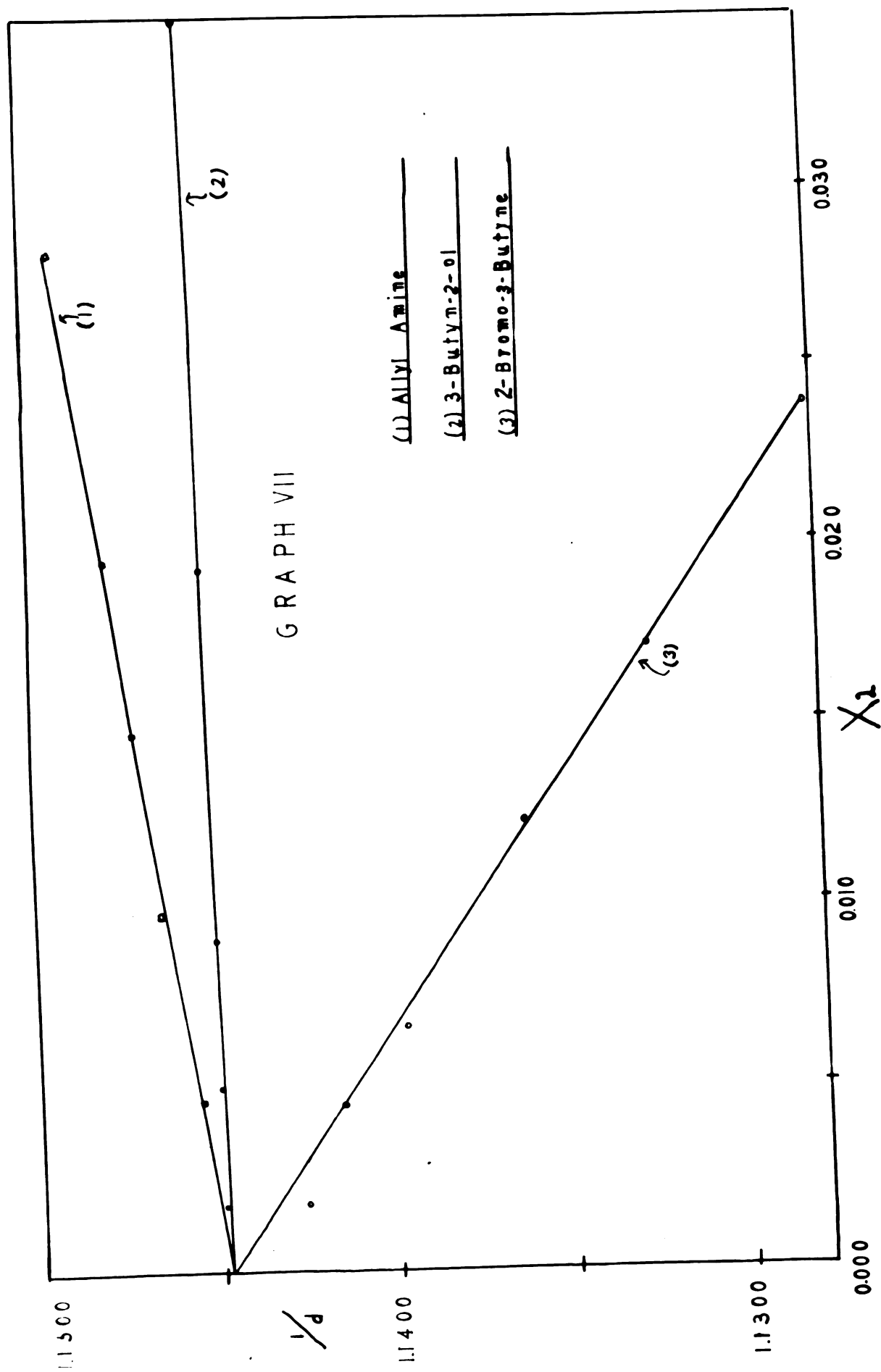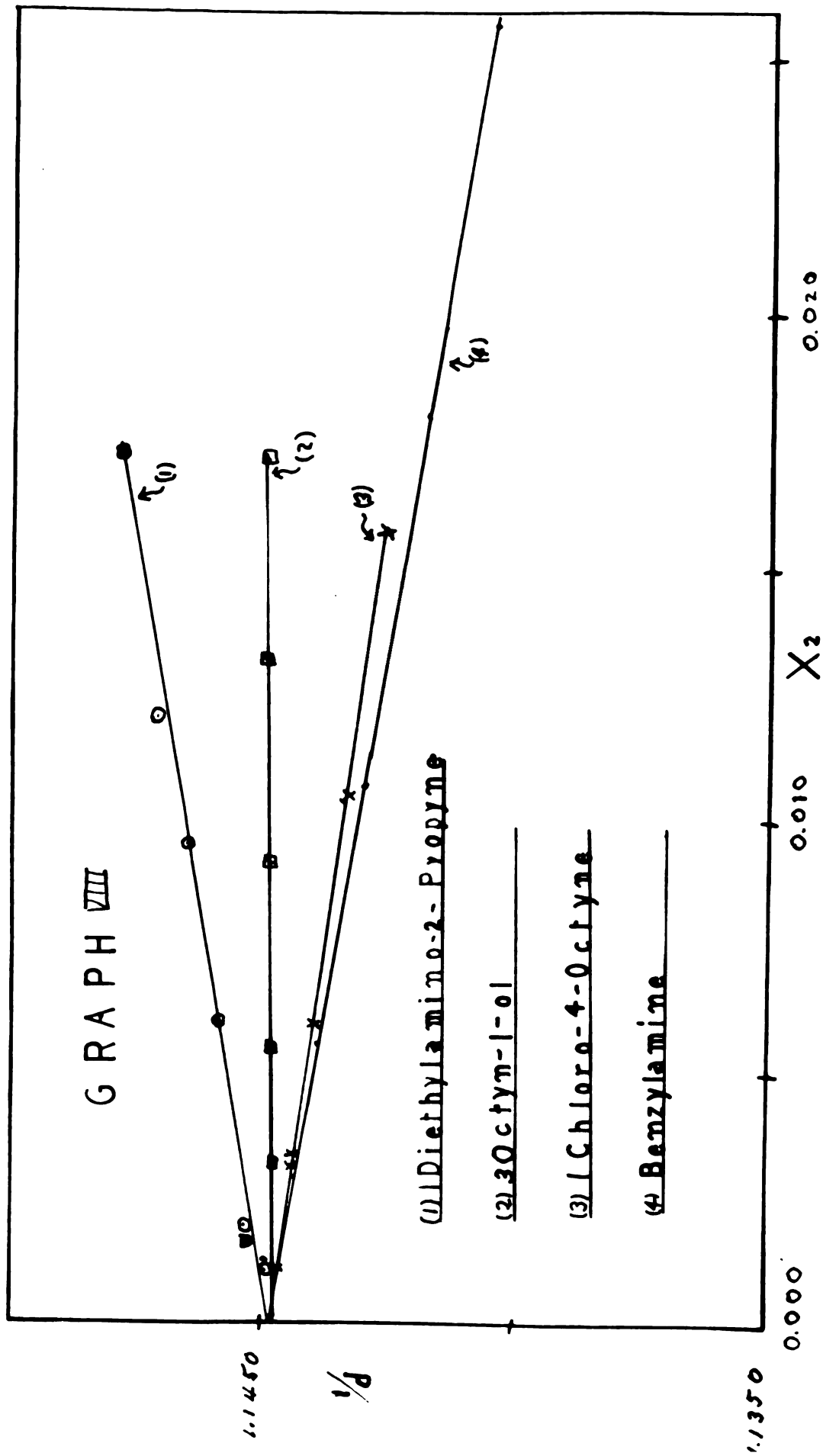(2) Propargyl Ethyl Ether
(3) Propargyl Iodide

