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THE DIPOLE MOMENTS OF A SERIES OF N,N-DIPHENYLBENZAMIDES

by

James William Cook

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Approved:

James E. Worsham, Jr.

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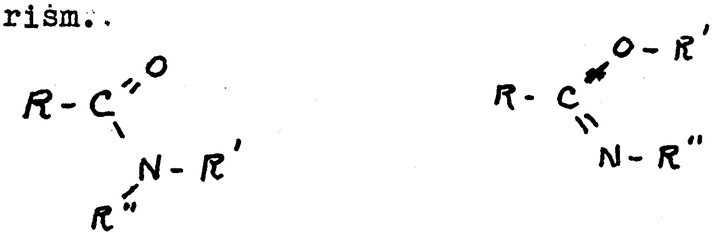
I) INTRODUCTION

In recent years amides have been used in synthetic fibers, plastics and in medicinal chemistry. Understandably, the literature contains many preparations and reactions of unsubstituted, monosubstituted and disubstituted amides, however, their structure has received very little attention. The information available on the amide group structure originates from studies made on the unsubstituted and monosubstituted compounds. The phenomenon of association of the amides has received considerable attention.

Structural determinations, using chemical methods, have been largely concerned with the lactam - lactim tautomerism.



(A) (B)

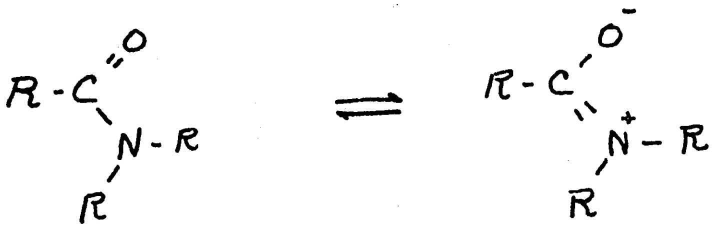
Figure I

Although amides are usually represented by the lactam form, A, there is a possibility that the lactim form, B, is also present (29).

In 1934, Kumbler and Porter (14) reported values of the dipole moments of a series of acetamides. The values found were:

Acetamide	3.72 D
Monoethylacetamide	3.87 D
Diethylacetamide	3.72 D
Dimethylacetamide	3.79 D

These workers attributed the discrepancy between the calculated and observed electric moments to the contributions from resonance forms based on the structure given by Pauling (21), Figure II.



(A) (B)

Figure II

It was found necessary to assume approximately a 10% contribution by the polar form, B, which has a calculated moment of 10D, to explain the moment measured for diethylacetamide. A 40% contribution of the resonance form is indicated by Pauling's equation (21) relating bond length to bond character.

Richards and Thompson have studied the infrared spectra of unsubstituted and disubstituted amides. They concluded that the compounds were in the keto form and that resonance caused a lowering in the frequency of the carbonyl absorption band(23).

Bates and Hobbs (1) measured the dipole moment of a series of aliphatic and aromatic unsubstituted amides. They found the following structure of the amide group.

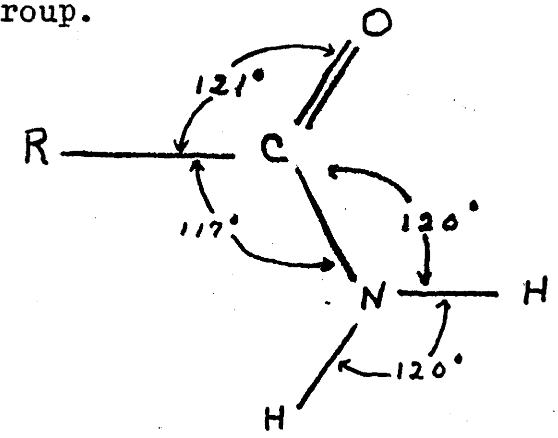


Figure III

They also observed that the polar resonance form makes a very small or negligible contribution to the structure of the amide group. Furthermore, the low basicity (21) of the amide group might be due to the presence of the large carbonyl dipole establishing a relative positive potential at the amido nitrogen.

Worsham and Hobbs measured the electric moments of N substituted benzamides. These investigators found that the calculated dipole moments and observed moments were in close agreement when the N - H bond was trans to the carbonyl group. Their observed and calculated moments are tabulated below:(31):

	Calculated		Observed
	N-H cis	N-H trans	
N Ethylbenzamide	1.8 D	3.6 D	3.6 D
N Ethyl p-chlorobenzamide	2.2 D	3.2 D	3.4 D
N -chloroethylbenzamide	2.1 D	3.3 D	3.4 D
Benzamilide	2.1 D	3.3 D	3.2 D
N Phenyl p-chlorobenzamide	2.6 D	2.8 D	3.2 D
N p-chlorophenylbenzamide	0.8 D	4.3 D	4.4 D
N p-chlorophenyl p-chlorobenzamide	2.3 D	3.3 D	3.3 D

Likewise dielectric constant measurements (16) determined at 10 mc., for methylforamide, methylacetamide, methylpropionamide gave high values of e, 167.1, 169.7, and 156.7 at 35° C. indicating trans configuration of the carbonyl and N - H group.

Recent dipole moment measurements by Kotera, Shibata, and Sone (13) for N phenyl amides have been made.

Their results are given as:

	25^{o} C.	40^{o} C.
Benzanilide	3.83 D	3.83 D
Phenylacetanilide	3.77 D	3.77 D
Phenylpropionanilide	3.62 D	3.62 D
Benzbenzlamide	3.93 D	3.90 D
Phenylacetbenzlamide	3.90 D	3.93 D
Phenylpropionbenzlamide	3.73 D	3.77 D
Phenylacephenethylamide	3.99 D	4.06 D

The authors note that since the difference between the observed and the calculated dipole moment is small, about 0.6 D., the highly polar form apparently contributes little to the structure provided the contribution of the π electrons to the bond moments is not overestimated, especially the C = O. Estimates of the resonance moment of the - CONH - group were made by LCAO method. A moment of 1.0 D was obtained for the C - O and 1.5 for the - CONH - group. In this manner there is an estimated 14% contribution from the polar form.

In 1940 Senti and Harker reported (24) the crystal structure of acetamide as planar and to exist in the keto form. Their structure is shown in Figure IV .

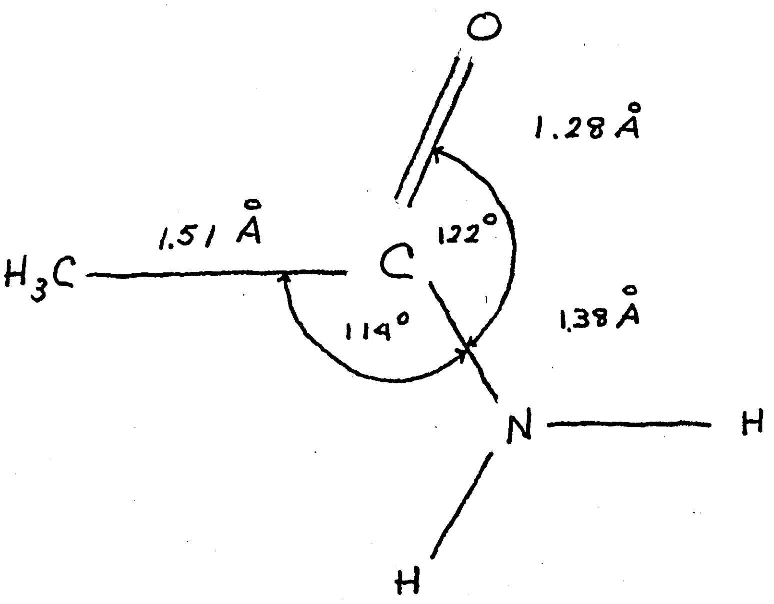


Figure IV

Having now discussed the major developments in amide structure, the topic of association between the molecules should be considered.

Meldrum and Turner (18), (19), (20) in an investigation of the Nerst - Thompson rule, using ebullioscopic methods, measured the apparent molecular weight of unsubstituted, monosubstituted and disubstituted amides in water, benzene, chloroform, acetone and diethylether. They arrive at the following conclusions.

(i) The molecules of the aliphatic amides are strongly associated.

(ii) The extent of association decreases with increasing molecular weight.

(iii) The phenyl groups depresses the tendency to associate, independent of the location in the molecule.

(iv) The substitution of both hydrogen atoms of the amide group yields a substance of normal molecular weight.

(v) a-Chloroacetamide associated less than acetamide

(vi) Association agrees with the Nerst - Thompson rule, water solutions being an exception to the rule.

Bates and Hobbs (2) have calculated the association constants of a series of unsubstituted amides from the molar polarizations. In contrast to Meldrum and Turner, see above, they found that association increased with molecular weight. It was found that the association was due to the formation of a cyclic structure, Figure V

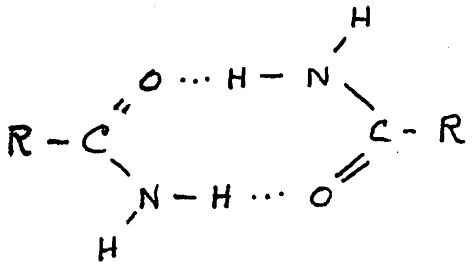


Figure V I

Worsham and Hobbs (31), in addition to the results cited earlier, found for the N monosubstituted benzamides, a linear association. This linear association also supports the trans structure of the monosubstituted amides as Worsham points out (30) that a cis structure would most probably result in the cyclic association. The chain linkage is in agreement with the dielectric measurements (16) of the monosubstituted amides.

Leader (16) has observed that the dielectric constant of N,N disubstituted amides is considerably less than the monosubstituted. He attributes this to the lack of association between the molecules.

The remainder of this work is devoted to the investigation of N,N diphenylbenzamides. The determination of the apparent molecular dipole moment has been used to study the amide group structure and the association of the amide molecules.

II) EXPERIMENTAL

A) Apparatus

The dielectric constant apparatus was of well known design (17), (26), (22). The variable oscillator of a beat frequency audio oscillator model number 197-A, serial number 609 manufactured by the Clough Brengle Co. was altered by removing about 1500 uuf of capicatance from its tank circuit. A General Radio Co., model number 722-D, serial number 5256, precision capicator and the cell were placed in parallel with the capacitance remaining in the oscillator circuit. Variations in the capacity of the experimental cell could be compensated for and determined by adjusting the precision condenser, the reference point being the setting of the precision condenser that gave a zero beat frequence between the oscillator circuits. The zero beat was determined by the electron eye tube mounted on the case of the oscillator. All connections between the oscillator and condensers were made with co-axial cables that were attached to the table to prevent any change in capacitance that might result from a change in position. Figure VI is a block diagram of the assembly.

The experimental cell was designed in this laboratory by Dr. James E. Worsham, Jr. and was built by Phipps and Bird, Richmond, Va. The cell condenser was a National Radio type TMS- 300 variable condenser. The condenser has 27 plates, 14 rotating plates and 13 stationary plates. The condenser plates were insulated from the chassis by two Pyrex glass insulators which were copied from the original steatite insulators. A short, heavy copper wire connected the plates to the coaxial connector firmly mounted on the cover of the cell, The rotor extended through the cover and was turned by a lever operating between two stops that permitted rotation through an angle of 180 degrees. The cover and solution container were constructed of nickle plated stainless steel. Figure VIIis a cross-section of the condenser and the cover plate. Here only a few plates are shown and the gap between the plates is greatly exaggerated. Figure VIIB shows the cover in position on the container.

The bath was a Sargent S-84805 bath. The apparatus consisted of a Pyrex glass container, a central heating unit and a mercury thermo-regulator. Switches and relays were contained in a separate unit connected to the central unit. The bath oil was a temperature stabilized oil purchased from Fischer Scientific Co., Washington, D. C.

The temperature of the bath was measured with a Beckman thermometer. The Beckman was calibrated by Dr. Worsham through the courtesy of the Chemistry Department of Duke University, Durham, N. C. The temperature was controlled with in ± .02° C.

The all glass pycnometers were made from a 100 milliliter cylinderical bulb having capillary tubes fused to either end. One capillary tube curved upward giving a U shape to the pycnometer. Both ends were closed with ground glass stoppers. Figure VIII is a drawing of the apparatus.

