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## Acknowledgements

The bulk of the text of the report is the M.S. thesis of Ms. Elizabeth Sugg with major revisions in the Results section and the addition of Appendix I. The thesis was prepared by Ms. Sugg as a Research Assistant on the subject project. Since the text had been rewritten and revised by both Ms. Sugg and the principal investigator, it was felt that the final form would not be improved by further revision.

A large number of pK measurements were performed by Mr. Charles Potter. Although the results reported here are numerically different from those calculated by Mr. Potter, the raw data obtained was used and was excellent. It is a pleasure to acknowledge his contribution to this work.

Mr. Magdy El-Faoumy was responsible for the synthesis of several compounds and preliminary kinetic measurements and it is a pleasure to acknowledge his contributions.

Mr. Roger Combs was responsible for the final computer programs utilized in the calculation of the pK values. It is a pleasure to acknowledge his very important contribution to this work.

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INTRODUCTION

Historical

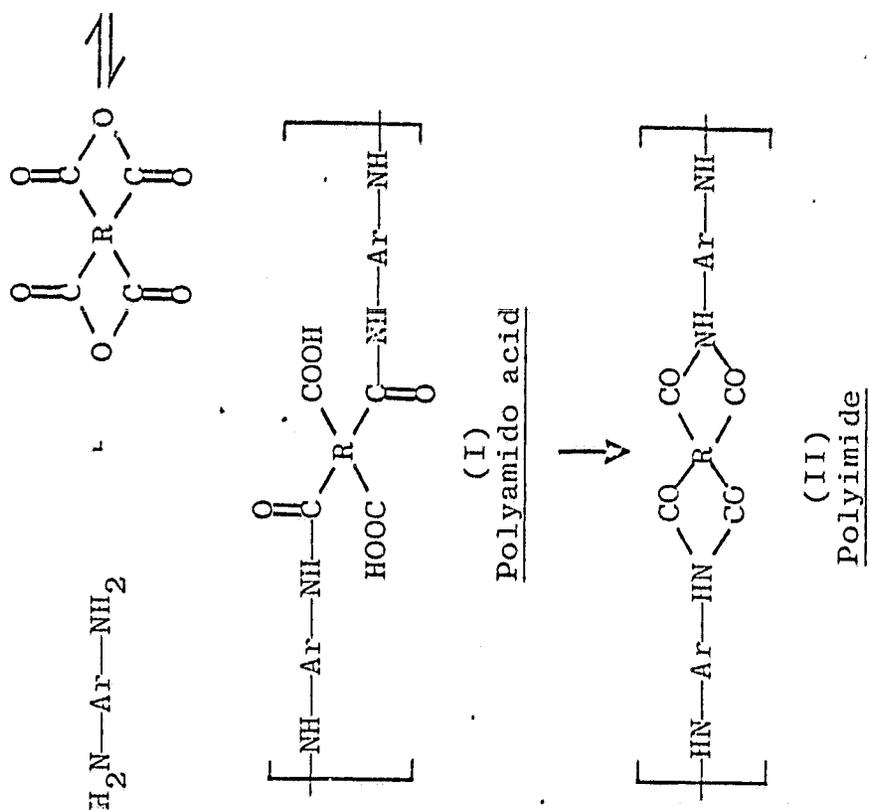
The fundamental reactions for synthesis of polymers containing an imide ring have long been known.<sup>1</sup> Aliphatic polyimides were prepared in the 1950's through condensations of salts of aliphatic diamines with tetracarboxylic acids and their esters.<sup>2</sup>

Appreciable interest in these compounds began to develop with reports<sup>2,3</sup> of the synthesis of aromatic polyimides from the reaction of dianhydrides with aromatic amines. This new class of polymers was found to have desirable electrical properties<sup>5</sup> and to possess exceptional thermal stability.<sup>1,2,4-6</sup>

Acylation of aromatic amines by acid anhydrides (Figure 1) was preferred over the nylon salt type of reaction used with aliphatic diamines because the low basicity of aromatic amines prevented the formation of well-defined salts.<sup>2</sup> The first step of the reaction was the formation of the polyamido acid (I) which was treated thermally to induce intramolecular cyclization to the polyimide (II).<sup>4</sup>

Highly polar solvents were required to dissolve these polymers<sup>3</sup> and N,N-dimethylacetamide (DMA) and dimethylsulfoxide (DMSO) were among the most commonly used solvents. These solvents have been shown to associate with both the polymer and the reactants.<sup>3,6,7</sup>

Kinetic experiments<sup>8,9</sup> to determine the mechanism of these polymerizations have revealed little about the rates of the individual steps and their degree of reversibility.<sup>10</sup> The reaction was found to be bimolecular,<sup>11</sup> with the rate determining step the formation of the amido acid. It was found that depending on the



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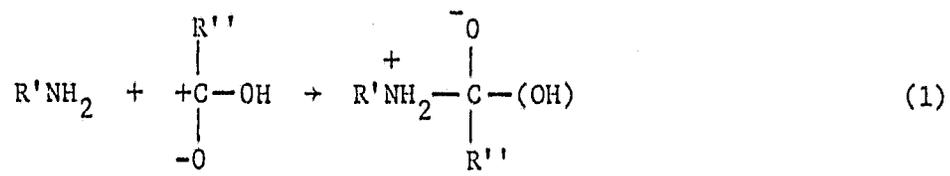
Figure 1: Overall reaction for formation of aromatic polyimides from aromatic amines and acid anhydrides.

degree of conjugation between the two amino groups, the reactivity of the residual amino group in the partially reacted compound could be much less than, or only slightly different from that of the amino group in the unreacted monomer.<sup>10</sup>

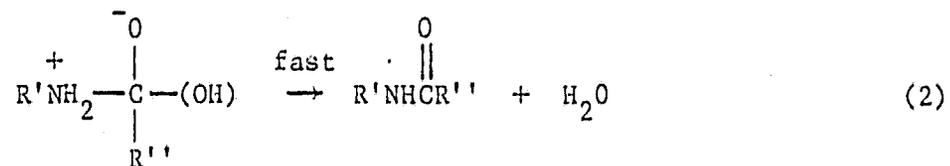
#### Mechanism for acylation of amines

The mechanism for acylation of amines by acid chlorides,<sup>14-16</sup> and acid anhydrides,<sup>13,17-19</sup> was examined in benzene,<sup>14-16,18</sup> and in tetrahydrofuran, cyclohexane and diethyl ether.<sup>19</sup>

According to Porai-Koshits,<sup>12</sup> one general scheme can be applied to the acylation and diazotization of amines, as well as to the formation of anils, diazo-amino compounds and iminazoles.<sup>12</sup> The first step (1) is the formation of a bond between the unshared electron pair on the amino nitrogen and an electron deficient atom, i.e.,



The final product is then obtained (2) through loss of a simple molecule (HCl, H<sub>2</sub>O):

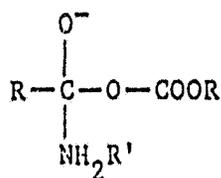


The rate of reaction for step (1) would depend on both the basicity of the amine and the polarizability of the electrophilic substrate.<sup>12</sup>

Studies<sup>14-16</sup> performed on the acylation of 4-aminobiphenyl by benzoyl chloride in benzene revealed some interesting information which

can easily be applied to a general understanding of acylation reactions. Litvinenko found that electron withdrawal decreased the reactivity of 4-aminobiphenyl and that disruption of the conjugated system of the biphenyl moiety through introduction of a sulfur or oxygen link increased the interaction between 4'-nitro and the 4-amino substituents.<sup>14</sup> The transmission of the electron-withdrawing effect of the nitro group was increased in the following order: diphenyl < diphenyloxide < diphenyl sulfide.<sup>14</sup> Further, distortion of the angle between the planes of the benzene rings, resulting from ortho substitution, led to a substantial reduction in the interaction between these two substituents.<sup>15</sup> Hypothesizing that the angle between the two benzene rings was somehow important in the transmission of electronic effect, Litvinenko<sup>16</sup> then studied the reactivities of 2-aminofluorene and 2-amino-7-nitrofluorene. In the case of the ortho-substituted diphenylamine, the angle between the benzene rings would be increased. In the fluorene molecules the angle would be decreased, but planarity would be maintained.<sup>16</sup> Since the reactivity of the 2-amino-7-nitrofluorene was the lowest of all the systems studied, it was concluded that maintenance of planarity of aromatic ring systems was an important factor in the transmission of electronic effects.

