

THE DETERMINATION OF THE ELECTRIC DIPOLE MOMENT  
OF CERTAIN ORGANIC COMPOUNDS

Thesis by Charles R. Daily

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## 1. Introduction:

The determination of the electric dipole-moment of molecules has assumed considerable importance in recent years as a means of recognizing and distinguishing various chemical structures. Recent experimental work in this field by Williams<sup>1,2,3,4,5</sup>, Smyth<sup>6</sup>, Errera<sup>7</sup>, Hojendahl<sup>8</sup>, and others on the basis of the Debye theory of binary liquid mixtures has shown that the dipole moment of polar molecules may be considered as a vector quantity. The magnitude of this moment may then be used in interpreting the molecular structure. The purpose of this paper will be to consider certain special chemical types containing CH<sub>3</sub> and Br groups in various molecular combinations.

The development of constant radio frequency oscillators constituted the first part of the experimental work undertaken and data is presented on two types which have been tested.

The construction and testing of the circuits used for the dielectric constant determinations is described in detail.

## 2. Theory of Electric Dipole-Moments.

The complete theory of the dipole moments of gases and dilute solutions was first presented by Debye<sup>9,10,11</sup> and his treatment of the subject forms the basis for most of the recent experimental work in this field. The Debye theory has since been checked theoretically by R. de L. Kronig<sup>12</sup> and Mensing & Pauli<sup>13</sup> on the basis of the new quantum mechanics. C. Manneback<sup>14</sup> has also derived the Debye equation using Schrödinger's wave mechanics. Thus it may be assumed that it is well verified by the more recent advances in physical theory.

According to this theory, if a dielectric is placed in an external field of force  $F$ , we may write for the molar polarization of a molecule which is free to assume a perfectly random orientation in either a gas or in a dilute solution:

$$P = \frac{e - 1}{e + 1} \cdot \frac{M}{d} = \frac{4\pi N}{3} \cdot \left( \frac{\mu^2}{3kT} + \alpha \right) = \frac{B}{T} + A \quad (1)$$

where  $e$  = dielectric constant,  $M$  = molecular weight,  $d$  = density,  $N$  = no. of grams in a gram molecule =  $6.062 \times 10^{23}$ ,  $\alpha$  = molecular polarizability,  $k$  = molecular gas constant =  $1.372 \times 10^{-16}$ ,  $\mu$  = electric dipole moment of a single molecule, and  $T$  = absolute temperature.

"A" is the polarization produced by the deformation, or shift of charges, in the structure of the molecule induced by the external field of force. The molecule is assumed to have an elastic structure and since the displaced electrons have a very small mass, this component of the

polarization will be maintained even for very high frequencies.

"B" is the polarization resulting from the induced moment per molecule produced by the acting field. It thus represents the effect of the orientation of the molecules in the field and is the only term of the polarization that is affected by temperature changes.

If now we have two components in solution, by the volume mixture law the molar polarization for the solution may be written:

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{(f_1 M_1 + f_2 M_2)}{d} = f_1 P_1 + f_2 P_2 \quad (2)$$

where  $f_1$  and  $f_2$ ,  $M_1$  and  $M_2$ ,  $P_1$  and  $P_2$  refer to the mole fractions, molecular weights, and molar polarizations of components 1 and 2 in the solution.

The validity of the volume-mixture law for the Clausius-Mosotti law which is involved in the derivation of this formula has been checked by Hubbard<sup>15</sup>, Hojendahl<sup>8</sup>, Philip<sup>16</sup>, and others, and may be assumed to be correct.

If  $P_1$  refers to a non-polar solvent such as benzene, then  $P_2$  which represents the molar polarization for the polar solute molecules may be obtained graphically by extrapolating the  $P_{12}$  curve to infinite dilution as shown by the dotted line in Figure 4 which is included in the experimental section of this paper. This extrapolation will give the molar polarization due to a single polar molecule completely surrounded by the non-polar solvent. The justification of this extrapolation and the interpretation of this form of curve is explained by Debye<sup>11</sup>.

As shown by Eq. 1, the polarization for the pure solute is composed of two parts which may be written:

$$P_2 = (P_2' + P_2^{n'}) + P_2^n \quad (3)$$

$P_2'$  corresponds to  $B/T$  in eq. 1 and represents the orientation polarization produced by the external field and it is this quantity that we wish to determine.

$P_2^n$  corresponds to  $A$  in eq. 1 and represents the polarization due to deformation and is called the molecular refraction or the molecular electron-polarization since only the displacement of electrons in the molecular structure have a part in determining it. It may be approximated by the Lorenz-Lorentz relation, the proof for which has been demonstrated by Lorentz<sup>17</sup>, Lange<sup>18</sup>, and Debye<sup>11</sup>.

$$P_2^n = \frac{N_0^2 - 1}{N_0^2 + 2} \cdot \frac{M}{d} \quad (4)$$

where  $N_0$  represents the index of refraction extrapolated to zero frequency and is valid providing no infra-red absorption occurs. Since little is known concerning this absorption, the value of  $P_2^n$  used may be in error by a small amount. But serves as a fair~~ly~~ approximation in the calculation of the dipole moment.

$P_2^{n'}$  represents the polarization produced by the displacement of polarized or ionized atoms and groups of atoms or radicals comprising the molecule. This quantity at low frequencies is generally negligible and has been neglected in this treatment.  $P_2^{n'}$  becomes zero in the solid state because the molecules are rigidly bound and will not be oriented by the external field. The justification for the omission of

this component of the polarization is treated by Lange<sup>18</sup>.

$P_2$  for the various concentrations used may be calculated from eq. 2, when it is assumed that  $P_1$ , the molar polarization for the solvent is constant.

$$P_2 = \frac{P_{12} - f_1 P_1}{f_2} = \frac{P_{12} - P_1}{f_2} + P_1 \quad (5)$$

Finally, since  $P_2^n$  is known from refractive data, and  $P_2$  is known from the extrapolated  $P_{12}$  curve obtained from dielectric data,  $P_2'$  may be calculated directly from eq. 3. From this value of  $P_2'$ ,  $\mu$  may be evaluated using eq. 1.

$$P_2' = P_2 - P_2^n = \frac{4\pi N \mu^2}{9kT} \quad (6)$$

$$\mu = \sqrt{\frac{9kT}{4\pi N} P_2'} = 2.196 \times 10^{-19} \sqrt{P_2'} \quad (7)$$

where  $T = 298^\circ \text{K}$  as this is the temperature used in most of the experimental work to follow.