The cooling curve apparatus, FigureIX, of the usual design was built by Wakefield Industries, Inc., Chicago, Ill. Thermometers graduated to a tenth of a degree were used. High resistance wire connected to a variable transformer heated the apparatus.

A Dufton column (7) was built for the distillation of benzene. The column was made by creating a spiral track in a narrow annulus between two Pyrex glass tubes. The outside tube had a length of 2.5 meters. The inner tube consisted of three 60 centimeter sections of sealed glass tubing around which was wound a spiral of copper wire so that contact was made with the outer tube. The upper section was of 34 millimeter outside diameter tubing wound to a pitch of 18 millimeters with number 28 B & S gauge copper wire. The middle section was 32 millimeter tubing spiraled to a pitch of 20 millimeters with 20 gauge wire. The lower section used 28 millimeter tubing and was spiralled with a wire made by wrapping a 12 gauge wire with 28 gauge wire. The pitch of the lower section was 22 millimeters. The takeoff arm, some 25 centimeters above the top of the inner tube, led to a West type condenser with an adapter that connected the condenser to the collection bottle. A Calcium chloride tube was attached to the adapter to prevent the entrance of moisture. A calibrated Beckman thermometer was suspended directly above the inner tube with its bulb well below the take-off arm. The boiling flask, condenser, adapter, calcium chloride tube and thermometer were connected by ground glass joints.

B) Experimental Procedure

The solutions were prepared in 250 milliliter, glass stoppered volumetric flasks, which had been cleaned with sodium dichromate sulfuric acid cleaning solution, rinsed and dried at 110° C. The flasks were then rinsed with benzene and redried before being used.

The more sensitive weighings were made with a Voland analytical balance using stainless steel weights that had been compared with a set of weights calibrated by the Bureau of Standards (4). Less sensitive weighings were made on a Harvard Trip balance that was reproducable to two tenths of a gram under a 200 gram load.

Before any of the amides were measured, the cell constant was evaluated by measuring ΔC in air. Five readings in each position were made, corrections furnished by the manufacturer of the precision condenser were applied and the difference between consecutive readings taken. The resulting ΔC values were averaged. Using 1.005 (9) as the dielectric constant of air the cell constant, ΔC in a vacuum, was calculated by

$$K = \frac{\Delta C \text{ air}}{1.005}$$

Once, between runs, the cell constant changed. A new value was determined and this second constant used for the remainder of the determinations.

The dielectric constant apparatus was checked with chlorobenzene at the beginning of the measurements, after four compounds had been measured and at the completion of the experimental work. The results are shown in Table X.

Solutions were prepared in the following manner. Approximately 250 milliliters of purified benzene was transferred to previously weighed volumetric flasks in the dry box. The flasks were stoppered and removed from the dry box. One of the samples of benzene was set aside. The remaining were weighed and known quantities of the compound dissolved in the solvent. The volume of pure benzene and the solutions were adjusted to 250 milliliters and 25 milliliters of solution removed from each with a volumetric pipette. The solutions along with the cell were returned to the dry box where they remained for a period of not less than one half hour. It was assumed that by this time the atmosphere was once again dry.

The solution to be measured was transferred to the cell and both the flask and the cell removed from the dry box. As the minimum change in ΔC occurred during a period of thirty-three to forty minutes after the cell filled with benzene was placed in the thermostat, the cell was allowed to remain in the bath for thirty-five minutes before any readings were taken. After making the capacitance measurements, the solution was returned to the flask, the cell rinsed with benzene and allowed to air dry before being returned to the dry box. A ΔC value was determined for each lot of benzene used.

The pycnometers were calibrated by the procedure given by Bauer (28). Their volumes at 30° C. were found to be;

#1	99.2205	±	.0001 ml.
#2	99.1750	±	.0005 ml.
#3	97.8140	±	.0012 ml.

The capillary level of the liquid was obtained by reading the graduations on the tube. Since the diameter of the tube was known as well as its height, the volume per graduation was obtained. The difference between the calibrated volume and the volume of the liquid was found by counting the divisions above the solution and then multiplying by twice the volume per division.

The density of the benzene solutions were determined as follows. About 125 milliliters of the solution was placed in a clean, dry beaker. A glass tube, having a ground glass joint that fitted into the ground glass joint of the apparatus, was used to transfer the liquid to the pycnometer. A second ground glass jointed tube connected the pycnometer to a vacuum bottle. By reducing the pressure within the pycnometer, the liquid was forced into the pycnometer until the solution level was in the capillary. They were capped immediately and placed in the constant temperature bath. About one half hour was allowed for the solution to come to the bath temperature. The caps were removed and the volume adjusted with a syringe and hypodermic needle. The inner surfaces of the pycnometer necks were wiped clean with pipe cleaners, the caps replaced, the pycnometers removed from the bath and cleaned of thermostat oil by dipping three times in each of three containers of ethyl ether. They were allowed to air dry to constant weight.

C) Preparation and Purification

Melting points of all compounds discussed in this section were made by the capillary method. Freezing points were taken from the cooling curves.

Aniline: Baker and Adamson purified aniline was distilled immediately before use.

p - Chloroaniline: Eastman practical grade p - chloroaniline was redistilled. The best fraction was allowed to crystallize slowly. When about two-thirds of the material had solidified, the liquid was poured off and the solid portion used.

Phenol: Baker and Adamson reagent grade phenol was distilled, the middle fraction collected and used.

p - Chlorophenol: Eastman pratical grade p-chlorophenol was purified in the same manner as the p - chloroaniline.

Diphenyl Amine: Dr. J. S. Pierce suggested the following procedure. A slurry of alcohol and amine were dissolved in hot concentrated hydrochloric acid. The mixture was poured into cold water and the resulting crystals washed with water.

Benzoyl Chloride and p - Chlorobenzoyl Chloride: Eastman white label chemicals were used without additional purification.

Anhydrous Ether: Metallic sodium ribbon was added to Baker and Adamson reagent grade ethyl ether, and used without any further treatment.

Anhydrous Alcohol: Commercial Solvents absolute ethanol was dried by the magnesium method as described by Feiser (8).

Benzanilide: Benzoyl chloride and purified aniline were reacted by the well known Schotten-Baumann procedure (11). The product of the reaction was recrystallized from 95% ethanol.

N-Phenyl p-chlorobenzamide: This compound was prepared by the Schotten Baumann reaction using p-chloro benzoyl chloride and purified aniline.

N-p - Chlorophenylbenzamide: Benzoyl chloride and purified p - chloroaniline were reacted in pyridine (12). The solvent was removed by distillation at reduced pressure. The product was washed with water and recrystallized from 95% ethanol.

N - p - Chlorophenyl p - chlorobenzamide: The reaction of p-chloroaniline and p-chlorobenzoyl chloride was carried out in pyridine. The product was purified as described earlier.

N-Phenyl benzimino p-chlorophenylether: Mole to mole ratios of benzanilide and phosphorus pentachloride were mixed in a round bottom flask. A reflux condenser was fitted to the flask. The mixture was heated gently until a melt was obtained, at which time there was a vigorous evolution of hydrogen chloride. When the reaction had subsided, the material was brought to a reflux. Refluxing was continued until the evolution of hydrogen chloride ceased. The mixture was cooled, the condenser removed, and the apparatus arranged for vacuum distillation. The low fraction was discarded and the high boiling fraction taken to be N-phenylbenzimino chloride.

The imino chloride was allowed to cool, dissolved in anhydrous ethyl ether and added to a mixture of dry ethanol, a slight excess of p-chlorophenol and the calculated amount of sodium metal. The mixture was stirred overnight. The solvent removed and the oil-like residue crystallized by adding to a large volume of water. Recrystallization from 95% ethanol yielded pale yellow crystals that were used without further purification.

N-p-Chlorophenyl p-chlorobenzimino p-chlorophenyl ether: This intermediate was obtained from the imino chloride of N p-chlorophenyl p-chlorobenzamide reacted with sodium p-chlorophenoxide. Recovery and purification were made by the usual procedure.

N-p-Chlorophenyl p-chlorobenzimino phenyl ether: This intermediate was obtained from the preceeding imino chloride reacted with sodium p-chlorophenoxide. Recovery and purification were made by the usual procedure.

N-Phenyl p-chlorobenzimino p-chlorophenyl ether: This compound was prepared from the imino chloride of p-chloro benzanilide reacted with sodium p-chlorophenoxide.

N-p-Chlorophenylbenzimino p-chlorophenyl ther: The imino chloride from N-p-chlorophenylbenzamide was reacted with sodium p-chlorophenoxide to give the desired ether.

N,N-Diphenylbenzamide: Benzoyl chloride and purified diphenyl amine were reacted in the same manner used in the preparation of N-p-chlorophenyl benzamide. The amide was purified by recrystallization from ethanol and then twice from benzene. The purified product was stored in the desiccator.

N,N-Diphenyl p-chlorobenzamide: This compound was prepared in the above manner. Final recrystallization was from a mixture of benzene and petroleum ether. The purified product was stored in the desiccator.

N,N-Di p-chlorophenylbenzamide: Pure, dry solid N-p-chlorophenylbenzimino p-chlorophenyl ether was placed in a round bottom flask. A 360° C. thermometer was clamped so that the bulb was well down into the powder. A loose cotton plug was placed in the neck of the glask. Using a heating mantle, the contents of the flask were heated for four hours between 280° and 310° C. The amber, plasticlike solid that formed was recrystallized from ethanol. Three crystallizations from ethanol and twice from a mixture of benzene and petroleum ether gave a light tan crystalline product that was stored in the desiccator.

N,N-Di p-chlorophenyl p-chlorobenzamide: Prepared from N-p-chloro p-chlorobenziminio p-chlorophenyl ether by the thermal rearrangement given above. Seven recrystallizations from both polar and nonpolar solvents gave a slightly colored product. The final crystallization was from benzene-petroleum ether. The product was stored in the desiccator.

N_o-Phenyl N_N-p-chlorophenylbenzamide: N-Phenyl N-p-chlorophenyl benzamide can be obtained from the two compounds, N-phenylbenzimino p-chlorophenyl ether and N-p-chlorophenylbenzimino phenyl ether. In order to distinguish between them, the subscripts o and n are used. The subscript o designates the group having the ether linkage in the imino compound and n designates the group attached to the nitrogen in the ether.

N_o-Phenyl N_N-p-chlorophenylbenzamide was obtained by rearranging N-p-chlorophenylbenzimino phenyl ether. Recrystallization was from acetone and water and finally from benzene and petroleum ether mixtures. Again the product was stored in the desiccator.

N_N-Phenyl N_O-p-chlorophenylbenzamide: Prepared by the rearranging N-phenylbenzimino p-chlorophenyl ether. Purification was from ethanol and finally from petroleum ether. The product was placed in the desiccator.

N_O-Phenyl N_N-p-chlorophenylbenzamide: N p-chlorophenyl p-chlorobenzimino phenyl ether was rearranged, purified and stored as above.

N_N-Phenyl N_O-p-chlorophenyl p-chlorobenamide: Rearrangement of N phenyl p-chlorobenzimino pOchlorophenyl ether was rearranged, purified and stored as above.

Benzene: Bakers reagent grade benzene was redistilled from over sodium before being used in dielectric constant measurements.

The treatment of benzene was as follows: About four liters of benzene was placed in a five liter round bottom flask along with fifteen to twenty grams of sodium ribbon. The mixture was refluxed overnight in a Dufton column. If the metal was tarnished at the end of the reflux period, fresh sodium was added and refluxed again. If the metal was bright, the lot was distilled through the column at the rate of approximately 300 ml. per hour. Throughout the distillation, the boiling point and the atmospheric pressure were recorded. The observed boiling points were corrected to 760 millimeter pressure (15). The value of $\partial t/\partial p$ used was 0.0427 deg./mm. (27).

The middle cut of the distillation was refluxed and distilled over sodium a second time. The center fraction was stored in a glass stoppered bottle and kept in a dry atmosphere. Freshly distilled benzene was used in the dielectric measurements.

Benzene was reclaimed from the solutions by two distillations through all glass apparatus containing a twelve inch Vigreaux column. The best fraction was redistilled through the Dufton column before being used.

Section E of Table I gives the observed boiling point and density of the benzene used. The benzene purified in this laboratory was observed to differ slightly from the accepted values of these constants. This was probably due to some inert impurity present in the samples. The consistency of the boiling range and density as well as the close agreement in C values for different lots of benzene led to the belief that the samples were identical.