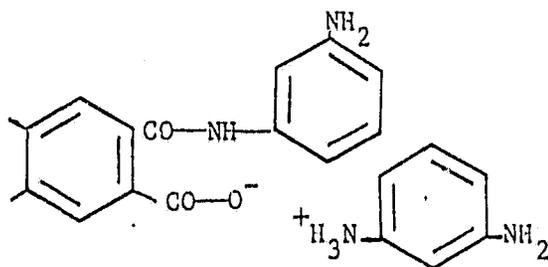
Denny and Greenbaum<sup>17</sup> have investigated the mechanism of acylation of aromatic amines by acid anhydrides through oxygen-18 tracer analysis in dimethylformamide, acetonitrile and diethyl ether. They proposed an equilibrium between the reactants and an intermediate complex (III).

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(III)

Ardashnikov<sup>20</sup> proposed a similar equilibration between the reactants and amic acid product, but calculated the equilibrium constant to be greater than  $10^5$  in highly polar solvents such as DMA.

The reaction between anhydrides and amines has also been examined in terms of the electron donor-acceptor properties of the amine and anhydride molecules.<sup>21</sup> Infrared spectra of proposed charge-transfer complexes obtained by cosublimation of various aromatic amines and anhydrides were reported.<sup>21</sup> It is interesting to note that the peak maximum assigned to the phthalic anhydride-*m*-phenylenediamine charge transfer complex (415-420  $\mu$ ) is very close to the peak maximum attributed<sup>11</sup> to a nylon type salt formed by the same amine upon equilibration with pyromellitic dianhydride in DMA (378-395  $\mu$ ).



The kinetics of the reaction of various substituted anilines with pyromellitic dianhydride (PMDA) and with 3,3', 4,4'-benzophenone-tetracarboxylic dianhydride have been examined in *N,N*-dimethylformamide, DMA and *N*-methyl-2-pyrrolidone.<sup>22</sup> Svetlichnyi<sup>22</sup> found that correlations

of substituent effects on the acylation rate obeyed the Hammett equations. Large negative  $\rho$  values (-3.4, -3.32, -3.0) indicated both acceleration of the reaction by electron donating substituents and a high sensitivity of the reaction towards structural changes in the amine molecule.<sup>22</sup> That the  $\rho$  value changed little on passing from one acylating agent to another indicated that only one type of acylation mechanism existed.<sup>22</sup>

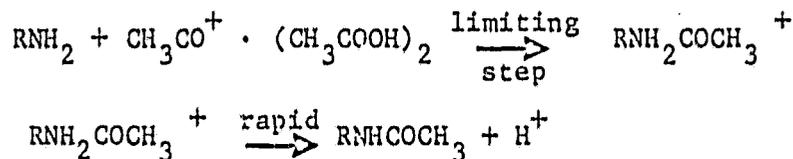
Litvinenko and Oleinik<sup>23</sup> also found correlation with the Hammett plot for the reactions of substituted anilines with acetic anhydride and benzoic anhydride in nitrobenzene and nitrobenzene-acetic acid. The reaction was unimolecular in each reactant for the uncatalysed reaction with a  $\rho$  value of  $-2.72 \pm 0.15$ . The rate law for the catalysed reaction included a rate constant for the catalysis by acetic acid. The  $\rho$  value for the catalysed reaction was  $-2.89 \pm 0.64$ .<sup>23</sup>

Catalytic effects on the reaction between anhydrides and amines have also been examined in benzene<sup>18,13</sup> and in acetic acid.<sup>21</sup> Loucheux and Bandaret<sup>18</sup> observed autocatalysis by the amic acid product for the reaction between aniline and various aliphatic and cyclic anhydrides at stoichiometric concentrations.

Litvinenko and Aleksandrova<sup>13</sup> found that benzoic acid catalysed the reaction of benzoic anhydride with aniline in benzene but that catalysis was dependent upon benzoic acid in its monomeric form alone. They did not propose the form of the reacting species.

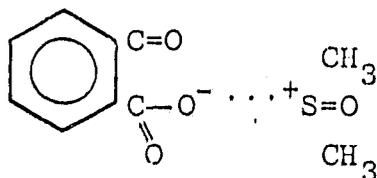
Bel'skii<sup>24</sup> proposed that acetic anhydride in a solution of acetic acid would react to form a positively charged species,

which then reacted with the aromatic amine in what was the



rate limiting step for the reaction.

Catalytic effects of the solvents normally used for polymerization have also been examined. Kolesnikov<sup>6</sup> suggested that a charge transfer complex was formed between the anhydride and a highly polar solvent such as DMSO. He proposed that the strength of this complex would be dependent upon the nucleophilicity of the solvent. The stronger the complex, the slower the reaction between the anhydride and amine molecules. This implied that DMA would retard the reaction considerably more than DMSO and that DMSO would retard the reaction more than dimethylformamide. However, he investigated only DMSO, so no comparisons could be made. He claimed to have isolated and identified DMSO-anhydride complexes such as



but the IR peak maxima, though in the same region as those previously reported for an anhydride-amine charge transfer complex and for the amine-carboxylic acid salt, are not clearly defined.

From this discussion, it may thus be concluded that acylation of amines by anhydrides is a second-order kinetic process, at times subject to acid catalysis. The reaction rate is related to the basicity of the amine molecule. A common mechanism for acylation exists which may be represented by Figure 2, where the formation of a bond between the anhydride and the amine to yield a tetrahedral intermediate (III) is the rate-determining step.

#### Basicity of aromatic amines

The following qualitative effects of substitution have to be considered as influencing the pKa values of primary aniline bases:<sup>25</sup>

- 1) Mesomeric and inductive effects of the substituent relayed through the bonds of the ring and of the substituent.
- 2) Bulk effect of substituents causing hindrance to approach or recession of the protons.
- 3) Combination effect of more than one substituent.
- 4) A direct spatial effect due to the interaction between the electron clouds of the amino groups and of the substituent.
- 5) Steric hindrance to solvation of the anilinium ion.

Brown<sup>26</sup> found that the relative base strengths of amine bases  $\text{NH}_3$ ,  $\text{RNH}_2$ ,  $\text{R}_2\text{NH}$  and  $\text{R}_3\text{N}$  as measured against an uncharged species  $\text{BR}'_3$  would depend mainly on the availability of the unshared pair of electrons on the nitrogen, but that other factors, such as weaker electrical forces and steric factors, should play an important role. Any effect which shifted electron density towards the nitrogen atom would enhance its proton attracting power through an increase in the electron density of the lone pair orbital.<sup>25</sup> Any effect which distorted this orbital would reduce the strength of the lone pair orbital, ". . . distortion



being concomitant with partial neutralization of the electronic charge around the nitrogen."<sup>25</sup>

These inductive effects help to explain the much weaker basicity of aromatic amines, as resonance with the phenyl rings reduces the availability of the unshared electron pair on nitrogen. Substitution of electron donating groups para to the amine function strengthens basicity while electron donation from a position meta to the amine is negligible. Substitution at the ortho position is complicated by the counteraction of resonance with steric effects between the amine and the substituents.

In addition to steric and inductive effects, however, an allowance must be made for the solvation and subsequent stabilization of the amine ions. In aqueous solvents, both the amine and the amine ion would be solvated, but hydrogen bonding to the ion would be stronger.<sup>27</sup>

Correlations of Taft  $\sigma^*$  values with pKa values of nonaromatic<sup>28</sup> and aromatic<sup>29</sup> amines have revealed that the amines fall into categories which are related to the number of hydrogens attached to the nitrogen atom. This suggested<sup>28,29</sup> that solvation did indeed play a role in determining base strength, in the sense that the steric requirements for solvation increased in the sequence: tertiary amines > secondary amines > primary amines due to an increase in the number of hydrogens which must be solvated.

Condon<sup>30-32</sup> has expanded upon these solvation theories through measurements of "net hydration energies", the difference in hydration energy between the amine and ammonium ion. The net effect of hydration is generally unfavorable to the dissociation of the protonated

amine, and is thus a base strengthening effect. The free energy of hydration by hydrogen bonding will depend on the nature of the substituents. Again, inductive and field effects, resonance, and steric factors will contribute to the hydration energy.<sup>31</sup> The estimation of absolute net hydration energies of anilines is complicated by resonance effects.<sup>30</sup> Withdrawal of the electron pair on nitrogen into the phenyl ring may either increase or decrease hydration of the amine function as compared with the corresponding aliphatic derivatives. However, the anilinium ion would be hydrated in the same manner as aliphatic ammonium ions.