GRAPH II

(1) Allyl Cyanide

(2) Allyl Bromide

(3) Allyl Iodide

X_2

GRAPH III

X_2

(1) 2 Methyl-2-Bromo-Butyn-3

(2) 2 Bromo-3-Butyn

(3) Allyl Ethyl Ether

(4) Allyl Amine

GRAPH IV

(1) 1 Chloro-4 Octyne
(2) 3 Octyn-1-ol
(3) Benzylamine
(4) 1 Diethylamino-2-Propyne

$\zeta_{(1)}$
$\zeta_{(2)}$
$\zeta_{(3)}$
$\zeta_{(4)}$

X_2

0.000   0.010   0.020

2.3500
2.3000
2.2500

GRAPH V

(1) Propargyl Alcohol

(2) 3-Butyn-2-ol

χ_2

(1)

(2)

η

2.4 500

2.3 500

2.2 500

0.000   0.010   0.020   0.030

GRAPH VI

(1) 3-Butyn-1-ol

(2) 2-Methyl-3-Butyn-2-ol

$\zeta_{(1)}$

$\tau_{(2)}$

X_2

GRAPH VII

(1) Allyl Amine
(2) 3-Butyn-2-ol
(3) 2-Bromo-3-Butyne

$\zeta_{(1)}$

$\zeta_{(2)}$

$\zeta_{(3)}$

X_2

$1/d$

1.1500

1.1400

1.1300

0.000   0.010   0.020   0.030

GRAPH VIII

(1) Diethylamino-2-Propyne
(2) 3 Octyn-1-ol
(3) 1 Chloro-4-Octyne
(4) Benzylamine