The vector theory for the interpretation of the dipole moments as above determined was first suggested for the case of di-substituted benzene compounds by J. J. Thomson<sup>19</sup> and approximate agreement has been obtained by several investigators including Errera<sup>7</sup>, Smyth & Morgan<sup>6</sup>, and Williams & Schwingel<sup>4</sup>. The experimental evidence available up to the present time indicates that in the p-disubstituted benzene molecule, the resultant moment is equal to the algebraic sum of the moments of the separate polar groups and this has been verified for p-bromotoluene within the limits of experimental error by the author. The steric effect present in the ortho and meta compounds which makes the calculation of the angles between

the vector dipole-moments in the molecule somewhat uncertain, is also present in the other molecules considered in this investigation and each will be discussed in the experimental section to follow.

### 3. Apparatus Development:

The dielectric constants of the solutions used were measured by means of a high frequency resonance system similar to those described by Williams<sup>1</sup> and Smyth<sup>6</sup>. The principle upon which this form of measurement is based is a very useful one in the field of physical measurements and a number of applications have been suggested by Wegstaff<sup>20</sup>, Belz<sup>21</sup>, Whiddington<sup>22</sup>, Dowling<sup>23</sup>, Sucksmith<sup>24</sup>, Scott-Taggart<sup>25</sup>, and others.

The general principle of the resonance method utilizes the fact that the beat frequency between two oscillators which are operating at approximately the same frequency may be accurately measured by comparing this beat frequency with a tuning fork, vibrating reed, or other constant low frequency generator.

In the apparatus as used, one oscillator utilized a quartz crystal to maintain a constant frequency of  $9.88 \times 10^5$  cycles per second. The oscillator used for the dielectric measurements was not crystal controlled because it is used to measure the changes in frequency produced by the introduction of a dielectric in the measuring condenser. Under normal operating conditions however its frequency should be very stable so that corrections would not have to be applied to the results obtained on the dielectric measurements.



Therefore the first part of the development program was to construct a suitable oscillator for this purpose.

First will be presented an analysis of the stabilized Hartley type of oscillator which offers considerable opportunities for future development, and second, an analysis of the Meissner type of oscillator which was finally adopted for dielectric measurements.

### 3. A. Stabilized Hartley Oscillator:

Following the accidental discovery by Mr. Rose of the Bell Telephone Laboratories that a certain impedance placed between the grid and the tuned circuit of an oscillator would render the frequency independent of the battery voltages, Mr. F. B. Llewellyn of the same organization suggested the following analysis for the Hartley oscillator.

The frequency of any oscillator will depend on all of the parameters in the circuit, namely, the self inductance  $L$  of the network, the mutual inductance  $M$ , the capacity  $C$ , the resistance  $R$  of the network, the plate resistance  $r_p$  of the tube used, the grid resistance  $r_g$  of the tube, and  $\mu$ , the amplification factor for the tube. With careful construction, all of these parameters may be considered as essentially invariant with the exception of  $r_p$  and  $r_g$  which of course depend directly on the battery voltages used. Assuming that  $r_g$  is arbitrarily made very large which is an easily realized condition experimentally, then any small change in  $r_g$  will have a negligibly small effect on the frequency compared with the changes which will occur simultaneously in  $r_p$ . Therefore the condition we wish to realize is that  $\frac{\partial \omega}{\partial r_p} = 0$ , where  $\omega \approx 2\pi f$ .

In Fig. 1 we have the schematic form of the circuit to be considered, with no special arrangements indicated for connecting in the batteries.

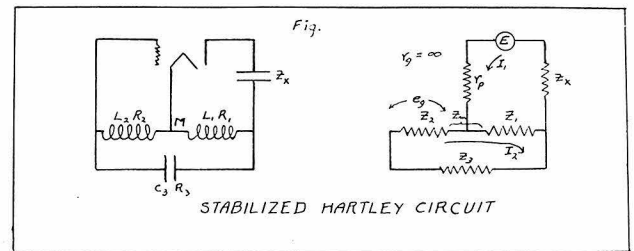


Fig. 1.

Using the current directions as shown by the arrows, we can write the circuit equations as follows:

$$\mu e_g = I_1(r_p + Z_x + Z_1) + I_2(Z_1 + Z_m) \quad (8)$$

$$0 = I_1(Z_1 + Z_m) + I_2 Z_0 \quad (9)$$

$$e_g = I_1 Z_m + I_2(Z_2 + Z_m) \quad (10)$$

where:

$$Z_0 = Z_1 + Z_2 + Z_3 + 2Z_m = A + iB$$

$$Z_1 = R_1 + i\omega L_1$$

$$Z_x = -1/\omega C_x$$

$$Z_2 = R_2 + i\omega L_2$$

$$A = R_1 + R_2 + R_3$$

$$Z_3 = R_3 - 1/\omega C_3$$

$$B = \omega L_1 + \omega L_2 + 2\omega M - 1/\omega C_3$$

$$Z_m = i\omega M$$

Solving equations 8, 9, and 10, eliminating  $e_g$ ,  $I_1$  and  $I_2$ , and substituting the equivalent quantities for the other variables as indicated above, we obtain:

$$(r_p - 1/\omega C_x)(A + iB) + (R_1 + i\omega L_1) \left\{ \left\{ (\mu + 1)R_2 + R_3 \right\} + i \left\{ (\mu + 1)\omega L_2 - 1/\omega C_3 \right\} \right\} - i\omega M \left\{ \mu R_3 - i \left\{ -(\mu + 1)\omega M + (\mu/\omega C_3) \right\} \right\} = 0 \quad (11)$$

The real part of eq. 11 gives the conditions under which oscillations will occur in the circuit while the imaginary part gives the conditions which determine the frequency of oscillations and it is this second part that we are interested in.