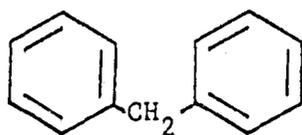
Condon has found that replacement of a hydrogen by a phenyl ring is responsible for a reduction in basicity by  $-0.37$  pK units due to inductive effects and approximately  $-2.0$  to  $-3.0$  pK units due to resonance effects.<sup>30</sup> Steric hindrance to hydration was found to operate with differing degrees of effectiveness.<sup>32</sup>

#### Correlation of amine basicity and reactivity

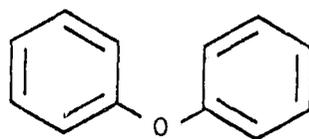
Correlations of basicity and reactivity have been performed by Kretov<sup>33</sup> for maleic anhydride and various monoamines in benzene, and by Koton<sup>34</sup> for a series of aromatic dianhydrides with 4,4'-diaminodiphenyl ether in dimethylformamide. Kretov established that the reaction rate for the acylation of amines with maleic anhydride was severely retarded with decreased amine basicity. The linearity of the relationship between pKa and the logarithm of the second-order rate constant was lost for amines whose pKa values were less than 3.0.

Koton found good linear correlation for amines with pKa values in the region of 4.3 to 5.2. This suggests that other structural effects, which are overshadowed in the reactions of the more basic amines with anhydrides, become substantial as basicity decreases.

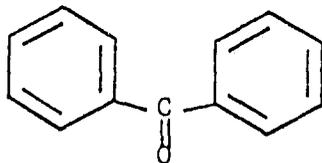
Work at NASA<sup>33</sup> with diamine derivatives of diphenylmethane (IV), diphenyl ether (V), benzophenone (VI), fluorene (VII) and fluorenone (VIII) revealed that polymerizations of these compounds with pyromellitic



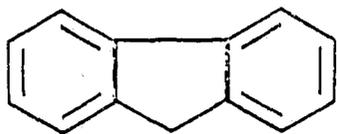
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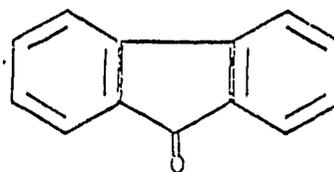
V



VI



VII



VIII

dianhydride in DMA were dependent on the basicity of the amine compound. This present study was initiated to determine what correlation existed between the basicity of the amine, and its reactivity with phthalic anhydride. Basicity measurements were to be made by potentiometric

titration of each amine in an acetonitrile-water solvent system, from which the pKa of the amine could be determined. Reactivity was defined in terms of the second-order rate constant derived from spectrophotometric examination of the reaction between each amine and phthalic anhydride in DMA. This reaction was expected to proceed in either one (for a monoamine) or two (for a diamine) stages as represented by Figure 3.

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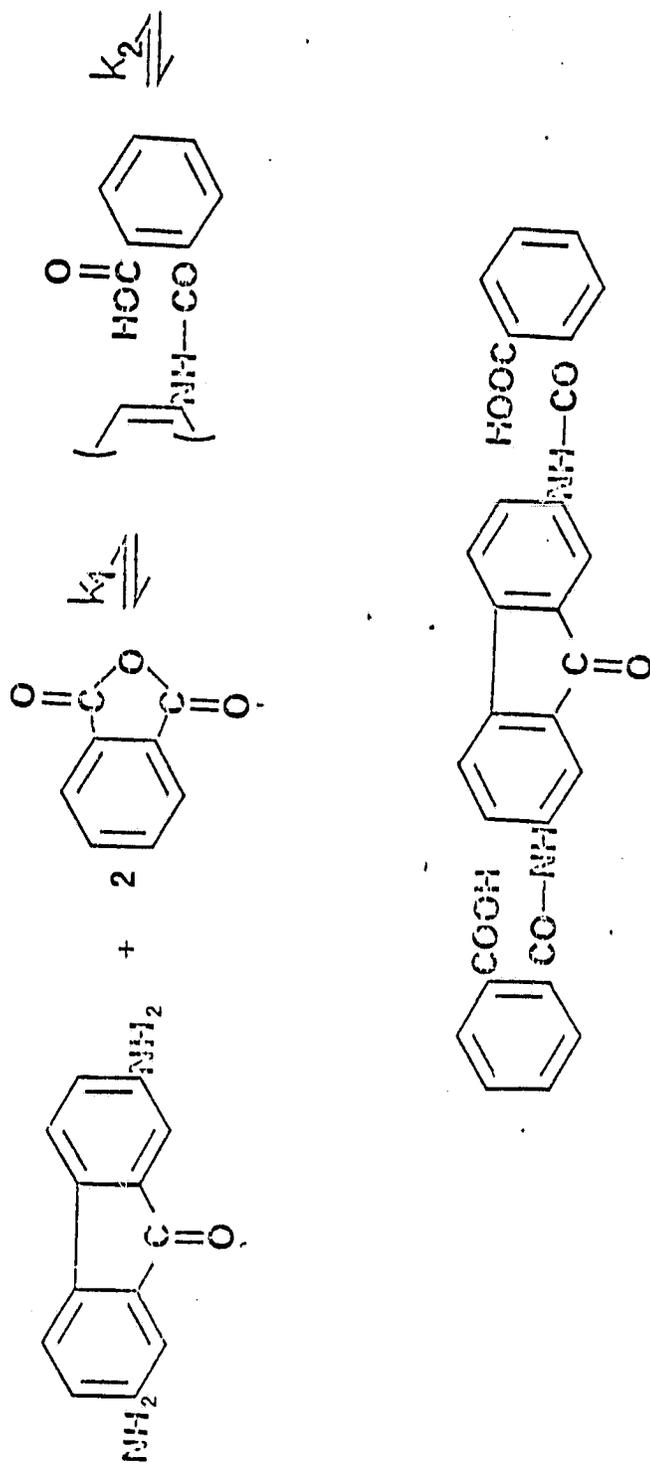


Figure 3: Formation of the monoamic and diamic acid derivatives of 2,7-diaminofluorenone from reaction with phthalic anhydride.

EXPERIMENTAL

Potentiometric determination of pKa values

1. Reagents

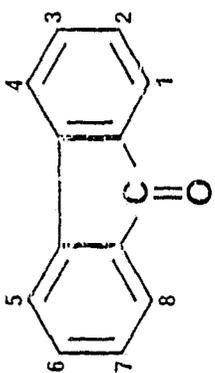
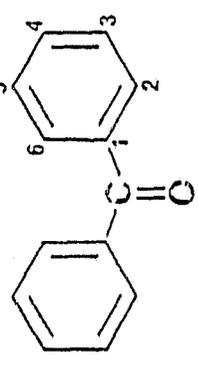
Reagent grade acetonitrile (AN) (Aldrich Chemical Co.) was used without further purification. Though this solvent could be contaminated with both acidic and basic materials, the residual acidity as measured by potentiometric titration was never large enough to warrant the extensive procedure required to obtain the pure reagent.

A stock solution was prepared of 90% AN, 10% water, and 0.10M tetraethylammonium perchlorate (TEAP) to maintain constant ionic strength. This solution was then used to prepare a one molar perchloric acid solution which was standardized against standard sodium hydroxide. The perchloric acid solution was restandardized for each series of titration and changes in molarity were never greater than 0.80%.

The amines were purified by recrystallization, usually from aqueous ethanol (Table 1). A 0.01M solution of each amine was prepared by dissolving the appropriate weight in 50 or 100 ml portions of the stock AN/water solution. This was then titrated with the perchloric acid solution using a 2.5 ml Gilmont micro-buret. Total volume change at the equivalence point was no greater than one per cent.

For each series of titrations, a titration of the stock AN/water solution was performed to determine the residual acidity of the solvent system. The data from this titration was also used to determine the formal potential ( $E^0$ ) of the electrode pair.

Table 1: Physical properties of the amines used in the kinetic study.

| Compound   | Source       | m.p. °C (Literature)        | Equivalent Weight<br>Calc. | Equivalent Weight<br>Found |
|--|--------------|-----------------------------|----------------------------|----------------------------|
| <br>Fluorenone    |              |                             |                            |                            |
| 2-amino  | Aldrich      | 161-162 (163) <sup>41</sup> | 195                        | 204.5                      |
| 2,5-diamino  | NASA         | 202-203 (200) <sup>44</sup> | 210                        | 210.8                      |
| 2,6-diamino  | NASA         | 202-203                     | 210                        | 218.7                      |
| 2,7-diamino  | NASA         | 284-288 (284-6)             | 210                        | 209.4                      |
| <br>Benzophenone |              |                             |                            |                            |
| 3-amino  | Pfaltz&Bauer | 86-87 (87) <sup>46</sup>    | 197                        | 196.9                      |
| 3,3'-diamino   | NASA         | 153-154                     | 212                        | 203.9                      |
| 3,4'-diamino   | NASA         | 127 (125-6)                 | 212                        | 213.8                      |
| 4,4'-diamino   | NASA         | 247-248                     | 212                        | 212.1                      |
| 2,4'-diamino   | NASA         | 126-127 (128-129)           | 48                         | 211.5                      |

## 2. Instrumentation

Changes in potential were measured using a Corning Model 12 pH meter with a glass-calomel electrode system. Saturated sodium chloride was used in the reference electrode instead of potassium chloride because the latter was known to form an insoluble salt in the presence of perchlorate ion.