GRAPH IX

$\gamma_{(1)}$

$\gamma_{(2)}$

$\gamma_{(3)}$

$^1/_d$

X_2

(1) Propargyl Ethyl Ether

(2) Propargyl Bromide

(3) Propargyl Iodide

GRAPH X

(1) Allyl Ethyl Ether

(2) 2-Methyl-3-Butyn-2-ol

(3) 2-Methyl-2-Bromo-3-Butyne

GRAPH XI

(1) Allyl Cyanide
(2) Propargyl Alcohol
(3) Allyl Iodide

GRAPH XII

(1) 3-Butyn-l-ol

(2) Allyl Bromide

$\frac{1}{d}$

X_2

DISCUSSION

VI DISCUSSION

Polarization Effects

It has been established previously[14] that the resultant moment of the -CH₃ group is equal to that of a C-H bond, therefore the replacement of a hydrogen by a methyl group should cause no change in the total moment of a molecule. Actually, however, the replacement of a hydrogen by a -CH₃ group will often cause a noticeable change in the dipole moment of a molecule. This effect is thought to be due to the polarization of the hydrocarbon radical by the more polar methyl group. An example of this is ethyl chloride which has a moment which is 0.15 D higher than that of methyl chloride. The moment due to polarization is in the same direction as that of the C-Cl bond, the carbon atom being made more negative by polarization.

To illustrate this we may draw two representative structures:

```
        H                               H
 (+)   |(-)                    (-) (+)  |
 H      C - Cl        and       H        C - Cl
        |                                |
        H      (A)                       H      (B)
```

the effect of the C-Cl bond being to increase the stability of structure A.

As the chain increases in length the increase in the dipole moment becomes negligible. However, it is still noticeable in adding secondary and tertiary groups, the increase from n-propyl bromide to 2-methyl-2-bromo butane being about 0.11 D. This is because the groups added are close to the C-Br bond.

In this work the dipole moments of a series of acetylenic compounds were run. Since these are comparable to the groups mentioned above it is interesting to see how the dipole moments vary on replacing H by -CH$_3$. We have:

$$HC \equiv C-CH_2Br \qquad HC \equiv C-\underset{CH_3}{\overset{H}{\underset{|}{\overset{|}{C}}}}Br \qquad HC \equiv C-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}Br$$

$$= 1.50D \qquad = 1.77D \qquad = 1.94D$$
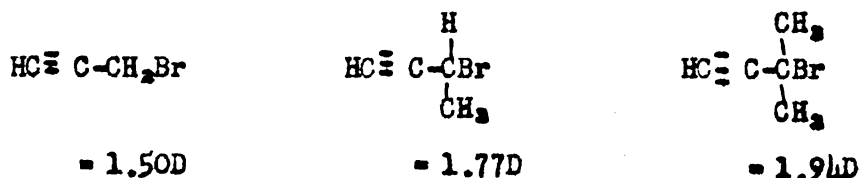
The total change in moment from the primary to the tertiary compound is 0.44D which is considerably larger than that of the saturated series. This seems to indicate that the -C$\equiv$C- group which is known to be more polarizable itself also tends to make the whole hydrocarbon radical more polarizable. Another explanation of this effect is that the increase in dipole moment in the acetylenic series is partially due to the supression of hyperconjugation structure VII (in the following discussion) upon replacement of H by -CH$_3$.

Resonance and Hyperconjugation Effects

For compounds such as the vinyl halides we would expect to find higher dipole moments than for the corresponding saturated halides if polarization were the only effect. Actually the dipole moments of these compounds are lower by about 0.7 to 0.8D than the unsaturated halides.[7] A similar effect is also noticed in the haloacetylenes where the moment is 1.7 to 2.2D lower than the value for the saturated halides. These effects are explained by resonance structures[7] such as:

$$H_2C-CH = X \qquad \text{and} \qquad HC = C = X$$
$${}^{-}{}^{+} \qquad\qquad\qquad {}^{-}{}^{+}$$

If the dipole moments of compounds similar to the above but with a
-CH$_2$- group between the unsaturated bond and the halogen are measured
the resonance or hyperconjugation effects in these compounds could be
studied also. In this work the dipole moments of some allyl and propargyl
compounds have been determined and compared with the saturated halides
for this purpose.

The dipole moment of n-propyl bromide is 1.94D[23] which moment may
be considered to be due only to the moment of the C-Br bond and polariza-
tion of the hydrocarbon radical.