Equating the imaginary part to zero we obtain:

$$-A/\omega C_x + Br_p + R_1 \left\{ (\mu+1)\omega L_2 - 1/\omega C_3 \right\} + \omega L_1 \left\{ (\mu+1)R_2 + R_3 \right\} - \mu \omega MR_3 = 0 \quad (12)$$

If changes in  $r_p$ , which are caused by battery voltage fluctuations, are not to affect the frequency of oscillation, then  $B = 0$  is a necessary conclusion. Therefore:

$$B = 0 = \omega L_1 + \omega L_2 + 2\omega M - 1/\omega C_3 \quad \text{which leads to}$$

$$\omega^2 = 1/C_3(L_1 + L_2 + 2M) = \omega_0^2 \quad (13)$$

Eq. 13 proves the very important fact that if the frequency of oscillation is to be independent of the plate resistance, then the frequency of the oscillation will be the natural frequency of the tuned circuit.

Solving the remainder of eq. 12, substituting for  $\omega$  its value as obtained in eq. 13, we obtain:

$$C_x = \frac{C_3 (R_1 + R_2 + R_3)(L_1 + L_2 + 2M)}{L_1 \left\{ (\mu+1)R_2 + R_3 - R_1 \right\} + L_2 (\mu R_2 - M(2R_1 + \mu R_3))} \quad (14)$$

= stabilizing impedance which will make the frequency independent of changes in battery voltages.

In practice this equation can be materially simplified.

For example, let:

$$L_1 = L_2 = L_0 \quad R_1 = R_2 = R_0 \quad R_3 = 0$$

Therefore:

$$C_x = C_3 \frac{(2L_0 + M)}{\mu L_0 - M} \quad (15)$$

and a still further simplification results if

$$M = 0.$$

$$\underline{C_x = 2C_3/\mu} \quad (16)$$

The result of eq. 16 may be checked very readily. A Hartley circuit similar to Fig. 1 was constructed having a natural frequency of  $10^6$  cycles per second,  $C_3 = 300$  mmf, and  $\mu \approx 8$  for the UX 201-A tube used. These quantities when substituted in eq. 16 yield the result that  $C_x = 75$  mmf is the capacity, which if inserted in the plate circuit, would render the frequency independent of battery voltages. This value was found to hold experimentally within the limits of error caused by neglecting the other variables in the circuit, especially the internal tube capacity, and so may be considered as a complete check on the theory.

In order to adjust  $C_x$  accurately to the proper value, a switch was provided which would increase the plate voltage by an amount  $\Delta E_p = 4.5$  volts. Having set  $C_x$  at approximately the right value, the change  $\Delta E_p$  would cause some corresponding change in frequency  $\Delta f$ . Values of the condenser readings  $C_x$  were then plotted against  $\Delta f$  for this constant  $\Delta E_p$  and the point found where  $\Delta f = 0$ .  $\Delta f$  could be made to change sign by continually varying  $C_x$  on either side of the point of stabilization. The adjustment of  $C_x$  to the proper value was very critical and the slightest error in setting would result in enormous frequency changes for the  $\Delta E_p$  used in the setting.

This circuit was not as useful as had been expected because after stabilization had once been effected, uncontrollable variations in other parts of the circuits would, in an hour or two, vary the constants so that  $C_x$  as adjusted no longer had the proper value for stabilization. When such a condition occurs, the resulting  $\Delta f$  is much larger than if the impedance  $C_x$  had not been used in the circuit. It is the small changes

produced in the circuit incident to the handling of the apparatus while making the dielectric measurements which change the various circuit parameters and so cause the unstabilization of the apparatus. For this reason such a circuit was not used in the final measurements, although the principle on which it is based is perfectly sound.

Development work which has been done on this type of circuit at the Bell Telephone Laboratories in conjunction with oscillators to be used in carrier frequency telephone apparatus have proven the value of the theory especially at low frequencies. The carrier channels have a minimum separation and it is absolutely necessary that the frequency of each channel remain constant in order that cross-talk and other attendant difficulties may be avoided. Such an oscillator constructed to operate at a frequency of 35000 cycles per second remained absolutely stable, with changes in frequency of the order of only 0.1 cycles resulting from a change in the plate voltage of 50%. At such a low frequency, the inductances and capacities are much larger than those used at radio frequencies and thus are correspondingly<sup>less</sup> influenced by small changes in capacity to ground, tube capacities, etc. which so markedly affect oscillators operating at radio frequencies. It is possible however that with quite different circuit constants, a better approach to permanent stability can be made at the higher frequencies.

### 3. B. Meissner Dielectric Oscillator:

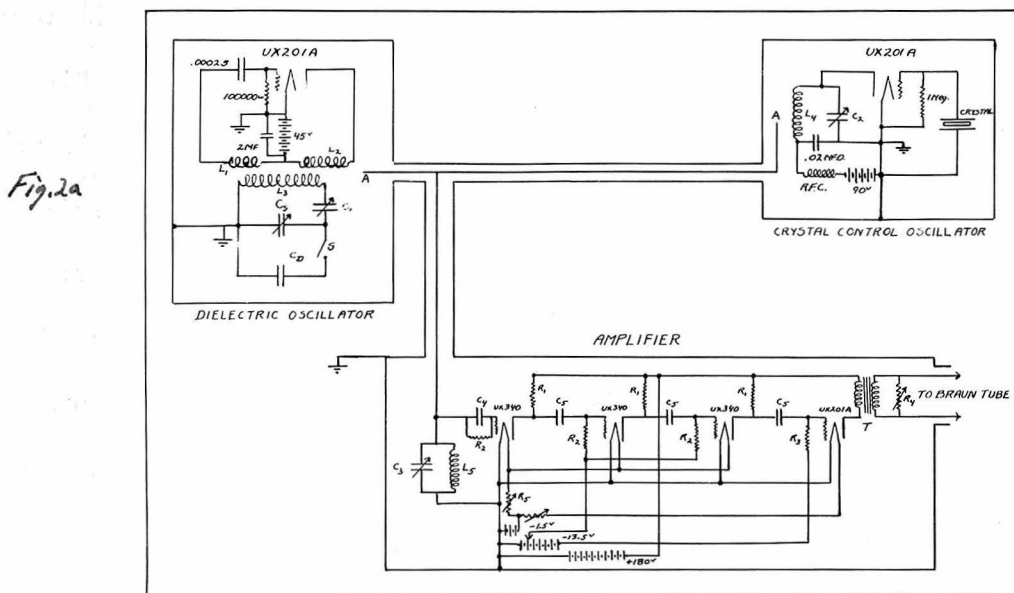


Fig. 2.