Measurements of the potential difference between the glass and calomel electrodes will be affected by the potential at the point of contact between the saturated sodium chloride-calomel electrode and the AN/water solution. The magnitude of the potential of this liquid junction is determined by differences in the activities and mobilities of all ions present in solution.<sup>36</sup> Because the mobility of the hydrogen ion is much greater than all other ions present in this system, potential readings at high concentrations of acid will be markedly influenced by the liquid junction potential, and the response of the electrode pair will appear to be non-theoretical.

To determine at what point deviation from theoretical response occurred as a result of the liquid junction potential, several titrations of the AN/water stock solutions were performed using a cell without liquid junction which consisted of a glass electrode-silver wire reference electrode with an electrolyte of 0.01M silver nitrate and 0.09M TEAP. Data from these titrations were then plotted and compared with data from titrations performed using the NaCl reference electrode. It was thus found that below a certain acid concentration, the response of the electrode pair was both linear and theoretical (Figure 4).

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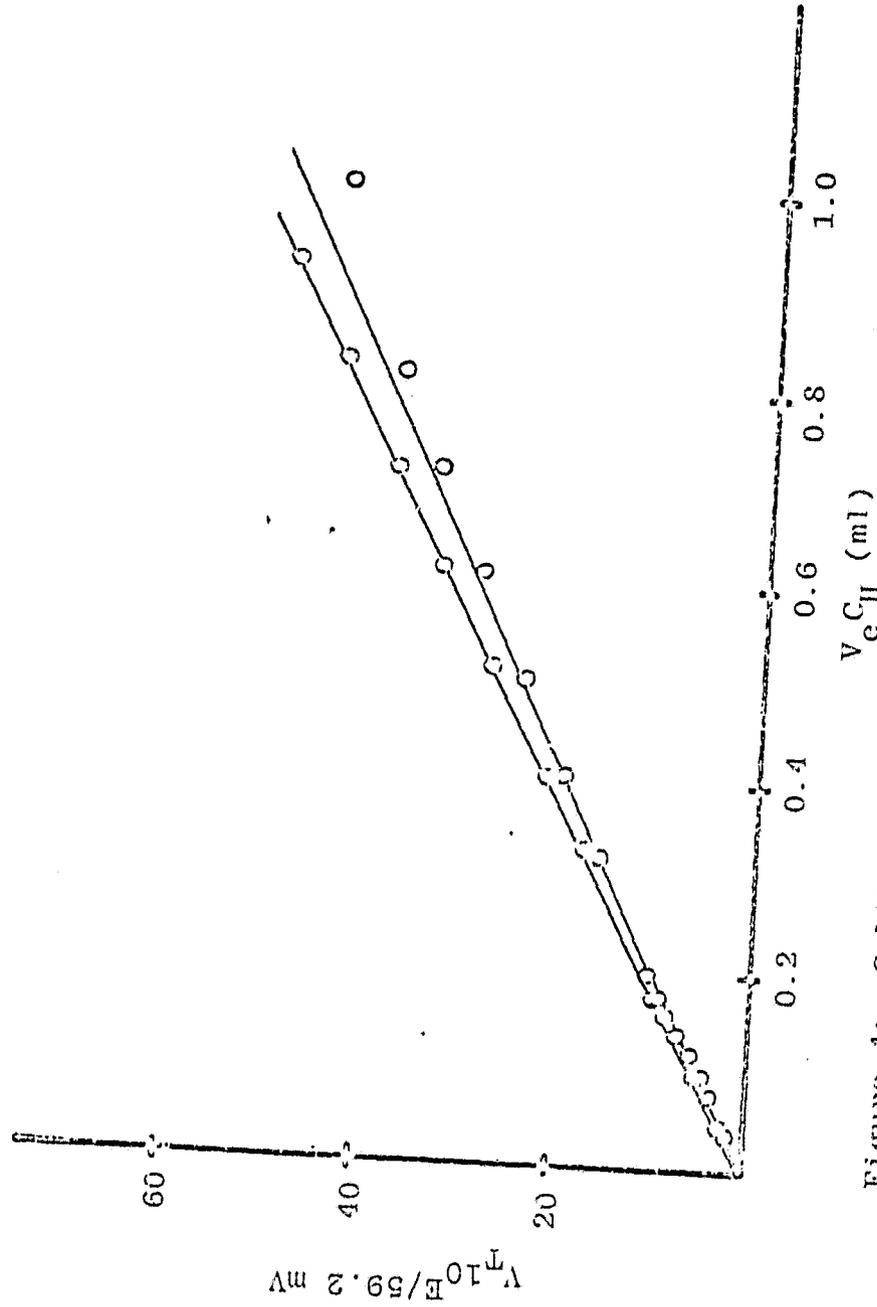


Figure 4: Calibration curve for the titration of (o) 50 ml and (o) 100 ml of the AN/water blank solution with 1.0M perchloric acid. (NaCl reference electrode.)

The potential curves obtained from most of these titrations (Figure 5) do not reveal a sharp break at the equivalence point. It was therefore necessary to manipulate the titration data in order to determine the equivalence point for each titration.

### 3. Calculations

#### (a) Calibration of the electrode pair

For data obtained after the expected equivalence point the following relations apply.

$$[\text{BH}^+] + [\text{B}] = V_e C_H / V_T \quad (1)$$

$$[\text{H}^+] + [\text{BH}^+] = V_H C_H / V_T \quad (2)$$

where  $[\text{B}]$  = unprotonated amine

$[\text{BH}^+]$  = protonated amine

$[\text{H}^+]$  = free hydrogen ion

$V_e$  = volume of acid required for equivalence

$V_H$  = volume of acid titrated

$C_H$  = concentration of acid

$V_T$  = total volume of the system.

Assuming  $[\text{B}]$  to be negligible, equations (1) and (2) were combined

$$[\text{H}^+] = V_H C_H / V_T - V_e C_H / V_T \quad (3)$$

to obtain an equation for the hydrogen ion concentration, which could then be substituted into the Nernst equation (4),