Chlorobenzene: Matheson Coleman and Bell's chlorobenzene was used to check the dielectric constant apparatus. The liquid was allowed to stand overnight over calcium chloride. After filtering, it was twice distilled through an all glass distilling apparatus containing a twelve inch Vigreaux column. The middle cut was stored in a glass stoppered bottle until time of use.

Table I

Physical Constants

Section A - Intermediates

	Melting Point °C.	Literature Value °C.
Benzamide	162.5-3.0	160.0 (25)
N-p-chlorophenylbenzamide	192.5-3.5	192.0 (25)
N-p-chlorophenyl p-chlorobenzamide	209.5-10.0	209.5 (30)
N-phenyl p-chlorobenzamide	195.0-5.5	194 (28)
N-phenylbenzimino p-chlorophenyl ether	109.5-10.0	110 (5)
N-p-chlorophenyl p-chlorobenzimino phenylether	83 - 4.5	85 (5)
N-phenyl p-chloro benzimino p-chlorophenyl ether	78 - 79.5	*
N-p-chlorophenyl p-chlorobenzimino p-chlorophenyl ether	105 - 6.5	*

Section B

Final Products

	Melting Point	Freezing Point	Literature
N,N-Diphenylbenzamide	179.5-8.0	177.95	180 (25)
N,N-Diphenyl p-chlorobenzamide	139.5-4.0	137.65	*

	Melting Point	Freezing Point	Literature
N,N-Di p-chlorophenylbenzamide	153 - 4.5	150.50	152 - 3 (25)
N,N-Di p-chlorophenyl p-chlorobenzamide	197 - 8	196.50	
N_o Phenyl N_N p-chlorophenylbenzamide	108.5°	109.65°	110° (5)
N_N Phenyl N_o p-chlorophenylbenzamide	108.5	109.60°	110° (5)
N_o Phenyl N_N p-chlorophenyl p-chlorobenzamide	131.0-2.5		*
N_N Phenyl N_o p-chlorophenyl p-chlorobenzamide	132.0-3.0		*
Chlorobenzene (boiling point)	132.0-2.1		132.0 (25)

Section C

Benzene

Boiling Point		Density	
Observed	Literature	Observed	Literature
80.035° ± .002°	80.094 (27)	.86732 ± 3×10^{-5}	.86814 (27)

* New compounds.

Figure VI

Diagram of The Apparatus Assembly

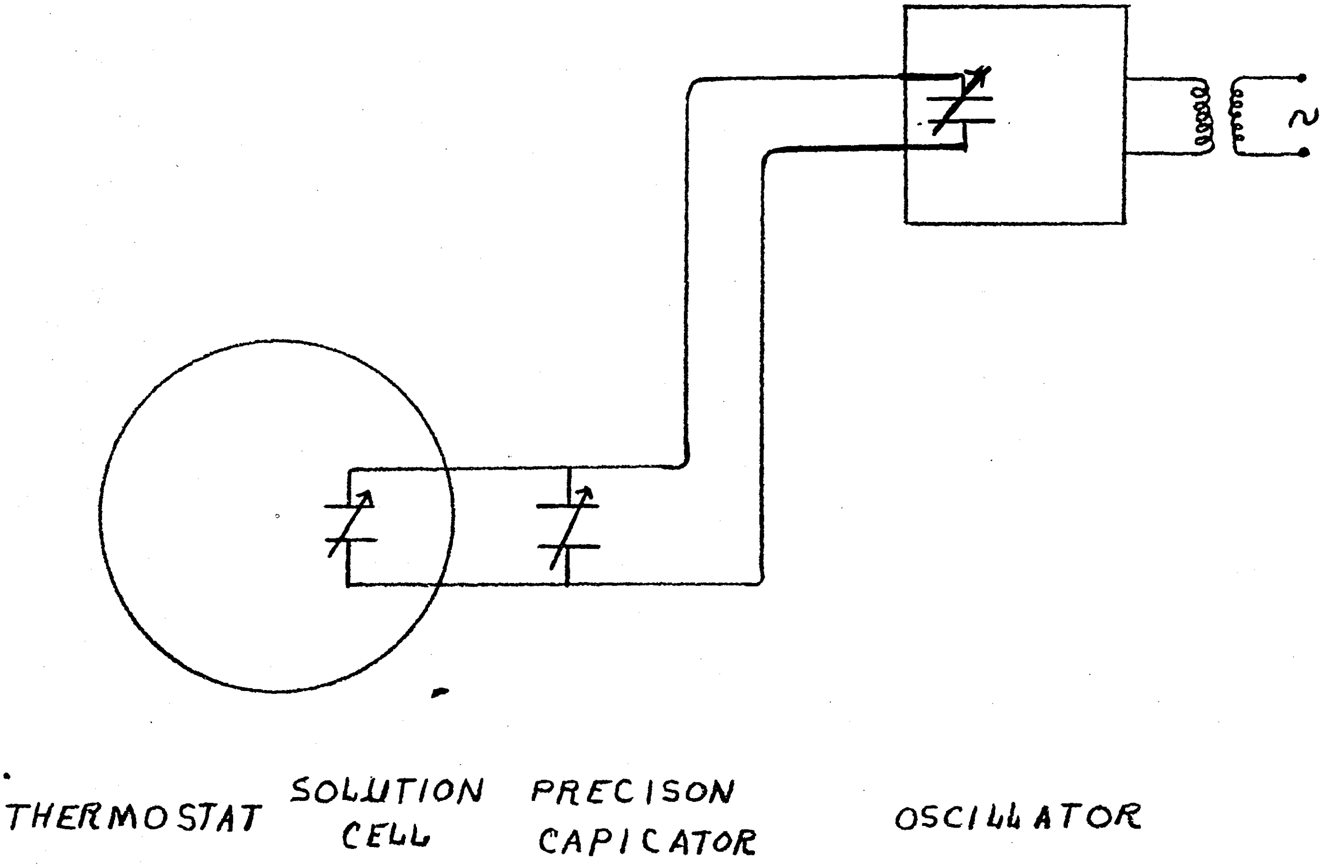
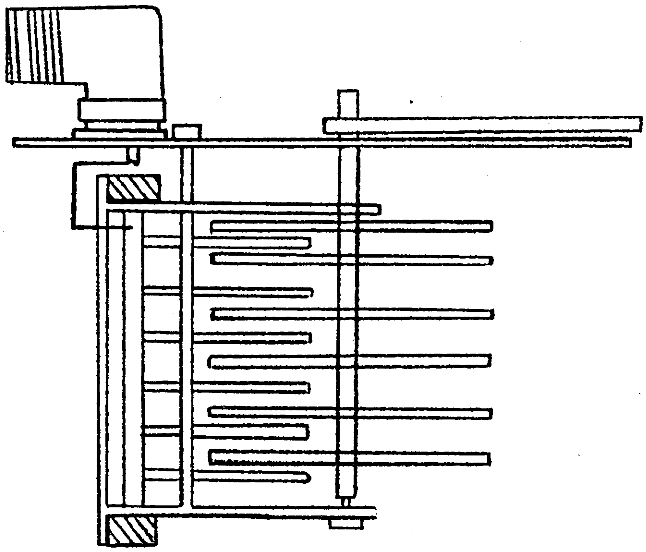

THERMOSTAT
SOLUTION CELL
PRECISON CAPICATOR
OSCILLATOR

Figure VII

A) Cross section of cell condenser and the cell cover plate.

B) The experimental cell

A



B

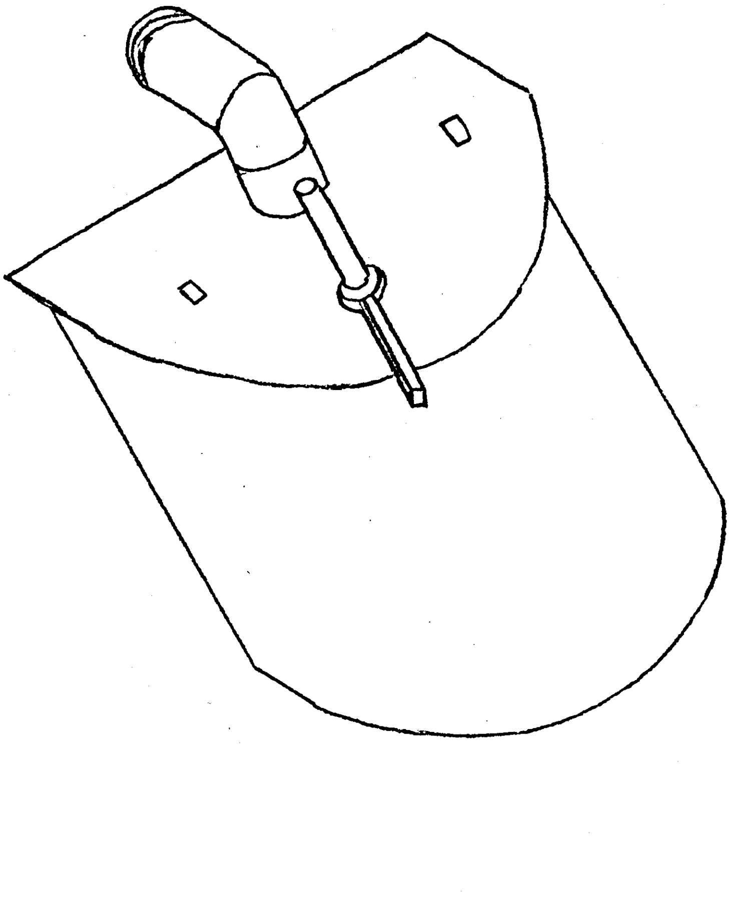


Figure VIII

Pycnometer Diagram

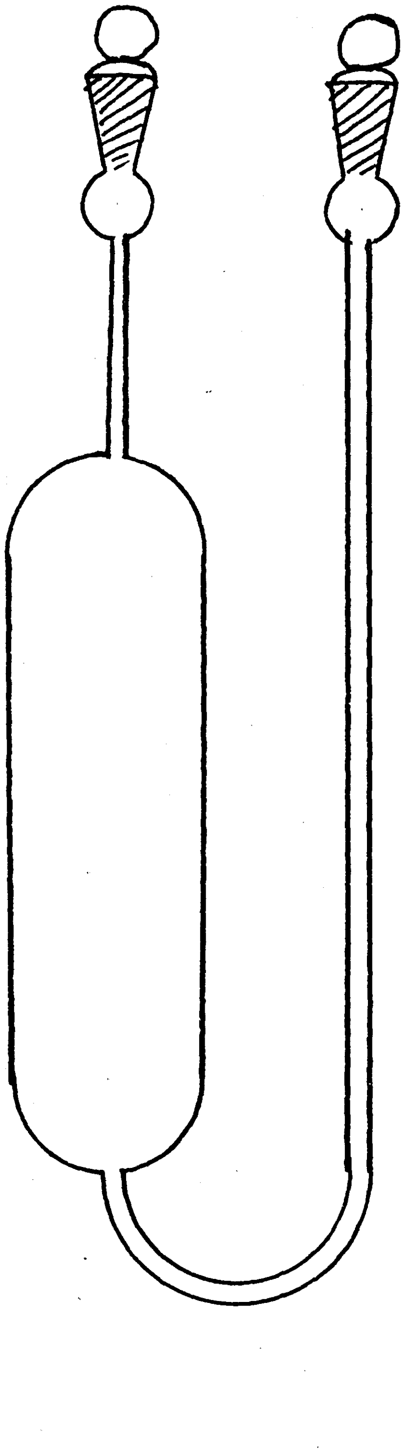
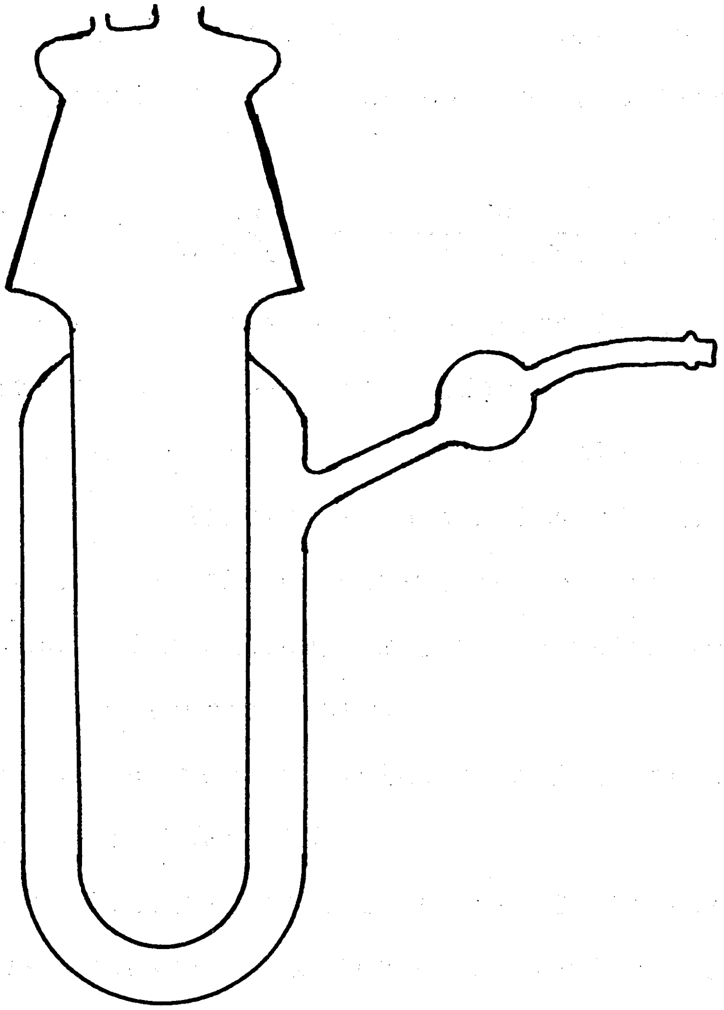