The moment of allyl bromide was determined in this work to be 1.82D.
This represents a lowering of 0.12D with respect to the saturated com-
pound despite the fact that the double bond would be expected to be more
polarizable and therefore to increase the dipole moment. This effect
can be partially explained on the basis of a hyperconjugation structure
which has not previously been mentioned for these compounds.

$$
\begin{array}{ccc}
\overset{H}{\underset{|}{\;}}\;\overset{H}{\underset{|}{\;}} & \overset{H}{\underset{|}{\;}}\;\overset{H}{\underset{|}{\;}} & \overset{H}{\underset{|}{\;}}\;\overset{H}{\underset{|}{\;}} \\
H_2C = C - C-H & H_2C = C - C-H & H_2C - C = C\;H^{(+)} \\
| & \underset{(+)}{\;}\;| & \underset{(-)}{\;}\;\;| \\
Br & Br & Br \\
& \underset{(-)}{\;} &
\end{array}
$$

$$
\begin{array}{c}
\overset{(+)}{\;}H \\
\underset{\;}{\overset{H}{|}} \\
H_2C - C = C-H \\
\underset{(-)}{\;}\;\;\;\;| \\
Br
\end{array}
$$

I   II   III
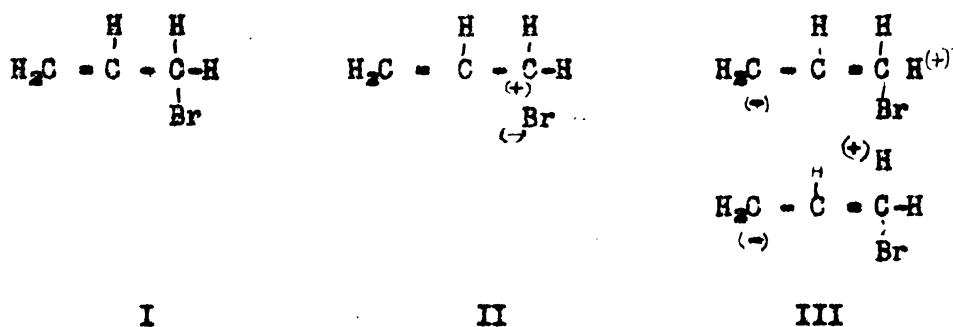
The suggested hyperconjugation structures III would account for a lower-
ing of the dipole moment. It is interesting to note that if we consider
the hydrocarbon propylene which has a dipole moment of 0.35D, the follow-
ing hyperconjugation structure which is analogous to III has been proposed:[15]

$$\overset{\underset{|}{H}}{H_2C} = \overset{|}{C} - CH_3 \qquad \qquad \overset{(-)}{H_2C} - \overset{\underset{|}{H}}{C} = CH_3 \overset{(+)}{H}$$
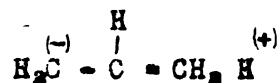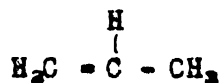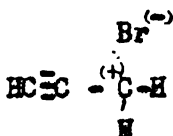
IV

It should be noted that structure III would have to be only a very small contributing factor to have a distinct effect upon the dipole moment because of its large charge separation. Not much can be said about the extent to which structure III lowers the total moment of the molecule since there are too many unknown quantities involved. Its actual contribution would depend among other things upon the magnitude and direction of the polarisation moment and upon whether or not there is free rotation of the -CH$_2$Br group.

The moment of propargyl bromide was determined in this work as 1.50D. The drop in the magnitude of the moment with respect to the saturated halide is 0.44D in this case. Since polarisation of the acetylenic group is even greater than in the allylic group a substantially larger dipole moment would be expected if hyperconjugation were not taken into consideration. The hyperconjugation structures proposed (VII) are analogous to structure III and as with the previous case a similar structure can be proposed for the hydrocarbon itself (VIII).[16] The dipole moment of methyl-acetylene (solution measurement) is 0.77D.

$$HC\overset{=}{=}C - \overset{\underset{|}{Br}}{\underset{H}{C}} - H \qquad HC\overset{=}{=}C - \overset{\underset{|}{Br^{(-)}}}{\underset{H}{\overset{(+)}{C}}} - H \qquad \overset{(-)}{HC}=\overset{\underset{|}{Br}}{\underset{H}{C}} \cdot H^{(+)}$$

V   VI

$$HC\equiv C - \overset{(-)}{\underset{H(+)}{\overset{Br}{C}}} - H$$

VII

$$HC\equiv C\equiv \overset{(-)}{CH_2}H^{(+)}$$
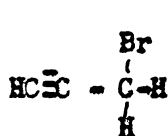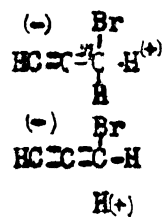
VIII

It should be noted that even a rough attempt at calculation of the contribution of structure VII would indicate immediately that the dipole moments of propargyl bromide and iodide are lower than can be explained on the basis of the indicated structures. The most probable explanation for this becomes evident if one considers the work of T. L. Jacobs[26] which was reported after the above experimental work was done. Jacobs has shown that if propargyl bromide is heated to 110°C in the presence of cuprous bromide a mixture of propargyl bromide and bromopropadiene is obtained. Jacobs has also shown that the "propargyl iodide" reported in the literature is actually a mixture of propargyl iodide and iodopropadiene. These facts give an immediate explanation of the extremely low dipole moment found for propargyl iodide and it is possible that they partially explain the low value obtained for the moment of propargyl bromide.