The Meissner oscillator<sup>26</sup> as shown in Fig. 2a was finally chosen for dielectric measurements because of its inherent frequency stability. Changes in plate voltage and filament current have an almost negligible effect on the frequency. Tests were conducted and it was found that with varying values of the grid leak resistance from  $10^5$  to  $10^6$  ohms, the maximum  $\Delta f$  observed was 20 cycles in  $10^6$  cycles for changes of plate voltage from 30 to 90 volts. Changes in filament current had a correspondingly small effect on the frequency.

The coils  $L_1$ ,  $L_2$ , and  $L_3$  were of a special construction suggested by Dr. Frayne who had used a similar circuit at the General Radio Company. Fifteen turns of #22 DCC wire were wound on a 3-inch bakelite tube for  $L_1$ , the grid coil, then fifteen turns for  $L_3$ , the oscillating coil, then 15 turns

for  $L_2$ , and so on until  $L_1 = 15$  turns,  $L_2 = 30$  turns,  $L_3 = 45$  turns. This staggered arrangement provides for a low distributed coil capacity with high inductive coupling between the plate and oscillating coils.  $C_1$  is a series tuning condenser of 250 mmf capacity;  $C_2$  is a General Radio Precision condenser, Type 222, 0-1500 mmf. It was provided with a 25 point calibration chart so that differences of capacity could be read directly to within 0.06 mmf.  $C_3$  is a concentric cylinder condenser used for the liquid dielectric. It was constructed of heavy walled brass tubing with bakelite end blocks to keep the inner cylinder accurately concentric with the outer cylinder. The effective length of the cylinders was 8.9 cms with a spacing between them of 1.3 mms. Its capacity in air was 91.5 mmf. The space between the plates contained all of the dielectric to be measured so that measurements could be made on as small as 25 cc of solution. This is a distinct advantage in that it reduces the quantities of materials that must be purified to a minimum. The liquid to be measured could be poured in at the top of the condenser thru a glass tube provided with a stopcock. This stopcock was closed while the liquid was being measured, thus preventing evaporation which would have continuously changed the mole fraction of substance in solution. After the measurement of the dielectric constant had been completed, the liquid was siphoned off thru a tube leading out of the bottom of the condenser.

The measuring condenser,  $C_d$ , was submerged in a water bath maintained at a constant temperature by means of a sensitive mercury thermostat. This water was circulated continuously thru the condenser bath as well as thru the bath used in connection with the density measurements, and finally thru the refractometer. The circulation was rapid, being maintained by a water pump, so that all three parts of the apparatus were kept at the same temperature. The difference in temperature between the various parts of the system was never greater than  $0.1^\circ\text{C}$  and the absolute temperature was kept ~~at~~ kept at  $25 \pm .05^\circ\text{C}$  except for the measurements on p-bromotoluene in which case the temperature was maintained at  $27.5^\circ$ . All thermometers used were carefully standardized.

The switch S in Fig. 2a was used to disconnect  $C_d$  from the circuit. In all cases, measurements were made on  $C_s$  with S open and closed alternately. In this way any change in the frequency of the oscillator caused by accidental jarring of the cases could be detected immediately and the dielectric measurements repeated if necessary.

The oscillator was allowed to operate continuously for several weeks while the necessary observations were being taken. During this interval there were noted only small frequency changes which were probably due to a slight warping of the table and the circuit supports, as well as small changes in the relative position of the shielding with respect to the circuit.



During the course of any individual dielectric determination, the frequency did not change by more than ten cycles in a million, which was well within the limits of experimental error in the determination of the dielectric constant.

The heterodyning beat note oscillator shown diagrammatically in Fig. 2b was crystal controlled because this type of circuit maintains a constant frequency, dependent almost entirely on the properties of the crystal itself. Extensive studies have been conducted in the field of piezo-electricity by G. W. Pierce<sup>27</sup>, W. C. Cady<sup>28</sup>, and others, and they have shown that the frequency of such oscillators is constant to one part in a million if the temperature, pressure on the crystal, and load are kept constant. The temperature coefficient is about 1 cycle in 50000 per degree. Since the fundamental frequency of the crystal used was  $9.88 \times 10^5$  cycles per second, a change in temperature of 1° C. would cause a frequency change of about 20 cycles. To minimize this effect, the entire room in which the apparatus was housed was thermostatically controlled to within 0.2°C. This precaution likewise prevented slow frequency changes in the dielectric oscillator due to expansion or contraction of the coil forms, condensers, and supports.

The circuit  $L_2C_2$  was tuned to the frequency of the crystal and this adjustment could be checked by noting the decrease in plate current when the circuit was adjusted to resonance.

The dielectric and crystal controlled oscillators were completely shielded. A brass rod A extended between the two oscillators to provide coupling between them to the beat note amplifier. This rod extended into the oscillator cases for about three inches and the coupling thus provided was so weak that the frequency of the two oscillators could be adjusted to within one cycle of each other with no synchronization taking place.

The coupling rod A was in turn connected to a tuned circuit  $C_3L_5$  in the first stage of the beat note amplifier as shown in Fig. 2c. This tuned circuit increased the voltage drop across the grid of the first tube which acted as a detector to separate the audible beat note from the radio frequency input. This audible frequency was then amplified in the circuit shown about 20000 times and the output obtained from the secondary of the transformer, T.  $R_4$  is a variable high resistance potentiometer used to control the amplitude of the output voltage which was applied to one pair of plates on a Braun oscillographic cathode ray tube. The other circuit constants were:  $C_4 = 0.1$  mmf fixed condenser,  $C_5 = 0.0005$  mmf,  $R_1 = 0.25$  megohms,  $R_2 = 2$  megohms,  $R_3 = 1$  megohm,  $R_5 = 6$  ohm filament resistances.