Figure IX

Cooling Curve Apparatus



III) DATA AND CALCULATIONS

Hedestrand (10) has shown that molar polarizations of solutes at infinite dilution can be calculated by the equation

$$P_{2\infty} = \frac{e_1 - 1}{e_1 + 2}\frac{1}{d_1}\left[M_2 - \frac{M_1}{d_1}\frac{\Delta d}{f_2}\right] + \frac{3M}{(e+2)^2 d_1}\left(\frac{\Delta e}{f_2}\right)_\infty$$

Here $P_{2\infty}$ is the molar polarization at infinite diltion; e, the dielectric constant: Δe, the difference between the dielectric constant of the solution and solvent; d, the density; Δd, the difference in density of the solution and solvent; M, the molecular weight; and f the mole fraction. The subscripts 1 and 2 refer to the solvent and solute, respectively.

The value of e used was the value of e for benzene found in the literature 2.267 (27).

d was found by density determinations of the solvent.

$\Delta d/f_2$ was the average value for a particular solute.

The Δe values were calculated from the relationship

$$\Delta e = \frac{\Delta C_{12} - \Delta C_1}{K}$$

where K is the cell constant and ΔC the change in capacitance of the cell when the plates were rotated from the fully meshed position to the open position.

The value of $(\Delta e/f_2)_\infty$ was the average of the $\Delta e/f_2$ terms for each solution.

The Clausius - Mosotti - Debye equation (6)

$$\mu = \sqrt{9kT/4\pi N}\,\sqrt{P_{2\infty} - R_D} \times 10^{18}$$

was used to relate the permanent dipole moment of a molecule to the molar polarization. In this equation, μ, is the dipole moment in Debye units (1 D x 10 e. s. u.); K, the Boltzmann constant in ergs/ deg. molecule; T, the absolute temperature; N, Avogadro's number; $P_{2\infty}$, the molar polarization as determined by the Hedestrand equation and R_D is the molar refraction for the sodium D line. Inserting the values of the constants gives

$$\mu = 0.223\sqrt{P_{2\infty} - R_D}$$

R_D values were calculated from the values given by Smyth (26) for the refraction of electron groups.

The data given in the tables below was obtained at 30° C.

Table II

N,N Diphenylbenzamide in benzene

$f_2 \times 10^3$	$\Delta e \times 10^3$	$\Delta e/f_2$	$\Delta d/f_2$
1.39	25.3	18.4	0.57
2.62	48.2	18.4	0.76
4.01	73.7	18.4	0.70
8.94	162.7	18.3	0.45
11.07	204.7	18.5	0.77

$(\Delta e/f_2)_\infty = 18.4$ ave. $\Delta d/f_2 = 0.65 \pm .13$

$R_D = 83.1$ $P_{2\infty} = 347.0$ $\mu = 3.62$ D

Table III

N,N Di p-Chlorophenylbenzamide in benzene

$f_2 \times 10^3$	$\Delta e \times 10^3$	$\Delta e/f_2$	$\Delta d/f_2$
1.11	14.8	13.3	1.26
2.46	30.7	12.5	1.20
3.06	44.6	13.6	1.31
5.75	76.5	13.3	1.30
7.74	102.7	13.3	1.29
10.34	137.7	13.3	1.34

$(\Delta e/f_2)_\infty = 13.3$ ave. $\Delta d/f_2 = 1.30 \pm .03$

$R_D = 92.8$ $P_{2\infty} = 274.7$ $\mu = 3.01$ D

Table IV

N,N Diphenyl p-chlorobenzamide in benzene

$f_2 \times 10^3$	$\Delta e. \times 10^3$	$\Delta e/f_2$	$\Delta d/f_2$
1.55	25.1	16.2	0.96
2.31	39.2	17.0	1.15
3.71	61.8	16.7	0.95
4.71	76.1	16.2	0.94
6.07	101.2	16.7	0.98
8.23	138.9	16.9	1.05
9.80	161.1	16.5	1.00

$(\Delta e/f)_2 = 16.7$ ave. $\Delta d/f_2 = 1.00 \pm .05$

$R_D = 87.9$ $P_{2\infty} = 322.7$ $\mu = 3.42$ D

Table V

N,N Di p-Chlorophenyl p-chlorobenzamide in benzene

$f_2 \times 10^3$	$\Delta e \times 10^3$	$\Delta e/f_2$	$\Delta d/f_2$
1.86	15.8	8.14	1.53
3.03	26.1	8.23	1.54
5.05	40.1	7.93	1.55
7.14	58.5	8.19	1.56
8.30	63.3	7.65	1.57
10.96	89.5	8.14	1.51

$(\Delta e/f)_\infty = 8.14$ ave. $\Delta d/f_2 = 1.54 \pm .02$

$R_D = 97.7$ $P_{2\infty} = 202.3$ $\mu = 2.28$ D

Table VI

N_N- p-Chlorophenyl $N_o$phenylbenzamide in benzene

$f_2 \times 10^3$	$\Delta e \times 10^3$	$\Delta e/f_2$	$\Delta d/f_2$
3.03	56.2	18.6	1.11
4.65	86.4	18.7	1.09
6.08	114.4	18.8	1.09
7.54	141.0	18.7	1.04
9.87	183.1	18.5	1.07

$(\Delta e/f_2)_\infty = 18.7$ ave. $\Delta d/f_2 = 1.08 \pm .02$

$R_D = 87.9$ $P_{2\infty} = 350.0$ $\mu = 3.61$ D

Table VII

N_N- Phenyl N_o-p-chloro phenylbenzamide in benzene

$f_2 \times 10^3$	$\Delta e \times 10^3$	$\Delta e/f_2$	$\Delta d/f_2$
1.93	35.0	18.1	1.20
2.36	43.2	18.3	1.09
5.39	97.8	18.1	1.12
6.08	111.8	18.4	1.15
8.05	147.7	18.4	1.20

$(\Delta e/f_2)_\infty = 18.3$ ave. $\Delta d/f_2 = 1.15 \pm .09$

$R_D = 87.9$ $P_{2\infty} = 341.9$ $\mu = 3.56$ D

Table VIII

N_N p-Chlorophenyl N_O phenyl p-Chlorobenzamide in benzene

$f_2 \times 10^3$	$\Delta e \times 10^3$	$\Delta e/f_2$	$\Delta d/f_2$
1.91	22.9	12.0	1.08
2.87	38.9	13.6	1.21
4.19	55.8	13.3	1.18
5.88	79.6	13.5	1.27
8.27	113.0	13.7	1.20
12.06	163.3	13.5	1.32

$(\Delta e/f_2)_\infty = 13.6$ ave. $\Delta d/f_2 = 1.21 \pm .06$

$R_D = 92.9$ $P_{2\infty} = 281.8$ $\mu = 3.07$ D

Table IX

N_O- p-chlorophenyl N_N- phenyl p-chlorobenzamide in benzene

$f_2 \times 10^3$	$\Delta e \times 10^3$	$\Delta e/f_2$	$\Delta d/f_2$
1.64	21.3	13.0	1.08
3.01	38.5	12.8	1.16
4.48	59.6	13.3	1.12
6.08	79.0	13.0	1.15
9.19	119.3	13.0	1.10
10.47	137.2	13.1	1.08
11.81	152.3	12.9	1.15

$(\Delta e/f_2)_\infty = 13.0$ ave. $\Delta d/f_2 = 1.12 \pm .03$

$R_D = 92.9$ $P_{2\infty} = 275.7$ $\mu = 3.02$ D

Table X

Chlorobenzene

$f_2 \times 10^3$	$\Delta e \times 10^3$	$\Delta e/f_2$
18.6	65.6	3.53
20.5	72.3	3.52
16.7	59.2	3.55

Hobbs (3) found $(\Delta e/f_2)_\infty = 3.52$

Table XI

Summary of Dipole Moments

N,N-Diphenylbenzamide	3.62 D
N,N-Diphenyl p-chlorobenzamide	3.42 D
N,N-Di-p-chlorophenylbenzamide	3.01 D
N,N-Di-p-chlorophenyl p-chlorobenzamide	2.28 D
N_o- Phenyl N_N- p-chlorophenylbenzamide	3.61 D
N_N-Phenyl N_o- p-chlorophenylbenzamide	3.56 D
N_o-Phenyl N_N- p-chlorophenyl p-chlorobenzamide	3.08 D
N_N-Phenyl N_o- p-chlorophenyl p-chlorobenzamide	3.03 D