It has not yet been possible to ascertain whether or not the propargyl bromide obtained from the Farchan Research Laboratories was subjected to such conditions as to have undergone the above mentioned isomerism. However, the physical constants of the propargyl bromide used in this work are in reasonably close agreement with those found for the pure propargyl bromide by Jacobs.[26]

The dipole moment of propargyl bromide has also been determined using material prepared by treating the alcohol with phosphorus tribromide. The value found was identical with that reported here (1.50D), although the physical constants of the propargyl bromides (n_D^{25} 1.4904, d_4^{25} = 1.576) differed. The physical constants reported by Jacobs[26] for material free from bromoallene were n_D^{25} = 1.4896, d_4^{25} = 1.562.

The above facts cast some doubt upon the validity of the results of this work with respect to the propargyl type halides and, in particular, propargyl iodide. In the case of the bromides the results of this work are probably valid, especially in light of the communication with Dr. Jacobs. In addition, the allylic halides also show dipole moments which are lower than expected. Since the allyl halides are better known than the propargyl halides, and since a similar isomerism has not been reported to occur in these compounds, it cannot be assumed that isomerism would be a valid explanation for their low dipole moment.

A study has been made of the bond lengths of the C-X bonds in the propargyl halides by Pauling and co-workers.[27] The bond lengths measured were slightly longer than the normal C-X bond lengths and the authors proposed the following resonance structure:

$$\overset{+}{HC} = C = CH_2 \ \overset{-}{X}$$

IX.

It is obvious that in order to account even partially for the lowering of the dipole moments this structure must be assumed to contribute even less than structure VII. It should be noted here that the indicated work of Pauling is subject to some doubt as a result of Jacob's work.

The dipole moments of two other acetylenic halides have been determined in this work. These compounds are 2 methyl-2-bromo-3-butyne (XIV), and 2 bromo-3-butyne (X) whose dipole moments are, respectively, 0.31D and 0.35D lower than those of the corresponding saturated compounds. Taking structures IV and VII into consideration the following resonance and hyperconjugation structures may be drawn:
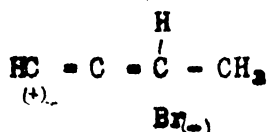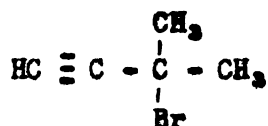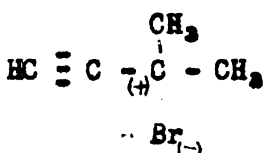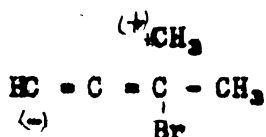
$$HC \equiv C - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}} - CH_3$$

X

$$HC \equiv C - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Br_{(-)}}{|}}{\overset{(+)}{C}}} - CH_3$$

XI

$$HC \overset{(+)}{=} C = \overset{\overset{\displaystyle H^{(+)}}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}} - CH_3$$

XII

$$HC \overset{(+)}{=} C = \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Br_{(-)}}{|}}{C}} - CH_3$$

XIII

$$HC \equiv C - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}} - CH_3$$

XIV

$$HC \equiv C \overset{(+)}{-} C - CH_3 \quad Br_{(-)}$$

XV

$$HC = C = \overset{\overset{\displaystyle (+)CH_3}{}}{\underset{\underset{\displaystyle Br}{|}}{C}} - CH_3 \quad (-)$$

XVI

$$HC \overset{(+)}{=} C = \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Br_{(-)}}{}}{C}} - CH_3$$
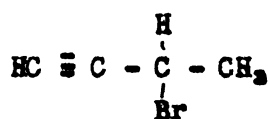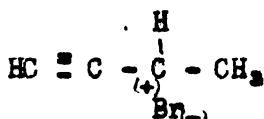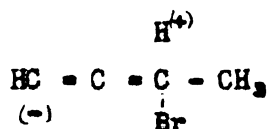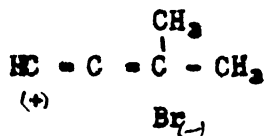
XVII

It should be noted that although structure XVI is not considered probable there is still an appreciable lowering of the dipole moment although not as great as in the propargyl compounds. This would seem to indicate that an inductive effect caused by the greater electronegativity of the carbon atoms in the triple bond might also contribute to the lowering of the dipole moment.[9] This inductive effect probably partially accounts for the very low moment of propargyl bromide.

The dipole moments of two of the ethyl ethers corresponding to the halogens discussed above have been determined in this work. The moment of allyl ethyl ether was found to be 0.22D higher than that ethyl,

n-propyl ether, and the moment of propargyl ethyl ether is 0.30D higher than that of the saturated ether. Since the magnitudes of the moments increased in this series a rough calculation will be made to determine whether a moment in the direction indicated by hyperconjugation structures of the same type as III and VII would account for this.