$$E = E^0 + 59.2 \log [\text{H}^+] \quad (4)$$

to yield the following expression,

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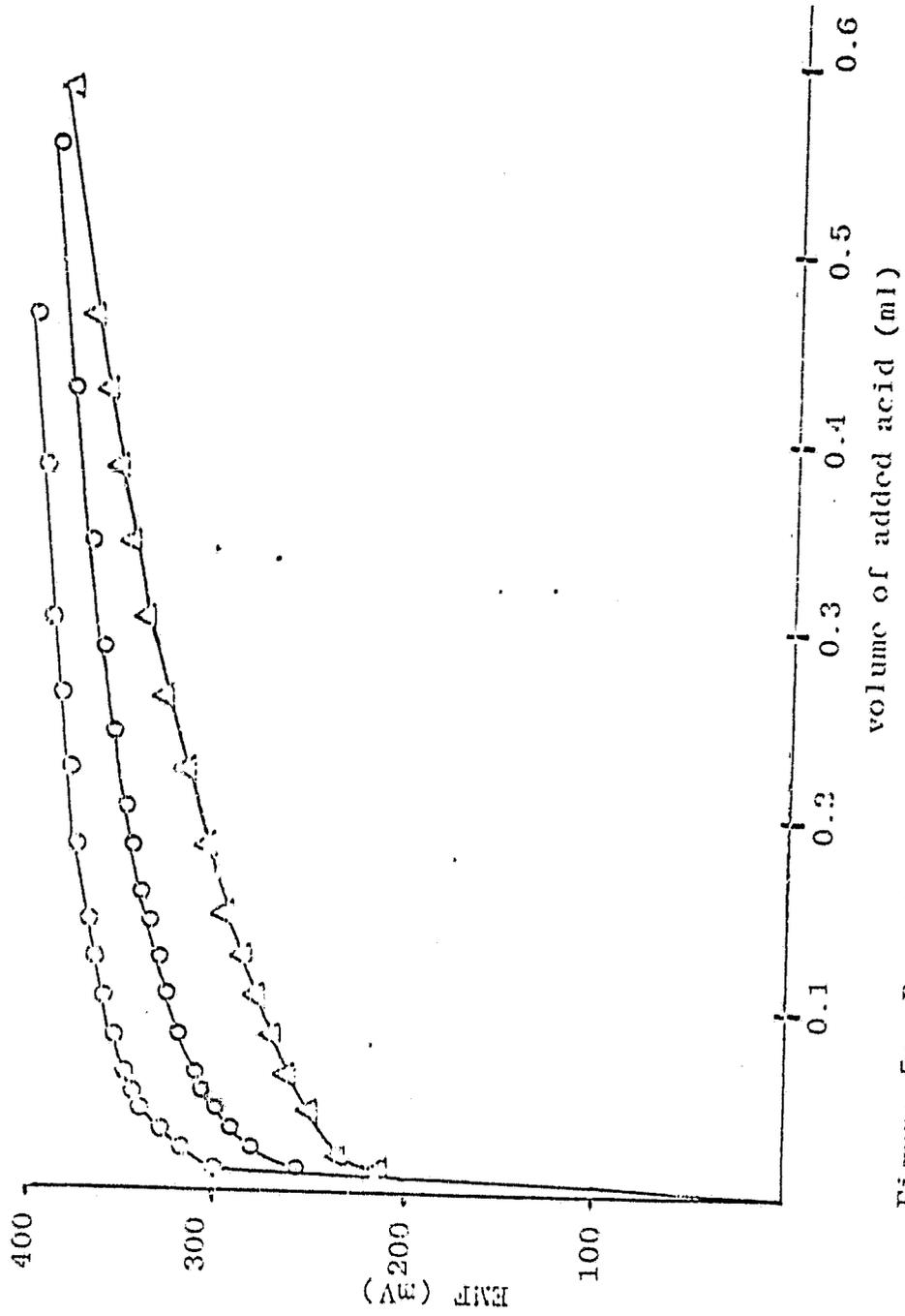


Figure 5: Potentiometric titration curve for (O) AN/water blank; (A) 2-aminofluorene; and (Δ) 2,7-diaminofluorene

$$E = E^0 + 59.2 \text{ mV} \log \left( \frac{V_H C_H}{V_T} - \frac{V_e C_H}{V_T} \right). \quad (5)$$

Rearrangement of (5) resulted in (6), an equation for a line,

$$V_T 10^{E/59.2} = V_H C_H / \Lambda - V_e C_H / \Lambda \quad (6)$$

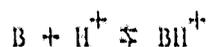
where E is the potential measured for each addition of acid,  $V_H$ , and  $\Lambda = 10^{-E^0/59.2}$ . The slope of (6) was used to obtain the formal potential,  $E^0$ , of the electrode pair (7).

$$\log (C_H / \Lambda) \times 59.2 = E^0 \quad (7)$$

The equivalence volume was obtained by dividing the intercept by the slope.

(b) Calculation of pKa values of monoamines and weakly basic diamines

The standard definition (8) of the dissociation constant for the reaction,



was used,

$$K_a = \frac{[BH^+]}{[B][H^+]} \quad (8)$$

restated as,

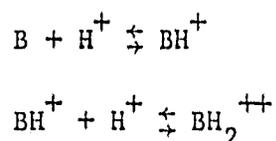
$$K_a = \frac{10^{(E - E^0)/59.2} (V_e C_H - V_H C_H + V_T [H^+])}{(V_H C_H - V_T [H^+])} \quad (9)$$

to determine the pKa values for both monoamines and those diamines which were so weakly basic that protonation of only one amino function was detected. The concentration of free hydrogen ion,  $V_T [H^+]$ , must

be taken into account for those monoamines and diamines for which protonation was not quantitative because of their weak basicity.

(c) Calculation of pKa values of basic diamines

For those diamines for which protonation of both amino groups could be detected, the formation constants for the mono-(10) and diprotonated (11) species for the reaction sequence,



were defined as,

$$\beta_1 = \frac{[BH^+]}{[B][H^+]} \quad (10)$$

and

$$\beta_2 = \frac{[BH_2^{++}]}{[BH^+][H^+]} \quad (11)$$

The fraction of protonated based,  $\bar{n}$ , was defined as,

$$\bar{n} = \frac{V_H C_H - V_T [H^+]}{V_e C_H} \quad (12)$$

where  $(V_H C_H - V_T [H^+])$  is the millimoles of mono- and diprotonated base in solution (13) and  $V_e C_H$  is the total millimoles of base present (14).

$$(V_H C_H - V_T [H^+]) = [BH^+] + 2[BH_2^{++}] \quad (13)$$

$$V_e C_H = [B] + [BH^+] + [BH_2^{++}] \quad (14)$$

Substitution of the expressions for the formation constants, (10) and (11), into (15) and rearrangement gave an equation for a line,

$$\frac{[H^+]}{\bar{n}} (\bar{n} - 1) = \frac{(2 - \bar{n})[H^+]^2}{\bar{n}} \frac{\beta_2}{\beta_1} - \frac{1}{\beta_1} \quad (16)$$

the slope of which is  $\beta_2/\beta_1$  and the intercept is  $1/\beta_1$ .<sup>37</sup> The reciprocals of the formation constants are the dissociation constants,  $K_1$  and  $K_2$ .

#### Spectrophotometric determination of pKa

A series of solutions of 2-amino-9-fluorenone (2-AFO) was prepared in the stock AN/water solvent with increasing concentrations of perchloric acid. Absorption spectra of these solutions were then obtained with a Cary 14 spectrophotometer.

The maintenance of an isobestic at 415 nm (Figure 6) suggested that only two species were present in solution, the protonated,  $[BH^+]$ , and unprotonated,  $[B]$ , forms of the amine. The observed absorbance at any wavelength was thus the sum of the absorbance contributions from both the unprotonated and the protonated species,

$$A_{\text{obs}} = \epsilon_{BH^+} [BH^+] + \epsilon_B [B] \quad (17)$$

where  $\epsilon_{BH^+}$  and  $\epsilon_B$  are the molar absorptivities for the protonated and unprotonated species and  $[BH^+]$  and  $[B]$  are the respective concentrations.

By defining

$$C = [BH^+] + [B] \quad (18)$$

and utilizing the standard definition of the dissociation constant,  $K_a$ ,

$$K_a = \frac{[B][H^+]}{[BH^+]} \quad (8)$$

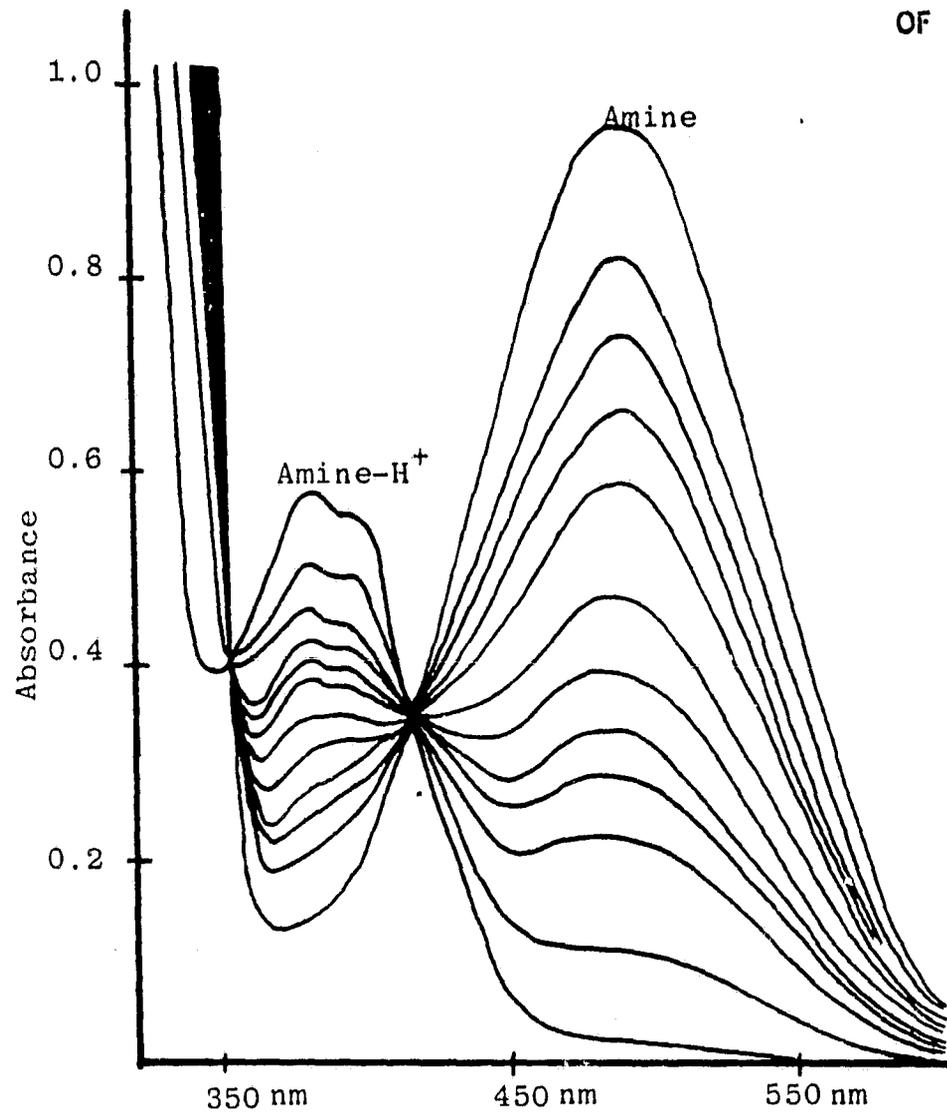
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Figure 6: Absorption spectra for 2-aminofluorenone as a function of added perchloric acid in AN/water.