In order to provide a comparison source of frequency for the beat note, a vacuum tube driven tuning fork drive was constructed as shown in Fig. 3. TF is a 435 cycle fork mounted in a heavy steel frame. The coupling and driving units to the fork were provided by two Western Electric phone units,  $P_2$ , adjusted so that the poles of their permanent magnets were

within 0.75 mms of the tuning fork. The d.c. component of plate current in the last tube is about 10 m.a. which would be excessive for the phone unit,  $P_2$ . Therefore

a General Radio Speaker Filter, S.F. was inserted so that only the a.c. component of the plate current flowed thru the plate driving coil. The output from this generator was obtained across an impedance  $P_1$ , suitably controlled by a variable resistance  $R_8$ . This output was connected to the second pair of plates in the Braun tube. It is interesting to note that with this arrangement, an a.c. output voltage of 75 to 100 volts on no load could easily be obtained, as was the case also with the beat note amplifier.

The other circuit constants in the tuning fork drive were:  $R_1 = 0.25$  megohms,  $R_3 = 1$  megohm,  $R_5 = 6$  ohm filament resistors,  $R_6 = 5$  megohm variable grid leak to control the input voltage to the grid of the second tube,  $R_7 = 0.5$  megohms, and  $C_3 = 1$  mfd coupling condensers.

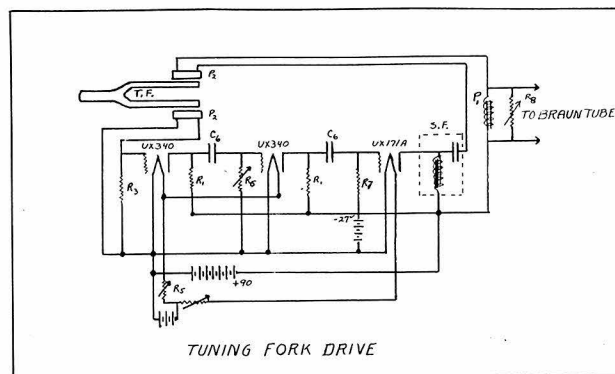


Fig. 3

#### 4. Experimental Procedure:

##### A. Purification of Chemicals:

All chemicals used were obtained from the Eastman Kodak Co. in a very pure form. Each was further purified as indicated.

Benzene: Thiophene free benzene was stirred with several portions of conc.  $H_2SO_4$  until no further discoloration took place. It was then washed with distilled water and dilute NaOH solution and stirred with clean mercury for 24 hours. The benzene was then dried over  $P_2O_5$ , distilled, and kept over metallic sodium. B.P.<sub>745</sub> 79.4-79.6°C. Benzene which was twice frozen out over ice before distilling showed no variation in dielectric constant.

Toluene: Toluene prepared from sulfonic acid was stirred with conc.  $H_2SO_4$ , washed with distilled water and NaOH, and allowed to stand over mercury for two days. It was then dried over  $P_2O_5$ , distilled and kept over metallic sodium. B.P.<sub>745</sub> 107.9-108.1°C.

Bromobenzene: The E. K. Co. product was dried over  $P_2O_5$  and distilled. B.P.<sub>745</sub> 152-153°C.

p-Bromotoluene: The E. K. Co. product was crystallized three times and dried over conc.  $H_2SO_4$  in a dessicator. M.P. 26-27°C.

n-Propyl Bromide: The E. K. Co. product was dried over  $P_2O_5$  and distilled. B.P. 68.6-69.4°C.

iso-Propyl Bromide: Same treatment as n-propyl bromide.  
B.P. 57.1-58.1.

Ethyl Bromide: Dried over  $P_2O_5$ .

#### 4. B. Determination of the Dielectric Constant.

In making dielectric constant determinations with the previously described apparatus, a pair of phones connected to the amplifier served to detect the beat note. With the switch S open, the beat note was adjusted by varying the condenser  $C_S$  to a frequency approximately equal to that of the tuning fork.  $R_4$  was adjusted so that the deflection on the Braun tube was about 3 cms. The deflection at right angles to the first, and produced by the tuning fork drive, was adjusted to about the same value by the controls  $R_6$  and  $R_8$ . If  $C_S$  is then varied carefully until the beat note exactly equals that of the tuning fork, the resulting Lissajou figure observed is either a straight line or a circle depending on the phase relations between the two frequencies. Changes in frequency of the beat note as small as 0.05 cycles can be readily detected, corresponding in the present case to a change in frequency of the dielectric oscillator of one part in  $2 \times 10^7$ , which approaches the order of accuracy obtainable with an interferometer. While such precision is not required in the measurement of the dielectric constants of liquids, it would be required in the accurate determination of the dielectric constants of gases.

Closing switch S increases the capacity of the resonant circuit and in order to bring the beat note back to its original value,  $C_S$  is readjusted. The change in  $C_S$  is then a measure of the capacity of  $C_d$  plus lead capacity. If a dielectric other than air is now inserted in  $C_d$ ,  $C_S$  is again adjusted to resonance and this second change in  $C_S$  will be proportional to the dielectric constant of the liquid used.

In the present work, the dielectric constant of benzene was used to calibrate the apparatus because it was to be used as the solvent for all of the liquids whose moments were to be determined. Absolute determinations of  $\epsilon$  for benzene have been made by Williams<sup>1</sup>, Hartshorn<sup>29</sup>, and others, and a value of  $\epsilon = 2.282$  for benzene at 25° C. has been used in this work.

Since the beat frequency was always made equal to that of the tuning fork, the fundamental frequency, and therefore the total capacity of the dielectric oscillator was necessarily kept constant for all measurements since no other changes occurred in the circuit. The equations for determining the dielectric constant of any liquid in terms of the dielectric constant of benzene might then be written as follows:

$C_{s1}$  = capacity of standard air condenser,  $\epsilon = 1$  for diel. in  $C_d$ .  
 $C_{s2}$  = " " " " " " ,  $\epsilon_1 = 2.282$  for  $C_6H_6$  in  $C_d$   
 $C_{s3}$  = " " " " " " ,  $\epsilon_2 = ?$  for unknown.

therefore:  $C_{s1} + C_d = K$

$C_{s2} + \epsilon_1 C_d = K$

$C_{s3} + \epsilon_2 C_d = K$

Solving we obtain:

$$\epsilon_2 = 1 + (\epsilon_1 - 1) \frac{C_{s1} - C_{s3}}{C_{s1} - C_{s2}} \quad (17)$$

Eq. 17 was used in the calculation of dielectric constants of the solutions in terms of  $\epsilon_1 = 2.282$ , the diel. constant of benzene.