In the following calculation[*] on propargyl ethyl ether polarization is neglected, free rotation about the C-O bond is assumed, the moment of the resonance structure corresponding to VII is assumed to be the same as that of the hydrocarbon (0.77D), and the moment of the C-O-H group is assumed to be the same as the moment of ethyl, n-propyl ether.

---
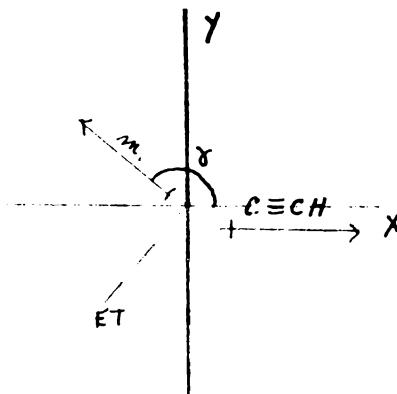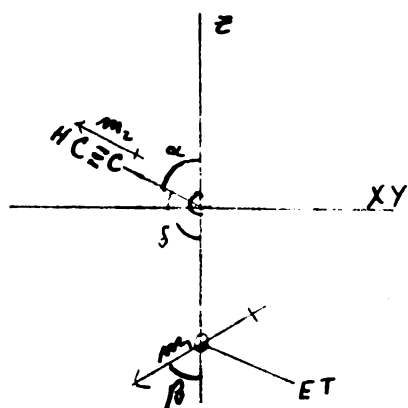
[*] See next page.

$$m_{\text{az}} = m_{1z} = m_z$$

$$m_{ax} + m_{1xy}\cos\gamma = m_x$$

$$m_{1xy}\sin\gamma = m_y$$

$$m^2_{\text{inst}} = m_z^2 + m_{ax}^2 + 2m_{ax}m_{1xy}\cos + m_{1xy}^2\cos^2\gamma + m_{1xy}^2\sin^2\gamma$$

$$= m_z^2 + m_{ax}^2 + m_{1xy}^2 + 2m_{ax}m_{1xy}\cos\gamma$$

$$\overline{m^2} = m_z^2 + m_{ax}^2 + m_{1xy}^2 + 2m_{ax}m_{1xy}\int_0^{2\pi}\frac{\cos\gamma\,d\gamma}{2\pi}$$

$$= m_{1z}^2 - 2m_{1z}m_{az} + m_{az}^2 + m_{1xy}^2 + m_{ax}^2$$

$$= m_1^2 + m_a^2 - 2m_{1z}m_{az}$$

$$= (0.77)^2 + (1.16)^2 - 2(0.77)(1.16)\cos\alpha\cos\beta$$

$$= \mu^2$$

If $\gamma = 110°$, $\alpha = 70°$, $\beta = 55°$ Then $\mu^2 = 1.59$

$\mu = 1.26D$

If $\gamma = 124°$, $\alpha = 56°$, $\beta = 55°$ Then $\mu^2 = 1.39$

$\mu = 1.18D$

Due to the large number of assumptions which had to be made it is doubtful whether this calculation is very significant.

---

*Definitions of the symbols used in the previous calculation are as follows:
m_x, m_y, m_z are the total moments along the x,y, and z axes.
m_1 -- The moment due to the C-O-Et group moment (1.16D).
m_a -- The moment due to the hyperconjugation structure (0.77D).
m_{1xy} -- The moment in the xy plane due to the C-O-Et group moment.
m_{ax} -- The moment along the x axis due to the hyperconjugation structure.
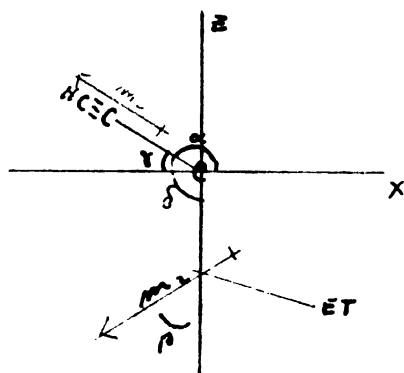m_{1z} -- The moment along the z axis due to the C-O-Et group moment.
m_{az} -- The moment along the z axis due to the hyperconjugation structure.
m_{inst} -- The instantaneous moment.
$\overline{m}$ -- The magnitude of μ (Average).
Angles α, β, γ, δ are as indicated in the calculation.