Figure X

N,N Diphenylbenzamide

A) Δe vs. f_2

B) $\Delta e/f_2$ vs. f_2

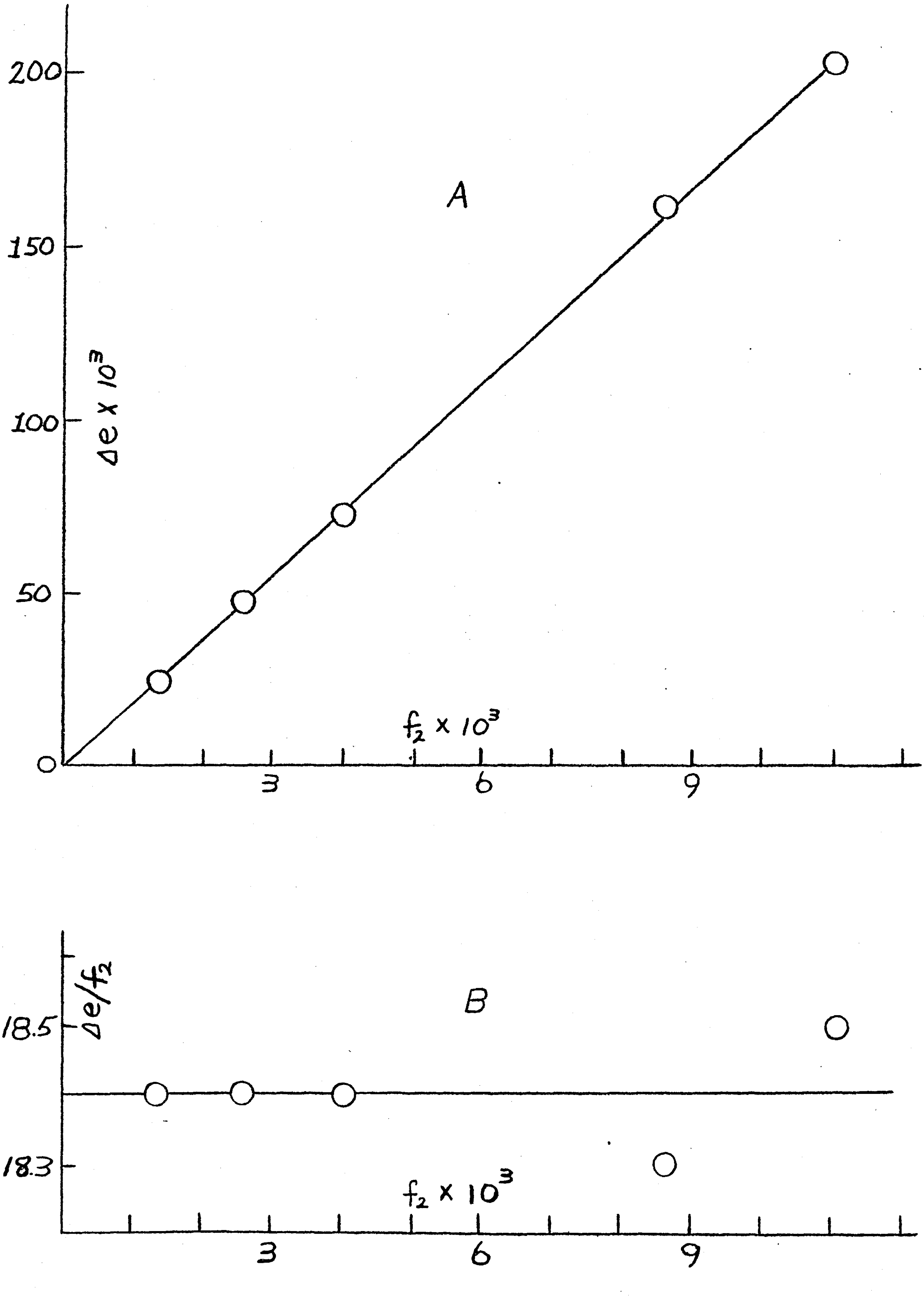

200
150
100
50
0
Δe x 10³
A
f₂ x 10³
3
6
9
Δe/f₂
B
18.5
18.3
f₂ x 10³
3
6
9

Figure XI

N,N Di-p-chlorophenylbenzamide

A.) Δe vs. f_2

B.) $\Delta e/f_2$ vs. f_2

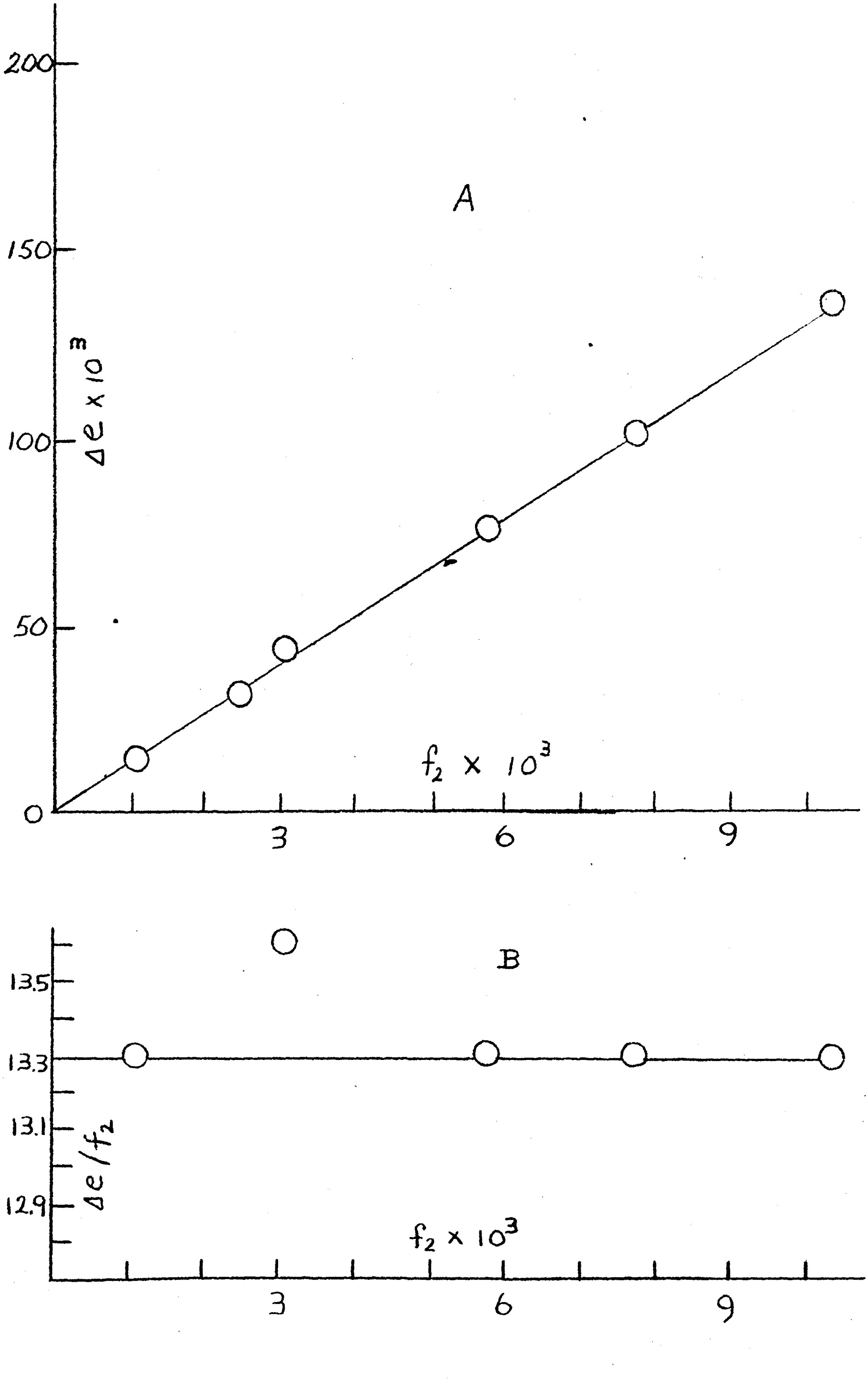

A
200
150
100
50
0
Δe x 10^m
f2 x 10^3
3
6
9
B
13.5
13.3
13.1
12.9
Δe/f2
f2 x 10^3
3
6
9

Figure XII

N,N Di phenyl p-chlorobenzamide

A) Δe vs f_2

B) $\Delta e/f_2$ vs f_2

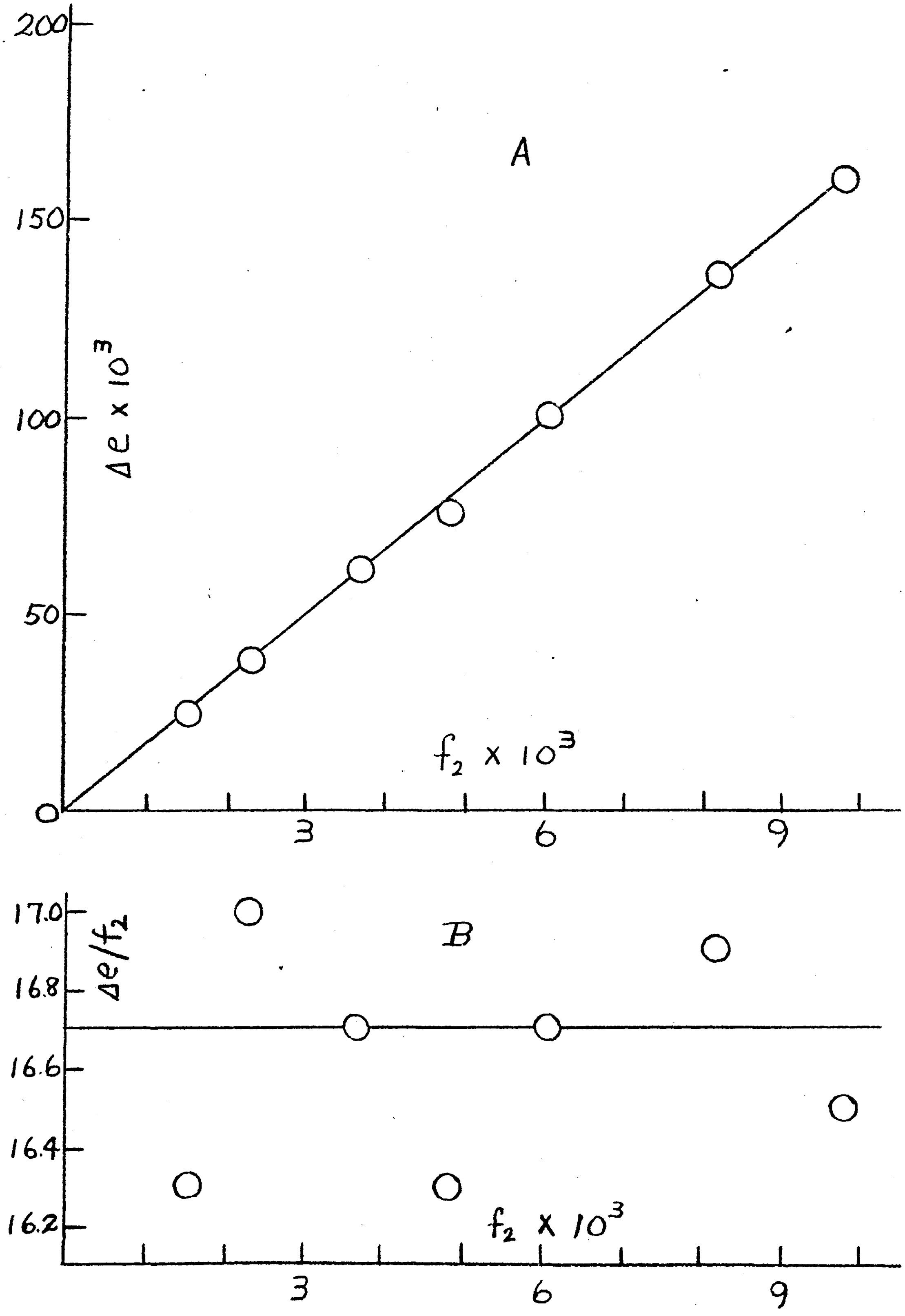
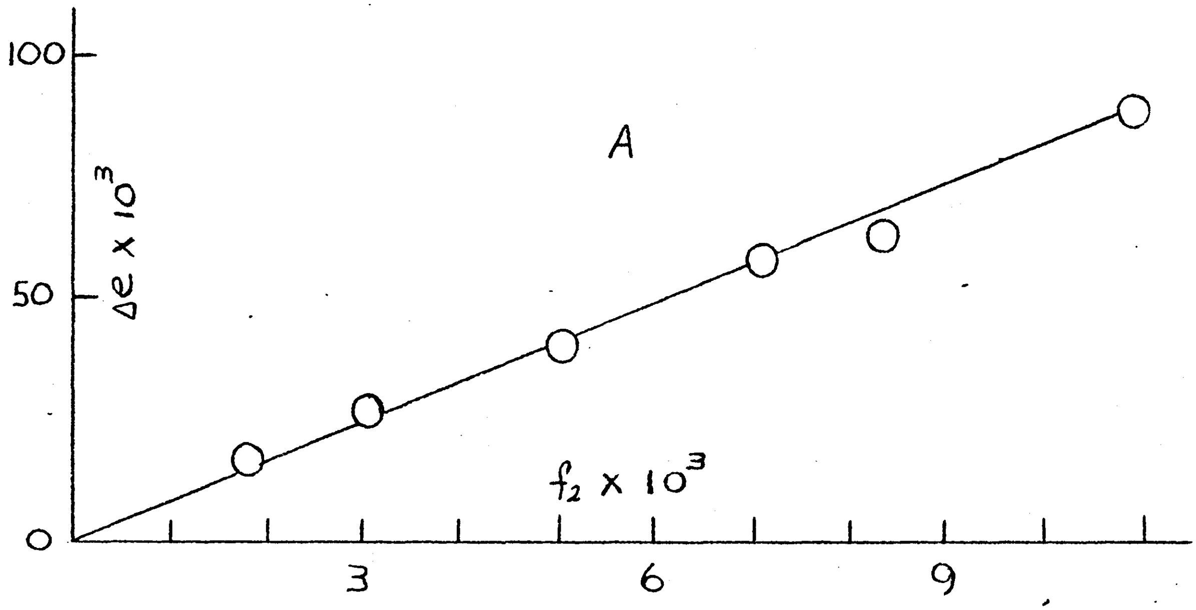