After each measurement, the condenser was washed with benzene, pumped out for ten minutes, and dry compressed air passed thru it to remove all impurities which might contaminate future solutions used. All compounds were readily soluble in benzene and no difficulty was experienced in checking readings.

#### 4. C. Measurement of Mole Fractions, Density, Index of Refraction

The compounds used were to be dissolved in benzene, and since most of these solutions differ from ideal solutions, particularly at the lower concentrations, only these values were studied because it is the value of the polarization at infinite dilution that is of interest. The liquid to be measured was carefully weighed in a volumetric flask fitted with a ground glass stopper; then weighed again after pure benzene had been added to make the total volume of solution approximately 50 cc. The mole fraction of the polar liquid in benzene could then be calculated very accurately.

Density measurements on the solutions were made by the usual pynknometer method immediately after the determination of the dielectric constant. The pynknometer used was provided with ground-in thermometer, and a glass cap with ground joint to fit over the capillary stem to prevent evaporation during the time required for weighing. The temperature of the bath in which the pynknometer was hung was regulated very carefully as has been described in a previous section.

The values of density obtained agreed very well with values taken by other observers and with values calculated from data in the International Critical Tables, Vol. III, p 27.

$d_4^{25}$	Table 1.			
	Benzene	Bromobenzene	Toluene	$C_2H_5Br$
Measured	0.8735	1.4885	0.8623	1.4490
Calc. I.C.T.	.8734	1.4887	.8610	
Williams (1)	.8731		.8593	
Smyth (30)				1.4479

Measurements of the index of refraction of the liquids used were made with an Abbe refractometer using a sodium flame for illumination. In calculating the optical polarization, the index of refraction should be extrapolated to zero frequency. In order to do this accurately, determinations of the index of refraction would have to be made at various wavelengths before the extrapolations could be made with certainty. This would require a Pulfrich refractometer which was not available. With this instrument, the dispersion of liquids can be measured with considerable accuracy.

Table 2 compares the data taken from an average of ten readings of  $n_d$  with those obtained by Williams<sup>1</sup> using a Pulfrich refractometer.

Table 2.

	Benzene	Bromobenzene	Toluene
Measured	1.49784	1.55702	1.49398
Williams	1.49780	1.55711	1.49392

##### 5. Experimental Results and Discussion:

Determinations of the dipole-moment of bromobenzene and toluene were first undertaken to obtain the probable value of the moment of Br and CH<sub>3</sub> groups singly before combinations of the two were studied.

The following pages give the results of the determinations on the various compounds studied with an analysis of each.



Table 3 presents the results obtained for the bromobenzene-benzene mixture. Figure 4 shows the variation of  $P_{12}$  with the mole fraction of  $C_6H_5Br$  in solution.

Table 3. Bromobenzene.

Mole Fract. $C_6H_6$	$d_4^{25}$	$n_d^{25}$	$e$	$P_{12}^{cc.}$	$P_2$
1.0000	0.8735	1.49784	2.282	26.75	93.25
.9528	.9068	1.50093	2.458	29.49	84.75
.9002	.9442	1.50444	2.640	32.16	80.96
.8027	1.0113	1.51094	2.972	36.71	77.24
.5711	1.1622	1.52542	3.727	45.85	71.28
.0000	1.4885	1.55702	--	--	--

$$P_2^n = 33.96$$

$$\mu = 1.69 \times 10^{-18} \text{ esu}$$

Hojendahl<sup>8</sup> obtains a value of  $\mu = 1.56 \times 10^{-18}$ ; calculations from dielectric constant measurements of Kerr<sup>31</sup> give  $\mu = 1.71 \times 10^{-18}$ , while Williams<sup>5</sup> obtains a value of  $\mu = 1.51 \times 10^{-18}$ .

These values are in agreement within the limits of

experimental error with that obtained by the author. The moment obtained for  $C_6H_5Br$  represents the moment of Br alone since the remainder of the benzene ring does not contribute to the moment. The moment of benzene has been found to be zero by several observers<sup>32,33</sup> using  $CS_2$ ,  $CCl_4$ ,  $C_6H_6$ , and  $C_6H_{14}$  as solvents.

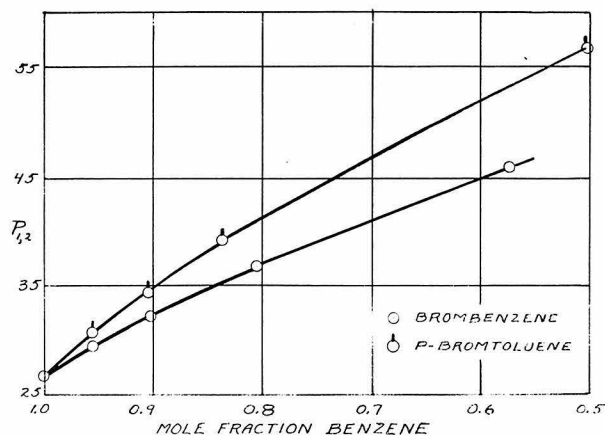


Fig. 4

The fact that benzene has a zero moment agrees also with experiments on p-dinitrobenzene, sym-trinitrobenzene, and sym-tribromobenzene<sup>8</sup>, all of which yield dipole moments which are not larger than the experimental error.

In this connection it should be mentioned that since it is  $P_2'$  that is measured, and since  $P_2'$  is proportional to  $\mu^2$ , a small value of  $\mu$  corresponds to a value of  $P_2'$  which is so small that it may not be distinguishable from zero.  $P_2'$  enters into the equation as a difference between  $P_{12}$  and  $P_2''$ , both of which are experimentally determined quantities, and an error in either, particularly in  $P_2$  which is obtained by extrapolation, will lead to a large error in  $\mu$  for small values of this difference.

Table 4. Toluene.