Substitution of these latter two equations into (17) gave,

$$A_{\text{obs}} = \frac{\epsilon_{\text{BH}^+} \times [\text{H}^+] C}{K_a + [\text{H}^+]} + \frac{\epsilon_B K_a C}{K_a + [\text{H}^+]} \quad (19)$$

which could be redefined in terms of absorbance,

$$A_B = \epsilon_B [B]$$

$$A_{\text{BH}^+} = \epsilon_{\text{BH}^+} [\text{BH}^+]$$

and rearranged to give a final expression for  $K_a$ .

$$K_a = \frac{A_{\text{obs}} - A_{\text{BH}^+}}{A_B - A_{\text{obs}}} [\text{H}^+] \quad (20)$$

The hydrogen ion concentration was obtained using

$$[\text{H}^+] = v_H C_H / v_T - [\text{BH}^+] \quad (2)$$

The total base concentration was known,

$$[B] + [\text{BH}^+] = C \quad (18)$$

where  $C$  is the molar concentration of the amine solutions. The concentration of protonated amine was defined as,

$$[\text{BH}^+] = \frac{A_{\text{obs}} - A_B}{A_{\text{BH}^+} - A_B} \times C \quad (21)$$

and substituted into (2) to yield an expression for the hydrogen ion concentration in terms of absorbance values.

$$[H^+] = V_e C_H / V_T - \frac{A_{obs} - A_{BH^+}}{A_B - A_{BH^+}} M \quad (22)$$

The values for  $A_B$  and  $A_{BH^+}$  were obtained from the absorption spectra and the intermediate values were then plotted according to equation (20).

$$\frac{A_{obs} - A_{BH^+}}{A_B - A_{obs}} = K_a \frac{1}{[H^+]} \quad (20)$$

The slope of this line was the dissociation constant,  $K_a$ .

### Spectrophotometric determination of rate constants

#### 1. Reagents

The amines were recrystallized as necessary. Phthalic anhydride (PA) was sublimed under vacuum. N,N'-dimethylacetamide (DMA) was distilled and the usual efforts were taken to assure that no water contaminated this solvent. The phthalic anhydride solutions were found to be stable and to give reproducible results for the same reaction run two hours apart. It was therefore assumed that hydrolysis to phthalic acid was not going to be a problem within a reasonable length of time.

Solutions of the amines at  $10^{-3}$  -  $10^{-4}$  M concentrations and three concentrations of phthalic anhydride were prepared in DMA and used within one hour of their preparation.

#### 2. Instrumentation

Initial measurements were made on a Cary 14 spectrophotometer to determine the most suitable wavelength for monitoring the reaction

course, and to determine that the reaction proceeded without complication. A Beckman DU UV-VIS spectrophotometer (Model #2400) with an Update Model 111 power supply and an Update Model 122 Digital Display log converter amplifier was then used to follow the reaction at 25°C.

### 3. Procedure

One milliliter of each of the reactants was placed in a Pyrocell split cell and an initial absorbance value was taken. Efficient mixing was accomplished within twenty seconds, and the reaction was thereafter monitored at a suitable wavelength until well beyond the reaction half-life. The usual length of time required to follow the reaction and acquire sufficient data was three to four hours.

The benzophenones were monitored in the region of 350-400 nm. At the concentrations used, the peak maximum was off scale and the reaction course was monitored along the side of the absorption peak (Figure 7). The fluorenone series was examined in the visible region between 430-510 nm. Both the amine reactant and the resulting amic acid were brightly colored and each gave a distinct absorption peak. It was thus possible to monitor both the disappearance of reactants and the formation of product as a check on the uniformity of the reaction (Figures 8-11). The absorption spectrum for phthalic anhydride did not overlap in these regions (Figure 12).

It was assumed that as long as an isobestic was maintained, only two components, the amine and the monoamic acid, were present in the reaction mixture. Phthalic anhydride did not contribute to the

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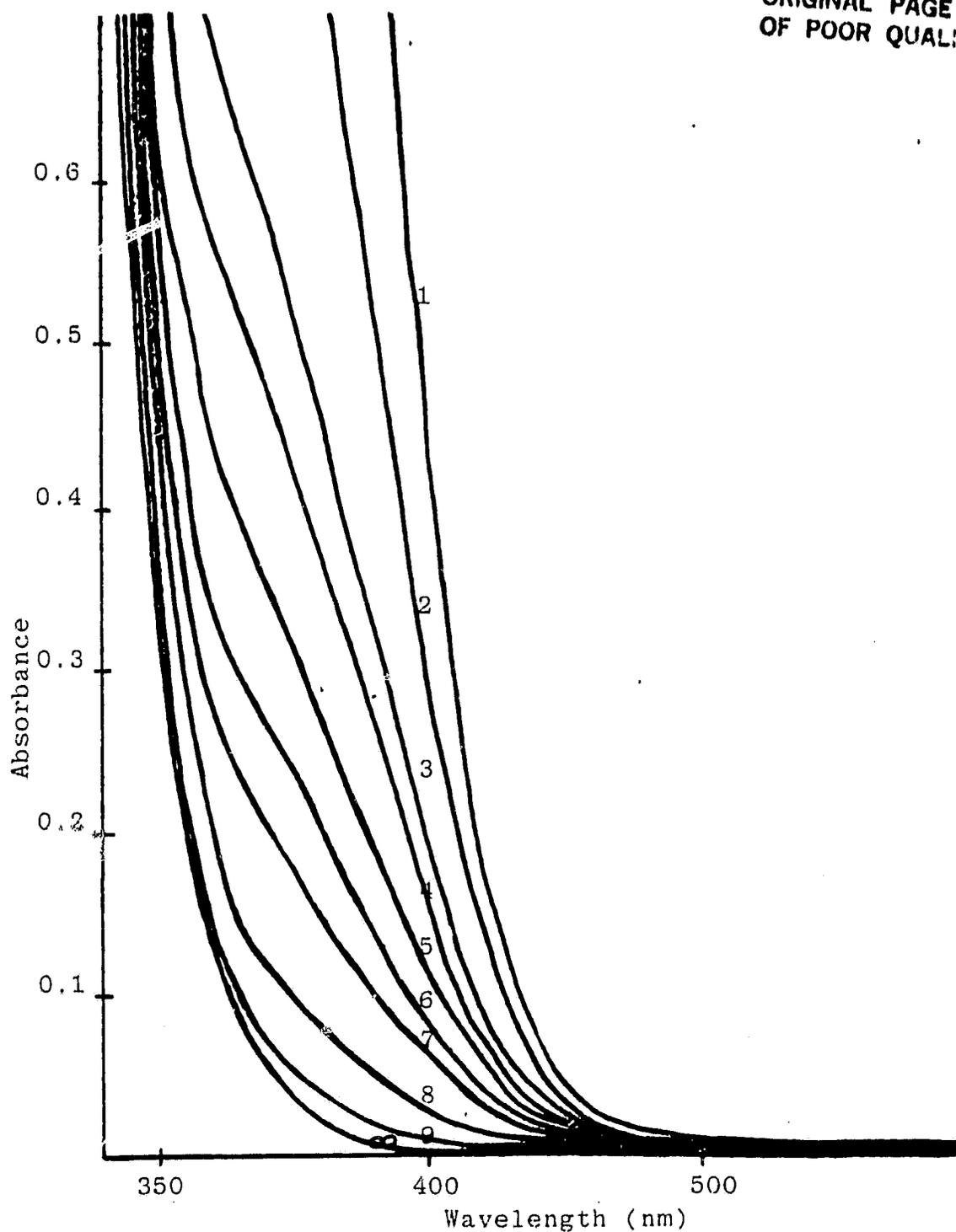


Figure 7: Absorption spectra for the reaction of 3,3'-diaminobenzophenone with phthalic anhydride in N,N-dimethylacetamide at 25°C.