A
200
150
100
50
0
$\Delta e \times 10^3$
$f_2 \times 10^3$
3
6
9
B
17.0
16.8
16.6
16.4
16.2
$\Delta e/f_2$
$f_2 \times 10^3$
3
6
9

Figure XIII

N,N Di p-chlorophenyl p-chloro benzamide

A) Δe vs f_2

B) $\Delta e/f_2$ vs f_2


A
100
50
0
Δe x 10³
f₂ x 10³
3
6
9

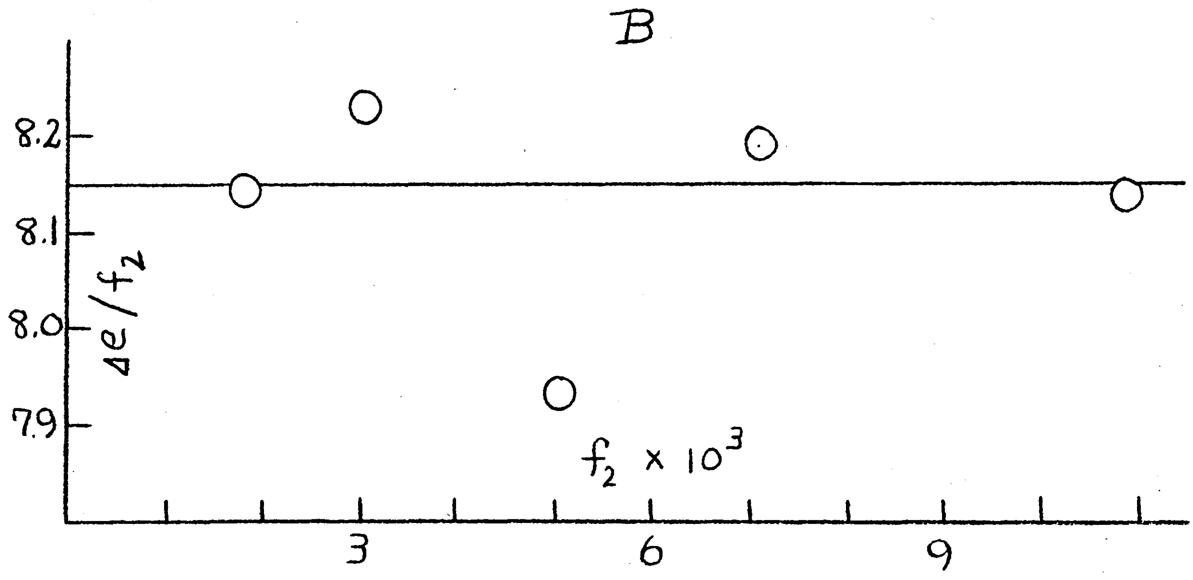

B
8.2
8.1
8.0
7.9
Δe/f₂
f₂ x 10³
3
6
9

Figure XIV

N Phenyl N p-chlorophenylbenzamide

A) Δe vs f_2

B) $\Delta e/f_2$ vs f_2

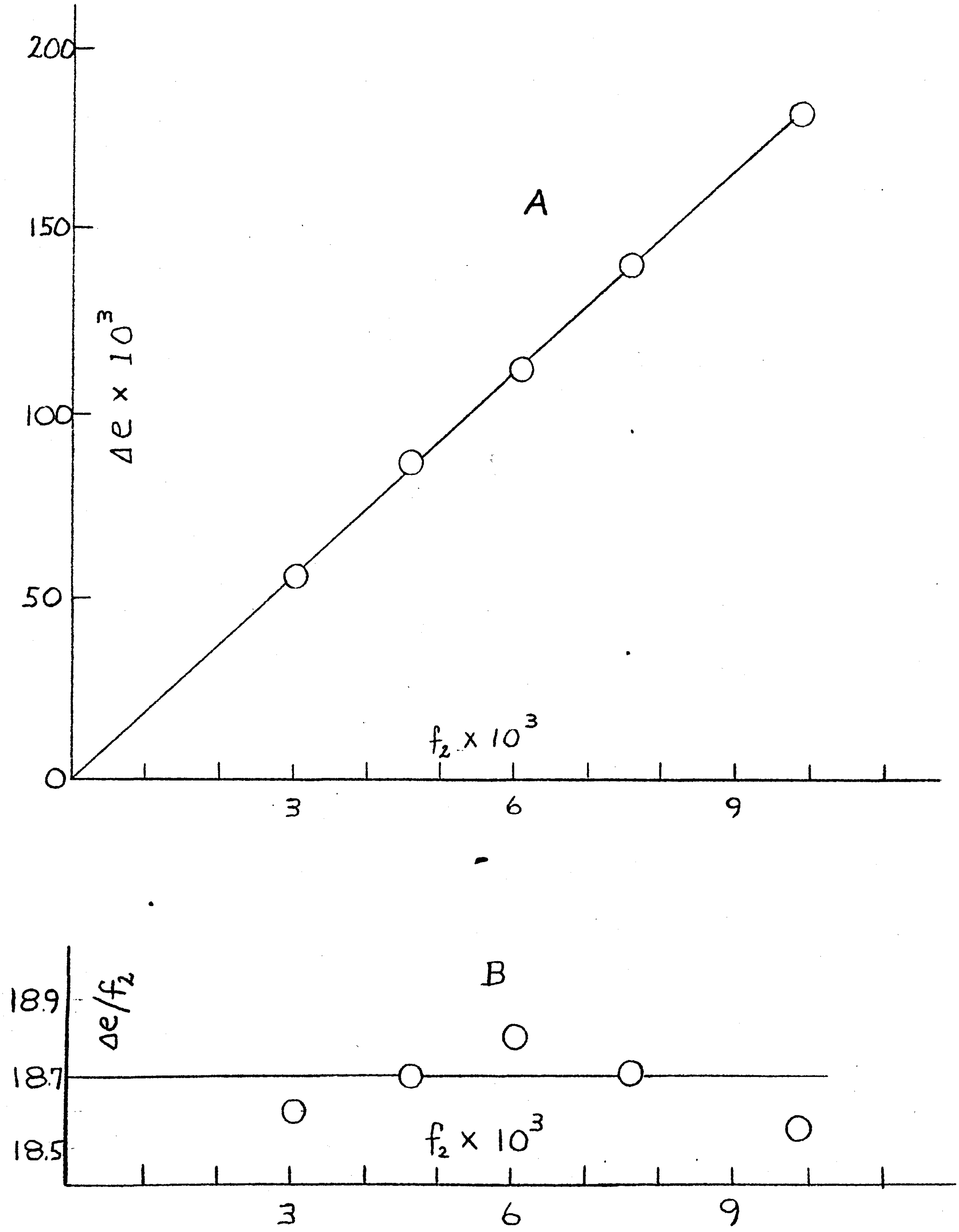
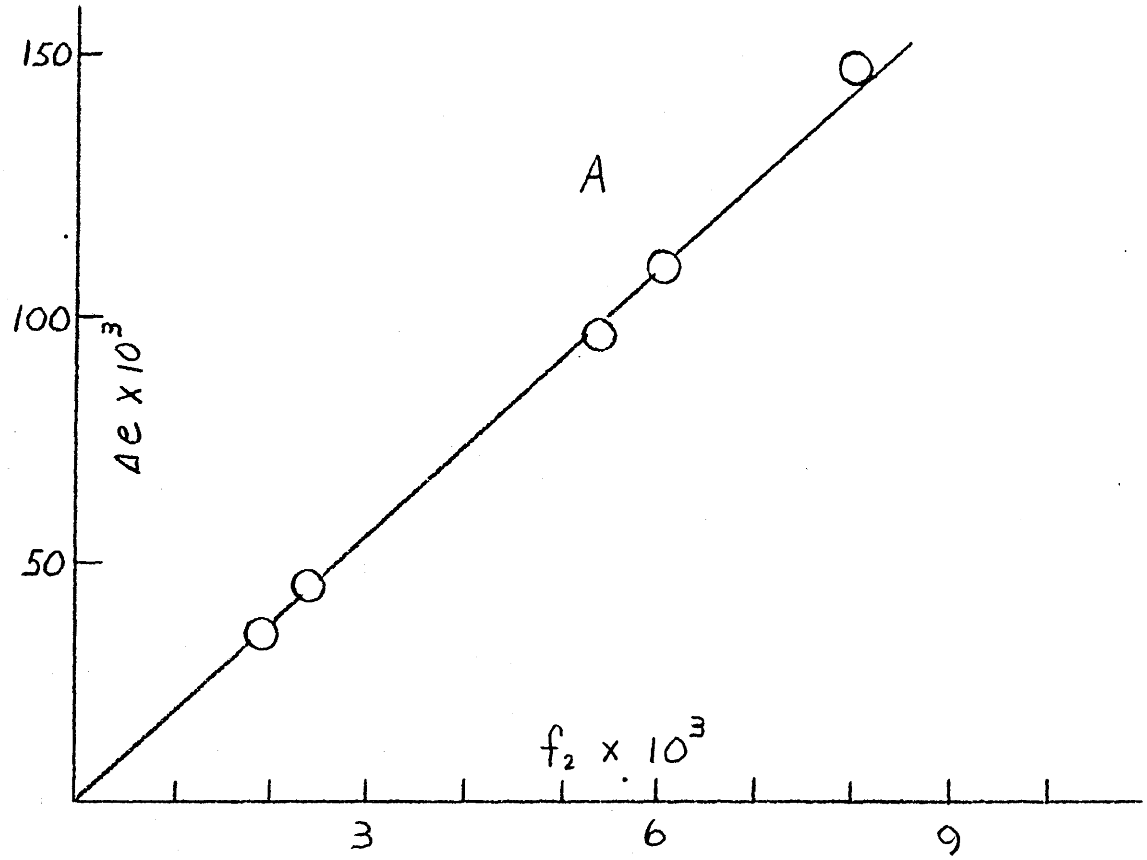