If assumption of free rotation were not valid, we could assume the orientation shown in the following calculation.[*]

$$m_{1z} = m_1 \cos\beta$$

$$m_{2z} = m_2 \cos\alpha$$

$$m_z = m_{1z} - m_{2z}$$

$$= 0.39 \text{ if } \alpha = 70° \ (\delta = 110°)$$

$$= 0.22 \text{ if } \alpha = 55° \ (\delta = 124°)$$

$$m_{2x} = m_2 \cos\gamma = 0.725 \text{ if } \gamma = 20° \ (\delta = 110°)$$

$$= 0.641 \text{ if } \gamma = 34° \ (\delta = 124°)$$

$$m_{1x} = m_1 \cos 35° = 0.951$$

$$\therefore m_x = 1.68 \text{ if } \delta = 110°$$

$$= 1.59 \text{ if } \delta = 124°$$

$$\therefore m = 1.73 \text{ if } \delta = 110°$$

$$= 1.61 \text{ if } \delta = 124°$$

Both of these values are higher than the experimental value (1.46D).

Although the results of these calculations depend upon many assumptions which render them very approximate, they might indicate that the rotation

---

[*]Definitions of the symbols used in the previous calculation are as follows:
m_x,m_z -- The total moments along the x and z axes.
m_1 -- The moment of the C-O-Et group (1.16D).
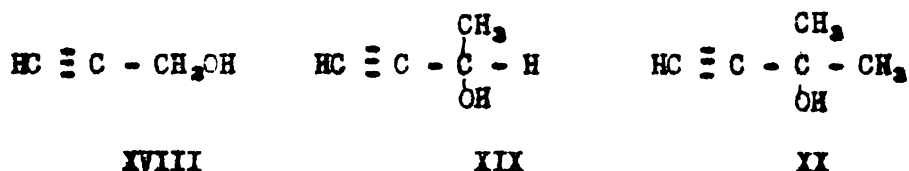m_2 -- The assumed moment for the hyperconjugation structure (0.77).
m_{1x} -- The moment of the C-O-Et group along the x axis.
m_{2x} -- The moment due to the hyperconjugation structure along the x axis.
   (Similar for z axis.)
Angles α , γ , δ are as indicated above.

about the C-O bond is somewhat restricted in the orientation indicated.
This is not very probable and there is probably some other effect which
has not been considered here. Similar calculations have not been
attempted for allyl ethyl ether because even more assumptions would be
necessary.

When the dipole moments of alcohols containing an acetylenic group
are considered it is found that in the series:

$$HC \equiv C - CH_2OH \qquad HC \equiv C - \underset{\overset{|}{OH}}{\overset{CH_3}{C}} - H \qquad HC \equiv C - \underset{\overset{|}{OH}}{\overset{CH_3}{C}} - CH_3$$

| XVIII | XIX | XX |

the dipole moment decreases very slightly (0.19) from XVIII to XX. This
is not like the bromides where there was an increase of 0.44D. It should
be noted that the alcohols would be expected to act more like the ethers
than the bromides and free rotation would be expected in the alcohols.
Comparison of the values obtained for the unsaturated alcohols with re-
ported values of the moments of the corresponding saturated alcohols shows
no definite trend from the saturated to the unsaturated cases, however all
are within 0.12D of one another. If we assume free rotation about the
C-O bond and assume that the orientation of the rest of the molecule is
similar to:

$$HC \equiv C - CH_2$$
$$124°$$ O-H
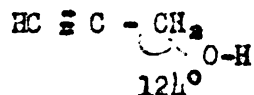
This orientation seems most probable because bond length measurements
in methylacetylene indicate that the bond between the methyl carbon

and the acetylenic carbon atom has a great deal of double bond character.[8]

If a calculation identical to that for the ethers, where free rotation was assumed, is made we obtain as before the equation:[*]

$$\bar{m}^2 = m_1^2 + m_2^2 - 2m_{1z}m_{2z}$$

A sample calculation with 3 butyn-2-ol is as follows:

$$\bar{m}^2 = \mu^2 = (0.77)^2 + (1.79)^2 - 2(0.77)(1.79)\cos56^\circ\cos55^\circ.$$

$$= 2.91$$

$$\mu = 1.70$$

TABLE IV

OBSERVED AND CALCULATED DIPOLE MOMENTS OF ACETYLENIC ALCOHOLS

Alcohol	μ Calc'd.	μ Determined	Difference
Propargyl alcohol	1.59D	1.78D	0.19D
3 Butyn-2-ol	1.70	1.69	0.01
2 Methyl-3-butyn-2-ol	1.59	1.59	0.00

It would seem that from the excellent agreement between the calculated and actual values that the assumptions made were essentially reasonable.

---

[*]m_1 -- The moment due to the C-O-H group taken as that of the corresponding saturated alcohol.
[*]All other symbols are identical with those in the previous derivation involving free rotation.
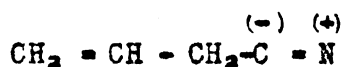
It should be noted that all values for the alcohols are subject to a greater error than the other compounds because their solution behavior is extremely non-ideal.