M.F. $C_6H_6$	$d_4^{25}$	$n_d^{25}$	$e$	$P_{12}$	$P_2$
1.0000	.8735	1.49784	2.282	26.75	35.90
.9072	.8720	1.49725	2.294	27.42	33.97
.8019	.8703	1.49597	2.314	28.29	34.52
.6025	.8679	1.49572	2.331	29.61	33.95
.0000	.8623	1.49398	2.387	33.75	33.75

$$P_2'' = 31.08$$

$$\mu \approx 0.48 \times 10^{-18} \text{ esu}$$

For toluene, the extrapolated value of  $P_2$  is somewhat uncertain and the final value of  $\mu$  may be in error by 10%. The above value for  $\mu$  however agrees with values obtained by other observers.

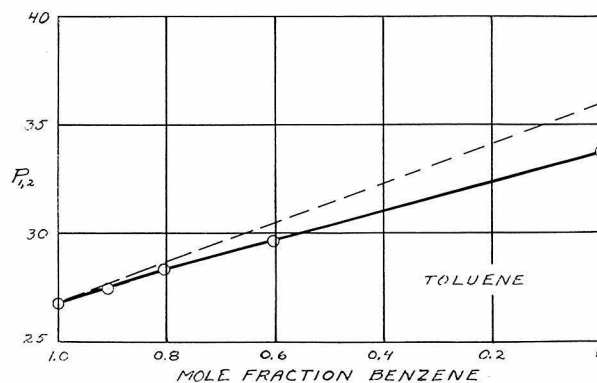


Fig. 5.

Williams<sup>2</sup> obtains  $\mu = 0.52 \times 10^{-18}$  while Smyth & Morgan<sup>6</sup> obtained a value of  $\mu = 0.40 \times 10^{-18}$ .

The dipole-moment obtained for toluene represents the moment of the  $\text{CH}_3$  group attached to the benzene ring. From the data obtained on toluene and bromobenzene, we can now discuss the results obtained for combinations of  $\text{CH}_3$  and Br in the case of the following compounds.

Table 5. p-Bromotoluene.

M.F. $\text{C}_6\text{H}_6$	$d_4^{27.5}$	$n_d^{27.5}$	$e$	$P_{12}$	$P_2$
1.0000	.8708	1.49784	2.280	26.80	118.4
.9550	.9002	1.50010	2.514	30.64	112.1
.9039	.9363	1.50330	2.765	34.41	106.0
.8352	.9816	1.50780	3.097	39.13	101.6
.5018	1.1721	1.52619	4.466	56.86	87.14
.0000	1.3993	1.54768	--	--	--

$$P_2^* = 24.51$$

$$\mu = 2.13 \times 10^{-18} \text{ esu}$$

If the steric effect is negligible in the para form of the di-substituted benzene ring, then we would expect a strictly additive result for the moments of  $\text{CH}_3$  and Br.

$$\begin{aligned} \mu &= (1.69 + .48) \times 10^{-18} = 2.17 \times 10^{-18} \text{ by vector addition} \\ &\approx 2.13 \times 10^{-18} \text{ measured.} \end{aligned}$$

The agreement obtained is remarkably close.

The sign attributed to the group polarity results from the charges on the atoms forming the group and the sign of the moment is taken as positive when the vector passes thru the negative to the positive pole of the group and points outward from the center of symmetry for the molecule.

In bromobenzene, the bromine atom is negatively charged with respect to the adjacent carbon atom in the benzene ring. In toluene the hydrogen atoms are positively charged with respect to the carbon atom in the  $\text{CH}_3$  group. If this is the case, then the moment of  $p\text{-CH}_3\text{C}_6\text{H}_4\text{Br}$  should be the algebraic sum of the moments of  $\text{CH}_3$  and  $\text{Br}$ .



A check on the correctness of this conclusion may be obtained by analyzing the results of other

investigators on similar compounds. Williams<sup>4</sup> obtained a value of  $\mu = 3.90 \times 10^{-18}$  for  $p$ -nitrobenzene and  $\mu = 4.50 \times 10^{-18}$  for  $p$ -nitrotoluene

The difference between these two values, ie  $\mu = .60 \times 10^{-18}$  should represent the moment of toluene and agrees within the limits of error with the value obtained by Williams and the author for toluene. While agreement is not as close in all cases, the general theory of vector additivity is seen to hold. Other cases which have been treated with success are  $p$ -chloronitrobenzene,  $p$ -bromonitrobenzene, and  $p$ -nitrotoluene.

Table 6.  $n$ -Propyl Bromide.

M.F. $\text{C}_6\text{H}_6$	$d_4^{25}$	$n_d^{25}$	$e$	$P_{12}$	$P_2$
1.0000	.8735	1.49784	2.282	26.75	107.1
.9554	.8939	1.49438	2.512	30.01	99.85
.9193	.9118	1.49199	2.698	32.38	96.51
.8995	.9209	1.49062	2.796	33.57	94.62
.8245	.9567	1.48535	3.193	37.93	90.45
.6734	1.0283	1.47497	4.013	45.18	82.18
.0000	1.3455	1.43197	--	--	--

$$P_2^m = 23.71$$

$$\mu = 2.00 \times 10^{-18} \text{ esu}$$

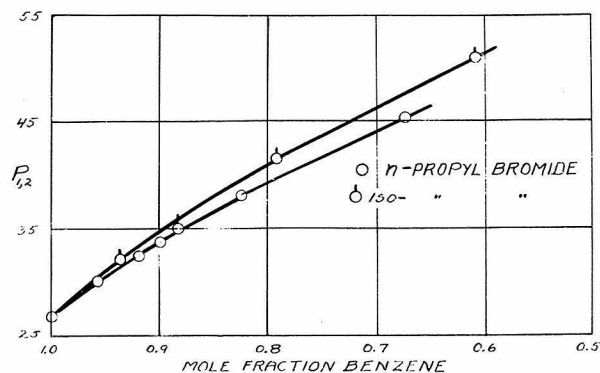
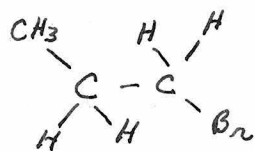


Fig. 6

The structure of n-propyl bromide might be represented as shown. In this case we would not necessarily expect the  $\text{CH}_3$  and Br groups to lie in a plane. However the moments of these two groups should be approximately additive and the value of  $\mu = 2.00 \times 10^{-18}$  is fairly in accord with the sum that would be obtained by vector addition, namely  $2.17 \times 10^{-18}$ . This difference may be partially explained by assuming that there is an angle between the vector moment for  $\text{CH}_3$  and Br but the interpretation of this angle, which is small, would be rather uncertain.