A
200
150
100
50
0
Δe × 10³
f₂ × 10³
3
6
9
B
Δe/f₂
18.9
18.7
18.5
f₂ × 10³
3
6
9

Figure XV

N Phenyl N p-chlorophenylbenzamide

A) Δe vs. f_2

B) $\Delta e/f_2$ vs. f_2


150
100
50
Δe x 10³
A
f₂ x 10³
3
6
9

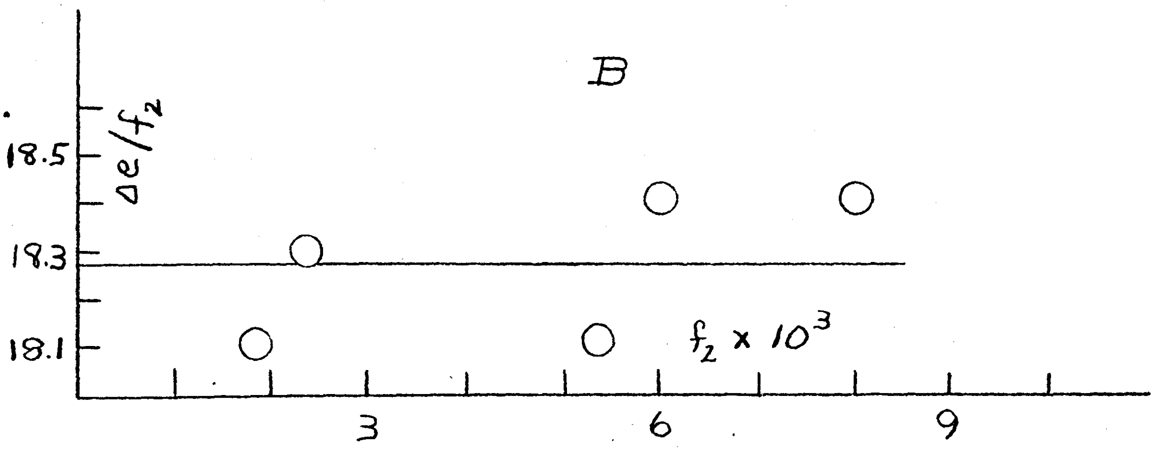
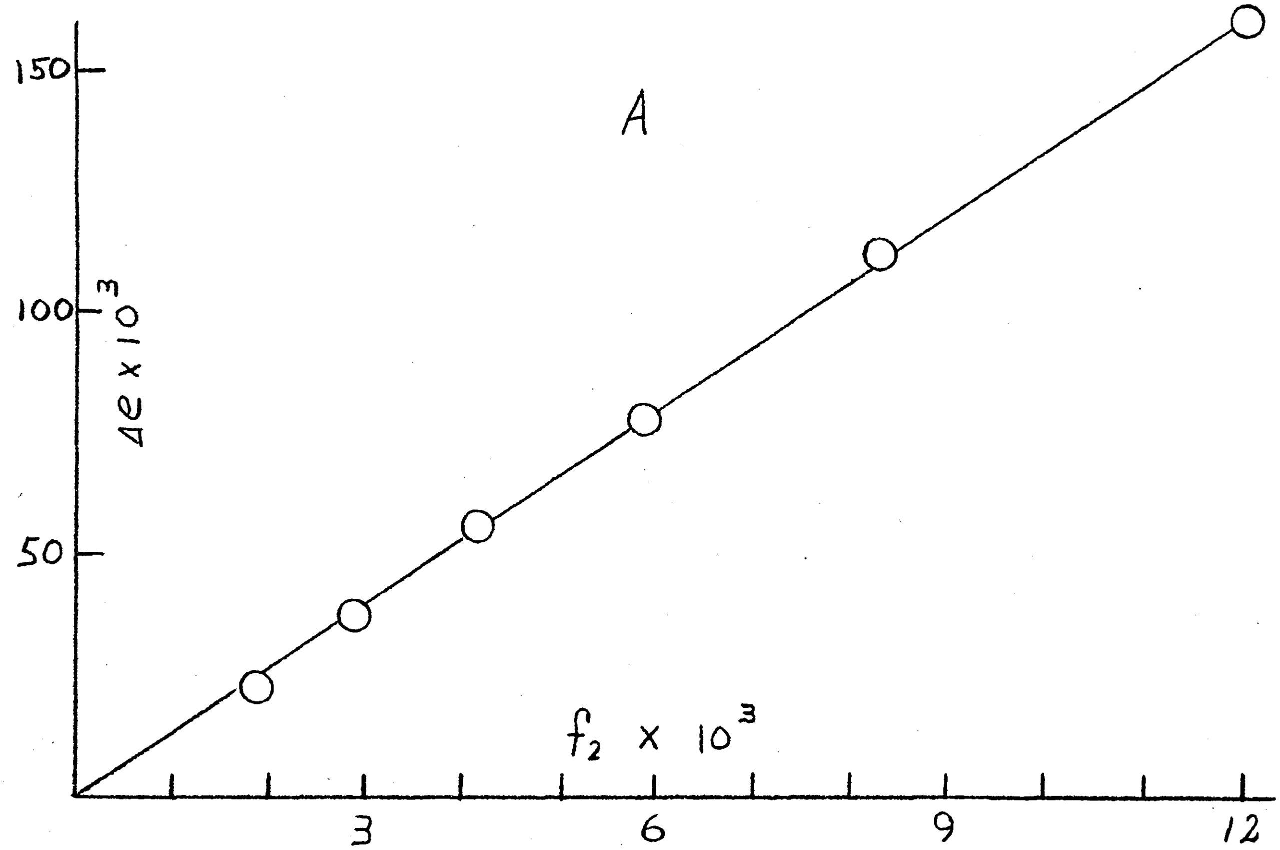

B
Δe/f₂
18.5
18.3
18.1
f₂ x 10³
3
6
9

Figure XVI

N Phenyl N p-chlorophenyl p-chlorobenzamide

A) Δe vs. f_2

B) $\Delta e/f_2$ vs f_2


A
150
100
50
Δe × 10³
f₂ × 10³
3
6
9
12

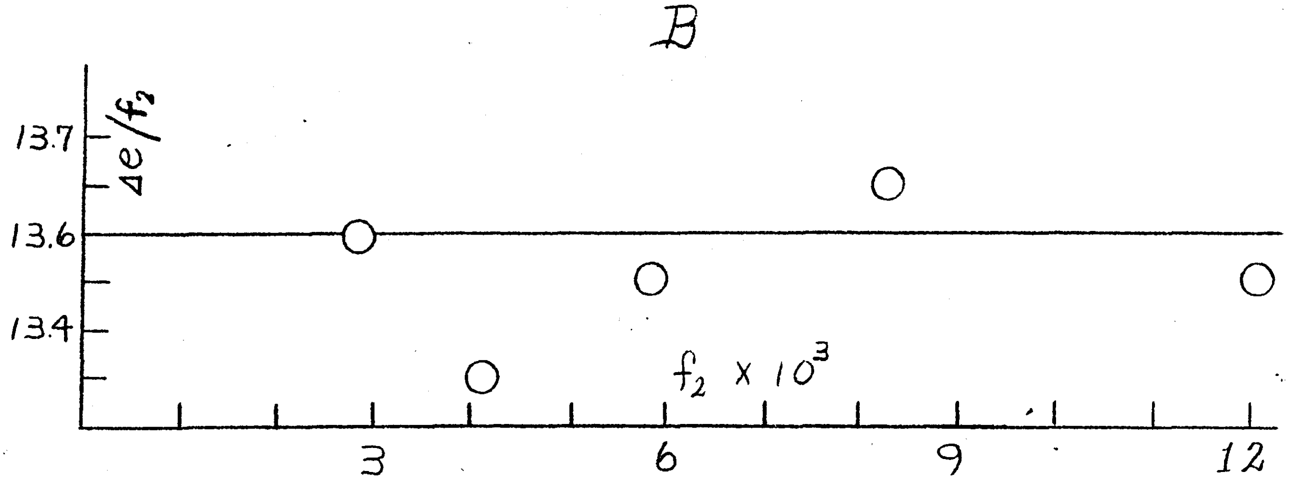
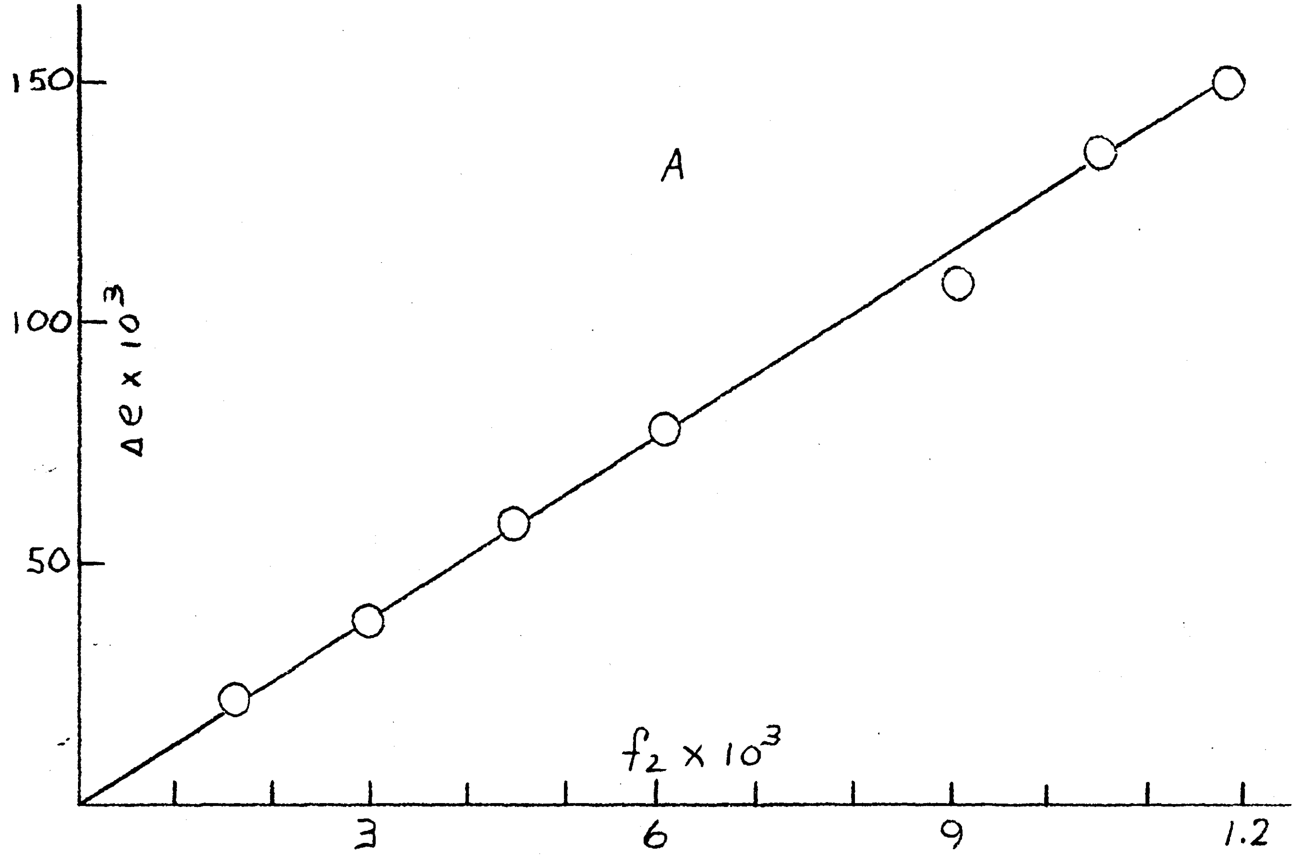

B
Δe/f₂
13.7
13.6
13.4
f₂ × 10³
3
6
9
12

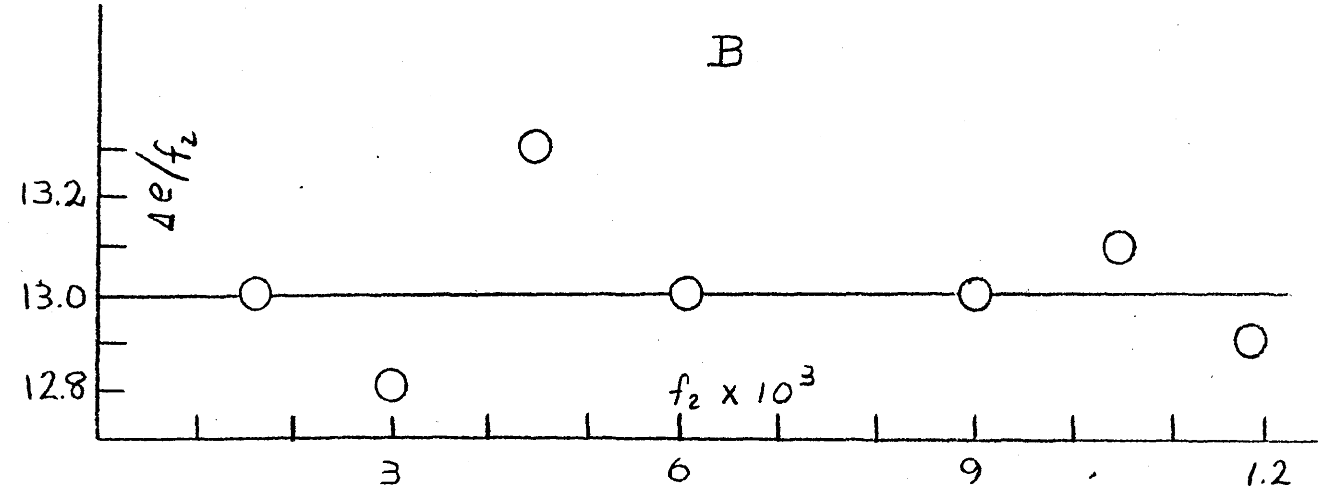
Figure XVIII

N Phenyl N p-chlorophenyl p-chlorobenzamide

A) Δe vs f_2

B $\Delta e/f_2$ vs f_2


A
150
100
50
Δe × 10³
f₂ × 10³
3
6
9
1.2


B
13.2
13.0
12.8
Δe/f₂
f₂ x 10³
3
6
9
1.2

IV ERRORS

The limiting factor determining the precision of the total polarization is the $\Delta e/f_2$ term of the Hedestrand equation. The $\Delta d/f_2$ contributes, in the case N,N diphenylbenzamide, about 6% to the total polarization.