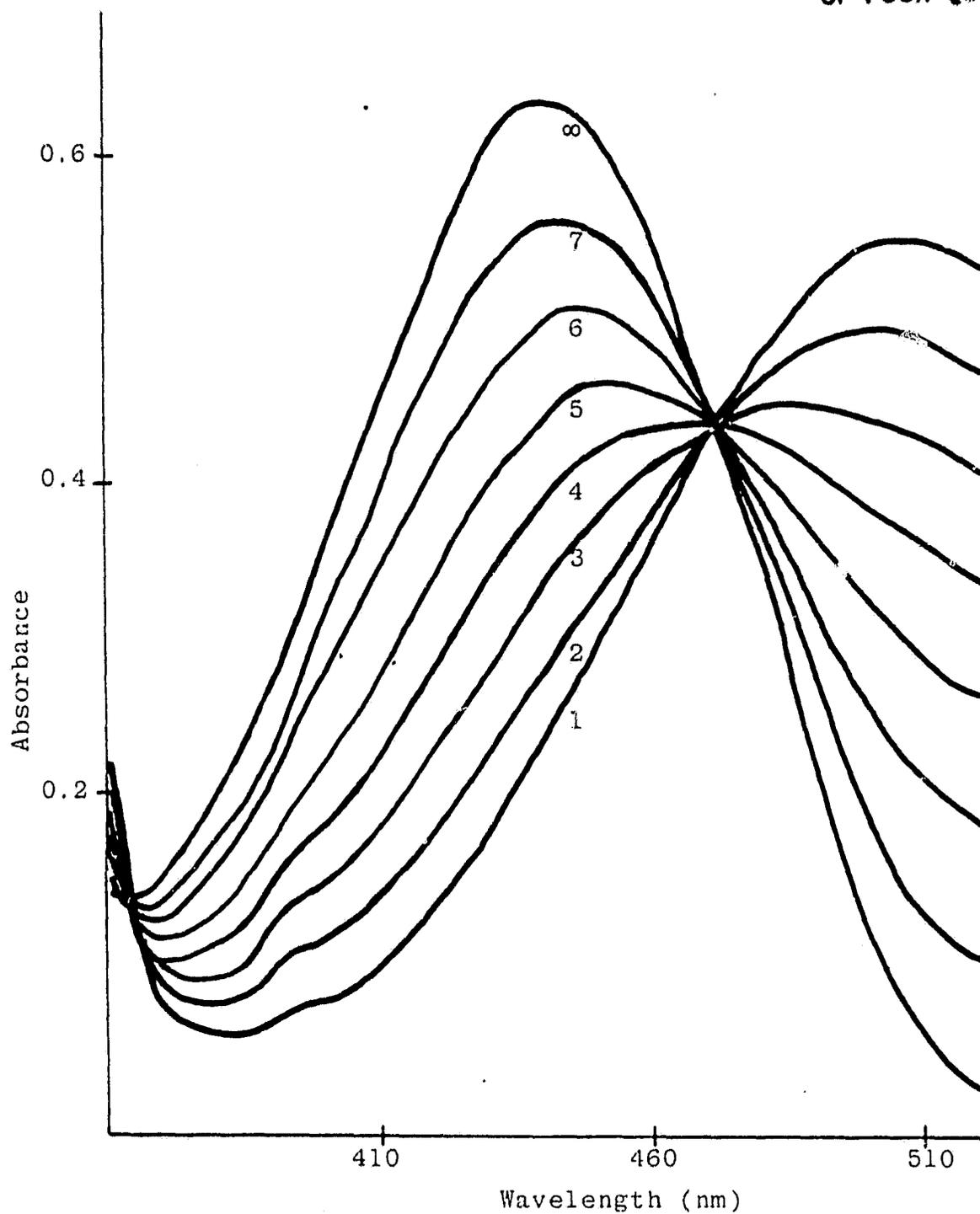
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Figure 8: Absorption spectra versus time for the reaction of 2-aminofluorenone with phthalic anhydride in N,N-dimethylacetamide; 2-aminofluorenone,  $1.004 \times 10^{-5}$  M; phthalic anhydride, 0.1 M; temperature, 25°C.

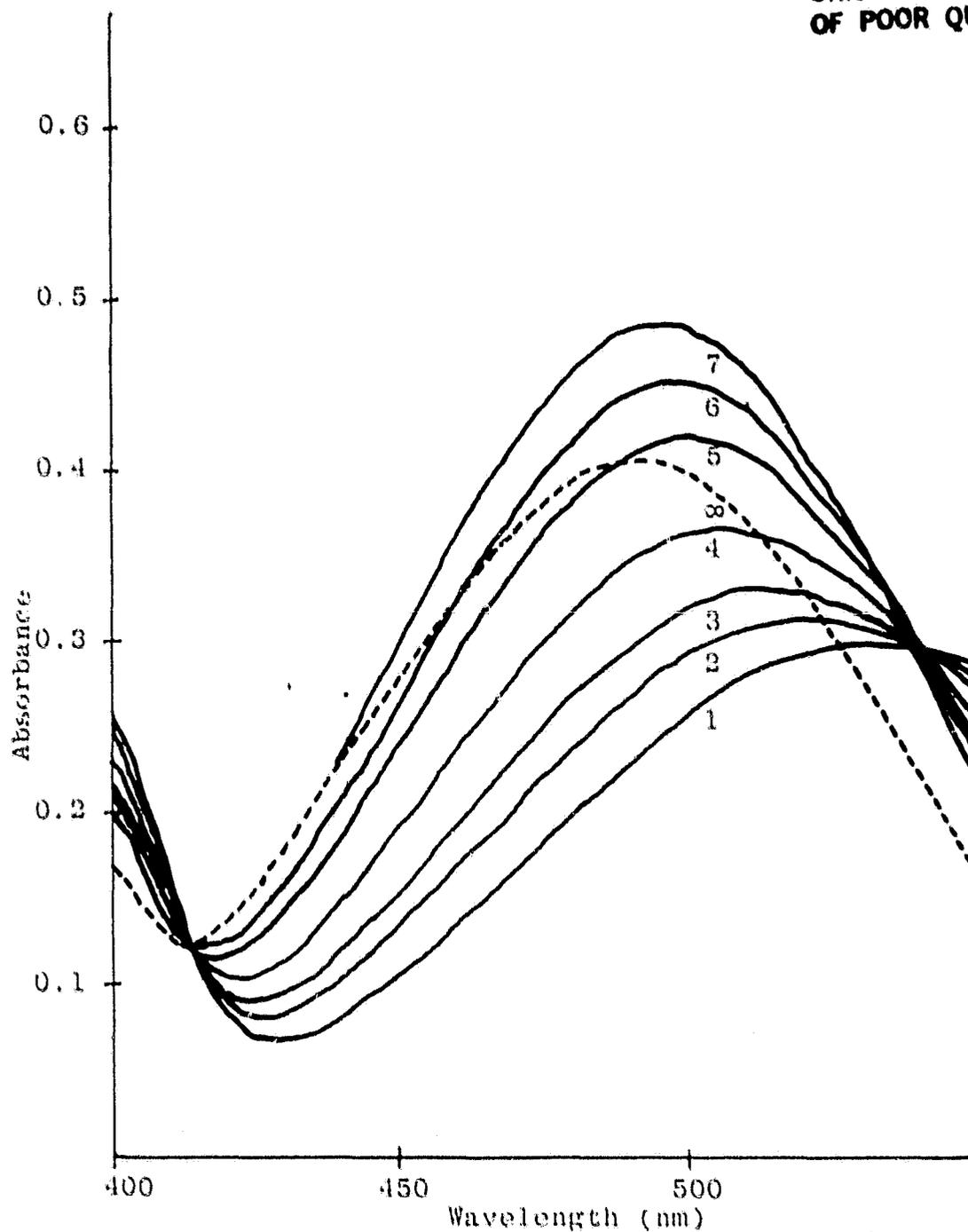
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Figure 9: Absorption spectra versus time for the reaction between 2,5-diaminofluorenone and phthalic anhydride in *N,N*-dimethylacetamide. Temperature, 25°C; 2,5-diaminofluorenone,  $2.475 \times 10^{-4}$  M; phthalic anhydride, 0.1 M.