The dipole moment of 3-octyn-1-ol was determined and found to be 0.14D higher than that of the saturated alcohol. This observation was not expected. This alcohol would be expected to have a moment essentially the same as that of the corresponding saturated alcohol. The difference of 0.14D is not very great, however, and might be due to experimental error.
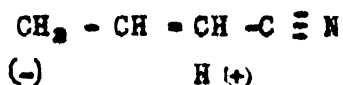
In the case of allyl cyanide the dipole moment is found to drop about 0.13 from the value for n-propyl cyanide. It is difficult to draw any definite conclusions about this due to the large discrepancies between reported values for n-propyl cyanide. However, the following resonance structures may be drawn:
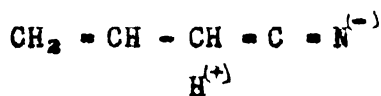
$$H_2C = CH - CH_2-C \equiv N \qquad CH_2 = CH - \overset{(-)}{CH_2}-\overset{(+)}{C} = N$$

$$\text{XVIII} \qquad\qquad\qquad \text{XIX}$$

$$\underset{(-)}{CH_2} - CH = CH -C \equiv N \qquad CH_2 = CH - CH = C = \overset{(-)}{N}$$
$$\qquad\qquad\quad \overset{}{H} (+) \qquad\qquad\qquad\qquad \overset{}{H}^{(+)}$$

$$\text{XX} \qquad\qquad\qquad\qquad \text{XXI}$$

Structure XX corresponds to the previously mentioned hyperconjugation structures and would account for a lowering of the dipole moment in this compound. Unfortunately propargyl cyanide seemed to decompose when attempts were made to prepare it. No measurements on that compound could be made.

The dipole moments of a few amines were run in this work. Due to the large number of assumptions which would have to be made in the interpretation of these moments, and the great variation in reported values for amines, no conclusions can be drawn regarding them.

SUMMARY

SUMMARY

The dipole moments of several series of unsaturated aliphatic compounds have been determined by the refractivity method. These moments provide evidence that hyperconjugation is important in allyl and propargyl derivatives. Resonance in the halides, the alcohols, and the cyanides has been discussed in detail. No conclusions could be drawn from the moments measured for the ethers and the amines.

REFERENCES

REFERENCES

1. N. V. Sidgwick, <u>The Covalent Link in Chemistry</u>, Cornell University Press, Ithaca, New York, 1933, Chapter V.

2. C. P. Smyth, <u>Dielectric Constant and Molecular Structure</u>, Chemical Catalog Co., New York, N. Y., 1931.

3. P. Debye, <u>Polar Molecules</u>, Chemical Catalog Co., New York, N. Y., 1929.

4. <u>Ibid.</u>, page 29.

5. G. W. Wheland, <u>The Theory of Resonance</u>, John Wiley & Sons, New York, N. Y., 1944.

6. <u>Ibid.</u>, page 168.

7. <u>Ibid.</u>, page 132.

8. <u>Ibid.</u>, page 298.

9. <u>Ibid.</u>, page 131.

10. R. J. W. LeFevre, <u>Dipole Moments</u> (2nd Edition), Methuen & Co., London, 1948, pg 5-6.

11. <u>Ibid.</u>, page 7-9.

12. Y. K. Syrkin and M. E. Dyatkina, <u>The Structure of Molecules</u>, Interscience Publishers Inc., New York, N. Y., 1950, page 197.

13. <u>Ibid.</u>, page 217.

14. <u>Ibid.</u>, page 211.

15. <u>Ibid.</u>, page 212.

16. <u>Ibid.</u>, page 180.

17. <u>Ibid.</u>, page 219.

18. I. F. Halverstadt and W. D. Kumler, J. Am. Chem. Soc., <u>64</u>, 2988 (1942).

19. J. Chien, J. Chem. Educ., <u>24</u>, 494 (1947).

20. H. Gilman and A. H. Blatt, <u>Organic Synthesis</u> (2nd. Edition), Collective Volume I, Wiley, New York, N. Y., 1941.

21. W. West and B. Paul, Trans. Faraday Soc., <u>28</u>, 688-97 (1932).

22. K. N. Campbell and J. T. Eby, J. Am. Chem. Soc., <u>62</u>, 1798-1800 (1940).

23. <u>Appendix on Dipole Moments</u>, Trans. Faraday Soc., <u>30</u> (1943).

24. R. A. Spurr and H. Zeitlen, J. Am. Chem. Soc., <u>72</u>, 4832 (1950).

25. E. G. Cowley and J. R. Partington, J. Chem. Soc., 604 (1935).

26. T. L. Jacobs and W. F. Brill. Abstracts of Papers Presented at Am. Chem. Soc. National Meeting Atlantic City, N. J., Division of Organic Chem., Sept. 14-19, 1952, and private communication.

27. L. Pauling, W. Gordy, J. H. Saylor, J. Am. Chem. Soc., <u>64</u>, 1753-6 (1942).

28. G. R. Robertson, Ind. Eng. Chem. Anal. Ed., <u>11</u>, 464 (1936).

29. M. T. Rogers and M. Patapoff, unpublished results.