The average deviation of the mean of ΔC measurements was 6×10^{-2} uuf. yielding an average deviation of the mean of Δe of about 2×10^{-4}. In Tables II through IX, the smallest Δe value is 14.8×10^{-3} and the largest is 183×10^{-3}. In the former, the deviation amounts to 1.3% error and in the latter, 0.11% error. This error then becomes about a 1% error in the total polarization. A 1% error in the $P_{2\infty}$ constitutes, in the present cases, between 0.5% and 0.6% error in the dipole moment.

The average deviation of the mean of the values of $\Delta d/f_2$ indicate a precision of about 3%, the worst case being 8%. An 8% error in $\Delta d/f_2$ term of the Hedestrand equation would be reduced to only about a 0.5% error in the total polarization.

V) DISCUSSION OF RESULTS

The dipole moment of the amides measured in this investigation are given in Table XI . They are being reported for the first time.

From the measured electric moments of N,N-diphenylbenzamide, N,N-di p-chlorophenylbenzamide, N,N-diphenyl p-chlorobenzamide, and N,N-di p-chlorphenyl p-chlorobenzamide, it is possible to determine the direction of molecular moment and to make certain deductions regarding the structure of these substances.

Theta, θ, is defined as the angle made by the moment of the molecule and a reference line in the molecule. This reference line is the line between the carbonyl carbon and the ring carbon to which it is bonded. Figure XVIII shows the location and general direction of the resultant.

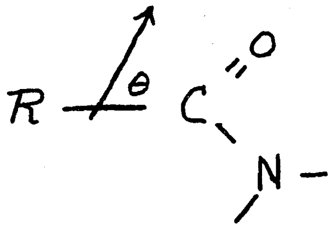


Figure XVIII

The experimental value of θ was determined in the following manner. Reference to Figure XX will assist the explanation. The vector representing the unsubstituted acid phenyl compound, viz. 3.62 D for N,N-diphenylbenzamide, was vectorially added to the vector representing the C - Cl bond moment plus the C - H moment, which is the moment of chlorobenzene, 1.58 D (3) as shown in the diagram. The experimental moment of N,N-diphenyl p-chlorobenzamide, 3.42 D, was then combined with the above vector in order to complete the triangle. The value of θ was then measured. The above procedure was repeated using N,N di p-chlorophenylbenzamide and N,N di p-chlorophenyl p-chlorobenzamide. The values of θ are given in Table XII .

Phi, ϕ , the angle that the resultant of the C - Cl moments para to the nitrogen atom makes with the reference bond is shown in Figure XIX . The measured magnitude and direction of this resultant is determined in the manner described below. Figure XX shows the vector diagrams

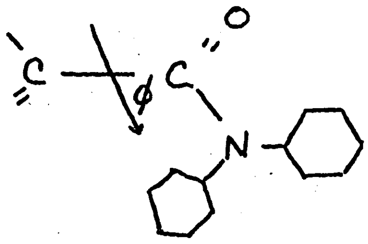


Figure XIX

used for this determination. The vector representing the moment of N,N, - di p-chlorophenylbenzamide is constructed, viz. 3.02 and 47^{o} for N,N-di p-chlorophenylbenzamide, and the moment of N,N-diphenylbenzamide is substracted, viz. 3.62 and 69^{o} for N,N-diphenylbenzamide, The diagram is completed by drawing in the resultant. The magnitude and direction of the resultant could now be measured. The above proceedure was repeated for the p-chlorobenzamides.

The value of ∅ obtained above was then used for determinations of alpha, α, the included angle of the phenyl groups attavhed to the nitrogen atom. This angle can be calculated from the cosine law. The angle was found to be 122^{0}, a value that is in close agreement with the value of the same angle in unsubstituted and N monosubstituted amides (1), (31), (24).

In applying these calculations to the data for the monochloro compounds, an impossible result was obtained. The resultant was considerably less than the absolute difference between the C - Cl bond moments and the C - H bond moment. The only explaination apparent at present is that the C -Cl bond para to the nitrogen atom is out of the plane of the amide group.

If the measured dipole moments of these amides in benzene solution are compared with the moments calculated from bond moment data (26) C=O, 2.3 D; C - H, 0.4 D; C - Dl, 1.58 D, a difference between the calculated and observed values is observed for some of these compounds, the largest being for N,N,di p-chlorophenyl p-chlorobenzamide

$$\mu_{calc} = 0.8\ D \qquad \mu_{obs} = 2.23\ D$$

This difference has been attributed to contributions of a highly polar form to the resonance hyrbid (21). The dipole moment of the polar form may be calculated from the distance between the nitrogen and oxygen atoms (24). In the case of N,N di p-chlorophenyl p-chlorobenzamide, this moment is about 8.3 D which gives an estimated 20% contribution of this form. Some of the difference between observed and calculated moment, probably about 0.2 D to 0.3 D, can be attributed to the solvent effect. As this is small, it was not taken into consideration in estimating the contribution of the polar form.

It was hoped that the thermal rearrangement of the imino ethers, N p-chlorophenylbenzimino phenyl ether and N phenylbenzimino p-chlorophenyl ether, would result in two different monochlorosubstituted benzamides, as earlier works (16), (30) had shown the lack of free rotation around the C - N bond. However, the compounds were found to have identical melting points, no depression of the mixed melting points and the measured dipole moment agreed within experimental error. The value of their moments is approximately that calculated from the structure in which the C - Cl bond is cis to the carbonyl bond. It is concluded that in this rearrangement the p-chlorophenyl group is preferentially oriented cis to the carbonyl group and that the two compounds are identical. The same result was observed with N p-chlorophenyl p-chlorobenzimino phenyl ether and N phenyl p-chlorobenzimino p-chlorophenyl ether.

Examination of the $\Delta e/f_2$ vs f_2 plots show no change with concentration. This is in agreement with earlier observations (2) (319) and indicates insignificant association of these compounds at these concentrations in benzene solution. This is expected as there is no amide hydrogen atom. Hobbs, Bates and Worsham (1), (2) (319) have previously shown that hydrogen bonding is principally responsible for the association of amides.

In summary the following points have been demonstrated:

(i) The directions of the dipole moment of N,N disubstituted benzamides are shown in Table

(ii) The angle between the two N - C bonds of the phenyl groups attached to the nitrogen atom is 122°.

(iii) A contribution of a polar form of less than 20% will explain all deviations between observed and calculated moments.

(iv) Association between molecules of N,N disubstituted benzamides is insignificant at concentrations less than a mole fraction of 0.01 in benzene.

(v) In the rearrangement of imino ethers, containing a p-chlorophenyl group attached to either the nitrogen or oxygen atom, the final product will have the p-chlorophenyl group cis to the carbonyl group.

TABLE XVI

Experimental Values of θ

N,N Diphenylbenzamide	69°
N,N Di p-chlorophenylbenzamide	47°
N,N Di p-chlorophenyl p-chlorobenzamide	79°
N,N Diphenyl p-chlorobenzamide	95°

TABLE XVII

Section A

Experimental Values of ϕ

N,N Di p-chlorophenyl benzamide	58°
N,N Di p-chloropheny p-chlorobenzamide	56°

Section B

Resultant Magnitude of C-Cl bond para to N-C bond

N,N Di p-chlorophenyl benzamide	1.38 D
N,N Di p-chlorophenyl p-chloro benzamide	1.41 D

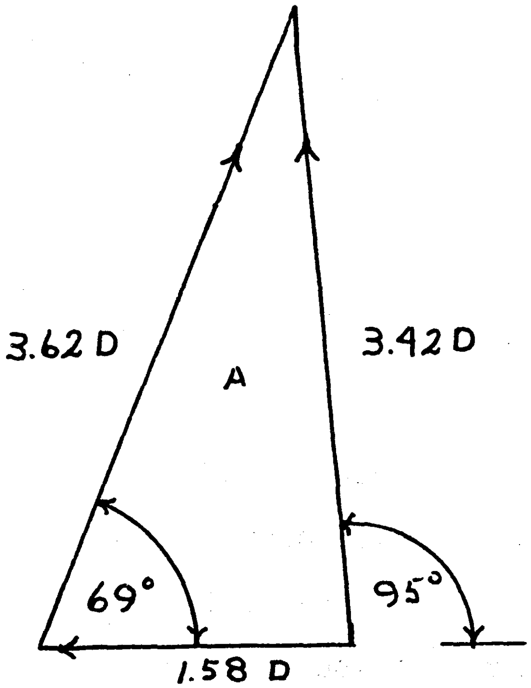
Figure XX

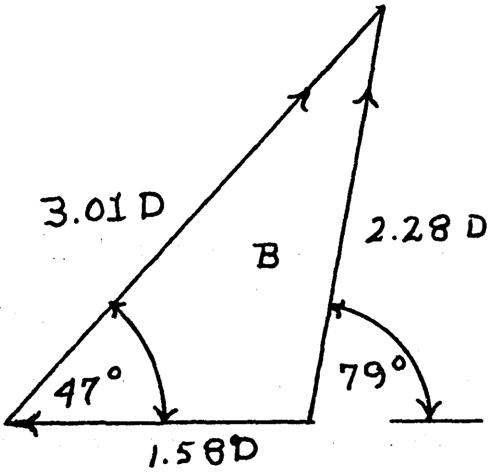
A) Vector diagram used in the determination of θ for N,N-diphenylbenzamide and N,N-diphenyl p-chloro benzamide.

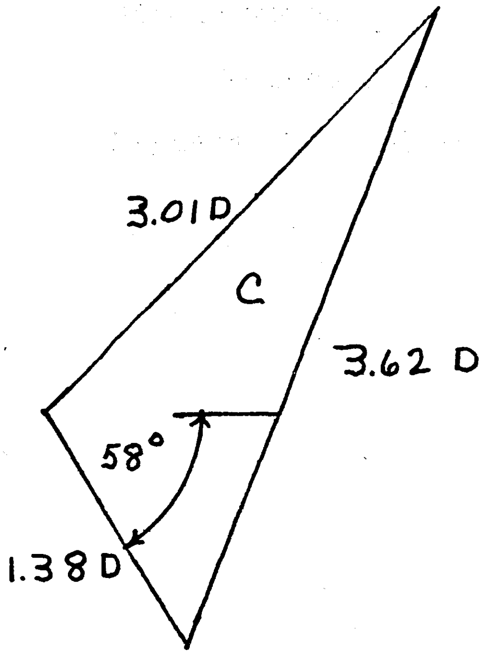
B) Vector diagram used in the determinationof θ for N,N-di p-chlorophenyl p-chlorobenzamide and N,N-di p-chlorophenylbenzamide

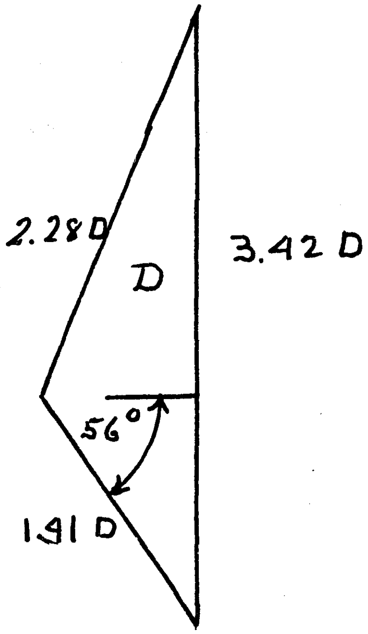
C) Vector diagram used in the determination of ϕ for N,N- di p-chlorophenylbenzamide and N,N-diphenylbenzamide.

D) Vector diagram used in the determination of ϕ from N,N-di p-chlorophenyl p-chlorobenzamide and N,N- diphenyl p-chlorobenzamide.


3.62 D
A
3.42 D
69°
95°
1.58 D


3.01 D
B
2.28 D
47°
79°
1.58D


3.01D
C
3.62 D
58°
1.38 D


2.28D
D
3.42 D
56°
1.91 D

SUMMARY

The dipole moments of six N,N-disubstituted benzamides were determined in benzene solution.

The structure of the amide group and its association in benzene solution were discussed in view of the aviable data. It appears that the N-phenyl groups are out of the plane of the carbonyl group. Resonance contributions of less than 20% explain the large dipole moment.

Unsaccessful attempts were made to prepare two N-phenyl N-p-chlorophenylbenzamide isomers.

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