The only check on the results obtained for n-propyl bromide is found in a calculation made by Hojendahl<sup>8</sup> on the basis of dielectric measurements on vapors at  $100^\circ$  made by Pohrt<sup>34</sup> in 1913. Calculation gives a value of  $\mu = 2.15 \times 10^{-18}$  on the basis of these earlier and possibly somewhat inaccurate bridge measurements. The check that is obtained however is close considering that one set of measurements was made on dilute solutions and the other on the vapor of the compound.

Table 7. iso-Propyl Bromide.

M.F. $C_6H_6$	$d_4^{25}$	$n_d^{25}$	$e$	$P_{12}$	$P_2$
1.0000	.8735	1.49784	2.282	26.75	124.3
.9358	.9013	1.49231	2.667	32.07	109.6
.8988	.9186	1.48950	2.884	34.68	105.1
.7932	.9660	1.48128	3.538	41.43	97.74
.6097	1.0470	1.46720	4.758	50.76	88.27
.0000	1.3040	1.42267	--	--	--

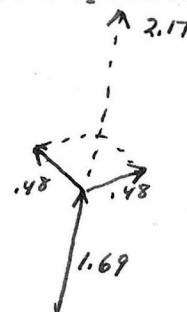
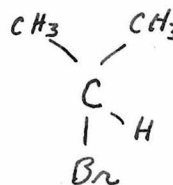
$$P_2^0 = 24.00$$

$$\bar{\mu} = 2.20 \times 10^{-18} \text{ esu}$$

The structure of iso-propyl bromide might be represented as shown. According to this

view, if the angle between the three vectors were each  $120^\circ$  and all lay in one plane, then the resultant moment for the molecule

would be that due effectively to one  $CH_3$  and one Br group in a line. This sum has been shown to be  $2.17 \times 10^{-18}$  on the basis of the measurements on toluene and bromobenzene, and is in close agreement with the value obtained above for this molecule.



The data on ethyl bromide is presented on page 31. its structure may be written as

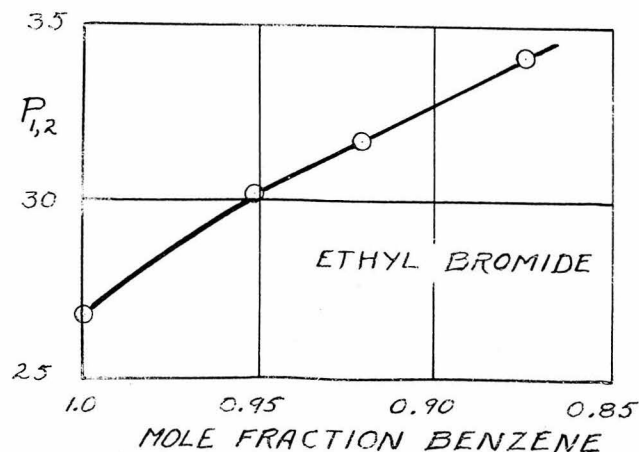
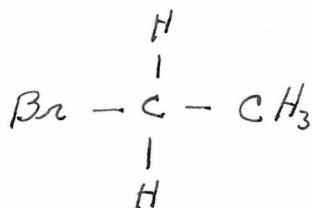


Table 8. Ethyl Bromide.

M.F. C <sub>2</sub> H <sub>5</sub> Br	$d_4^{25}$	$n_d^{25}$	$\epsilon$	$P_{12}$	$P_2$
1.0000	.8735	1.49784	2.282	26.75	101.7
.9514	.8966	1.49423	2.548	30.20	97.73
.9212	.9125	1.49210	2.687	31.75	90.23
.8745	.9344	1.48904	2.915	34.16	87.82
.0000	1.4490	1.42122	--	--	--

$$P_2^n = 19.09$$

$$\mu = 1.99 \times 10^{-18} \text{ esu.}$$

If the configuration as shown on page 30 is assumed to lie in a plane, the moment of this compound would be the same as that obtained for p-bromotoluene,  $\mu = 2.13 \times 10^{-18}$ , and agreement is obtained within 7%. Hojendahl calculates the value of the dipole moment for this compound to be  $2.09 \times 10^{-18}$  using the vapor data of Pohrt as mentioned in the case of n-propyl bromide. Smyth & Morgan<sup>30</sup> obtain a value of  $\mu = 1.86 \times 10^{-18}$  for ethyl bromide in a hexane solution. They used a bridge method for measuring the dielectric constant and also investigated this compound at several different temperatures.

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## 6. Summary:

A brief review of the Debye theory of dipole-moments is presented with a view toward interpreting the structure of certain organic compounds. A discussion of a new theory for constant frequency oscillators is presented which will be of interest in the adaptation of the apparatus to the measurement of the dielectric constants of gases. A constant frequency dielectric oscillator has been developed together with the associated heterodyning oscillator, amplifier, tuning fork drive, and Braun tube oscillographic circuit.

The second part of the investigation considers the relation between the dipole moment and the structure of the molecule. It is found that the group moments of the aliphatic compounds investigated, namely  $n\text{-CH}_3\text{CH}_2\text{CH}_2\text{Br}$ ,  $\text{iso}-(\text{CH}_3)_2\text{CHBr}$ , and  $\text{C}_2\text{H}_5\text{Br}$  can all be ascribed to the vector addition of the moments obtained for  $\text{CH}_3$  and  $\text{Br}$  in the mono-substituted hydrocarbon, benzene.  $n$ -propyl bromide is a pliable molecule, ie free rotation can occur about the single bond joining the carbon atoms and so accounts for the moment obtained which is slightly lower than the algebraic sum of the separate moments. The moment obtained for  $p$ -bromotoluene is in excellent agreement with the vector addition which would be expected for the case of the plane hexagonal benzene ring. A list of the dipole-moments obtained

includes:	Molecule	$\mu \times 10^{18}$ e. s. u.
	Bromobenzene	1.69
	Toluene	.48
	$p$ -bromotoluene	2.13
	$n$ -Propyl Bromide	2.00
	$\text{iso}$ -Propyl Bromide	2.20
	Ethyl Bromide	1.99



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