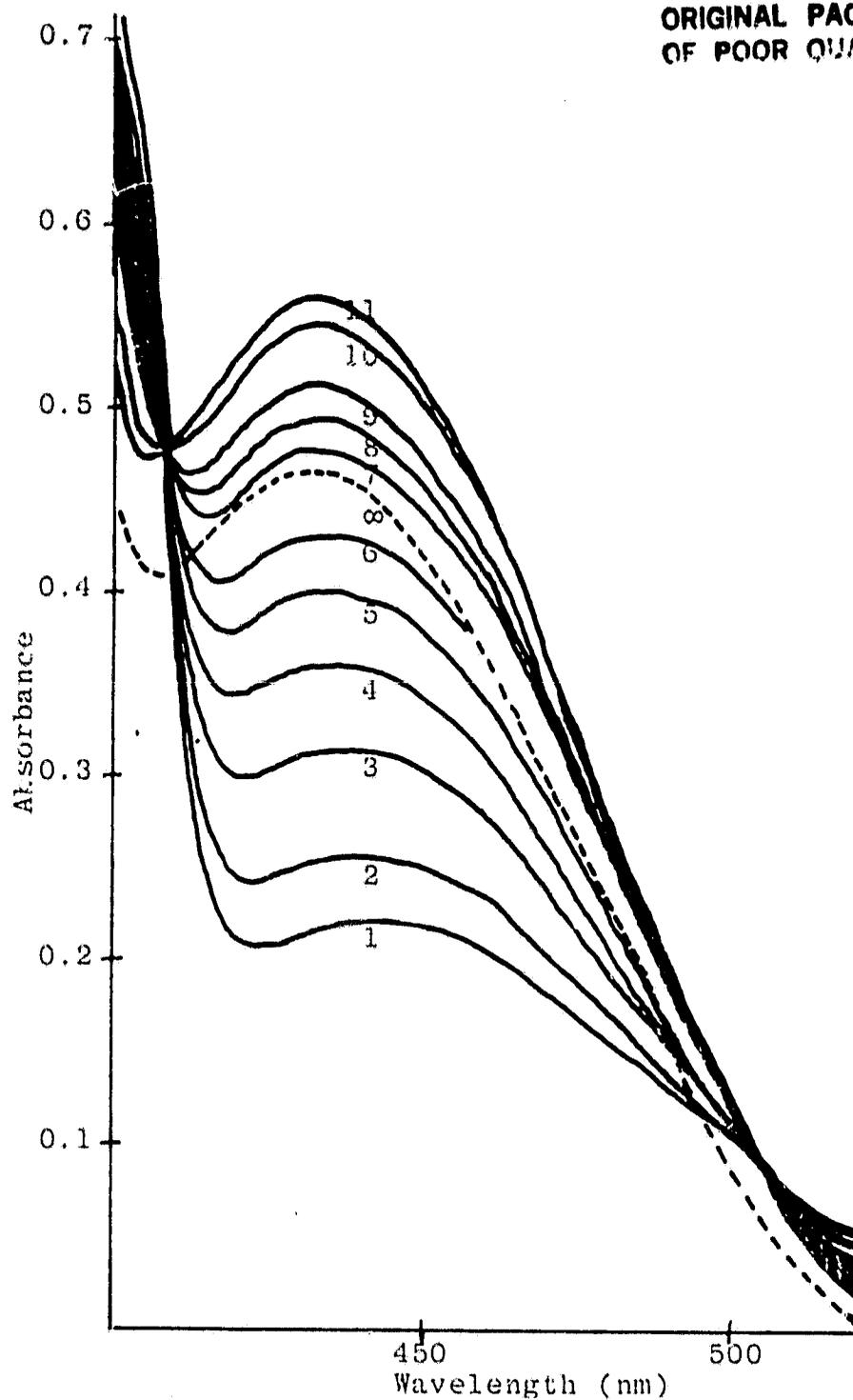
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Figure 10: Absorption spectra versus time for the reaction of 2,6-diaminofluorenone with phthalic anhydride in *N,N*-dimethylacetamide. Temperature, 25°C; 2,6-diaminofluorenone,  $2.475 \times 10^{-4}$  M; phthalic anhydride, 0.1M.

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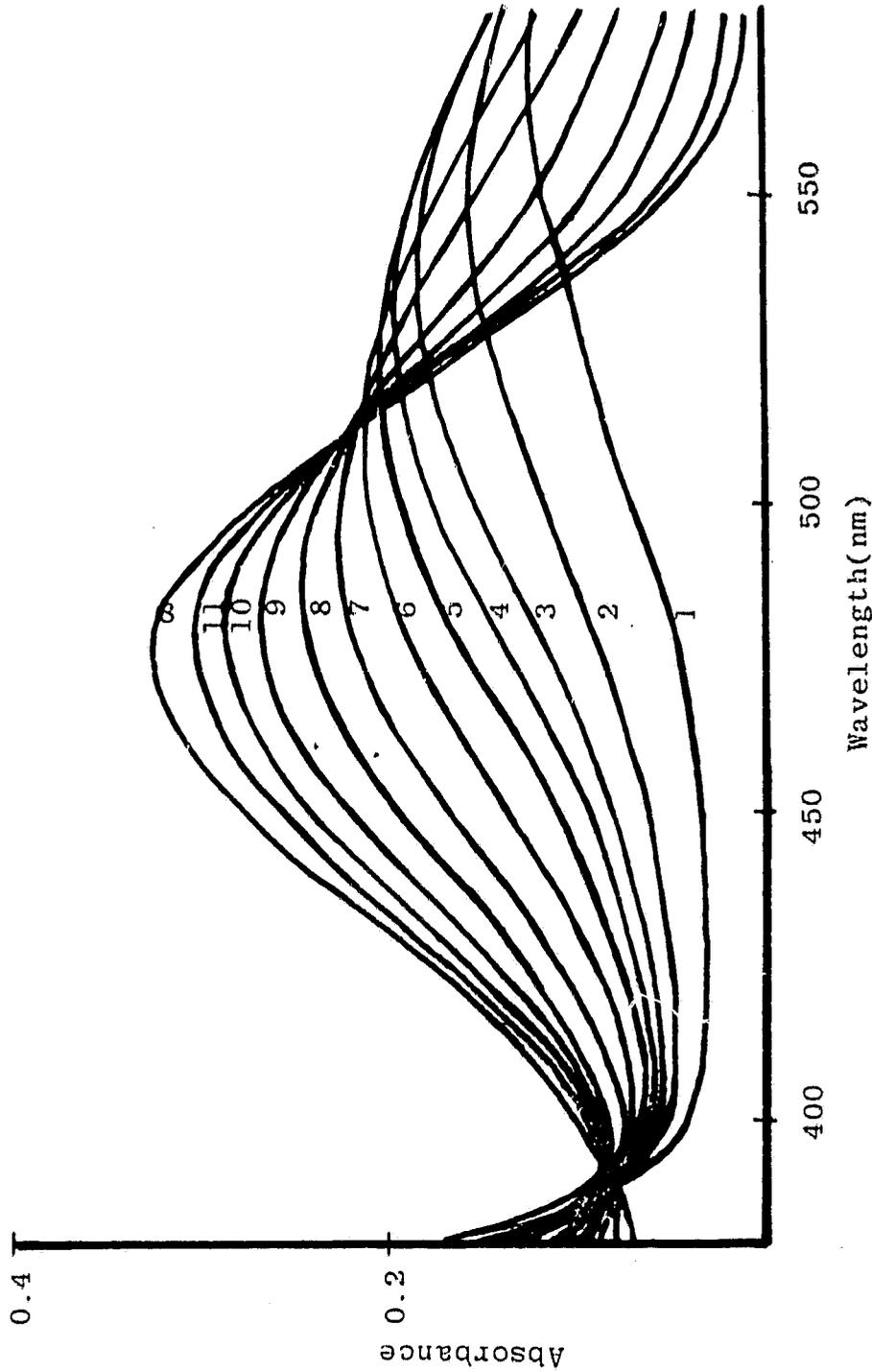


Figure 11: Absorption spectra versus time for the reaction between 2,7 diaminofluorenone and phthalic anhydride in N,N dimethylacetamide; 2,7 diaminofluorenone,  $2.453 \times 10^{-3}$  M; phthalic anhydride, 0.1M; temperature, 25°C.

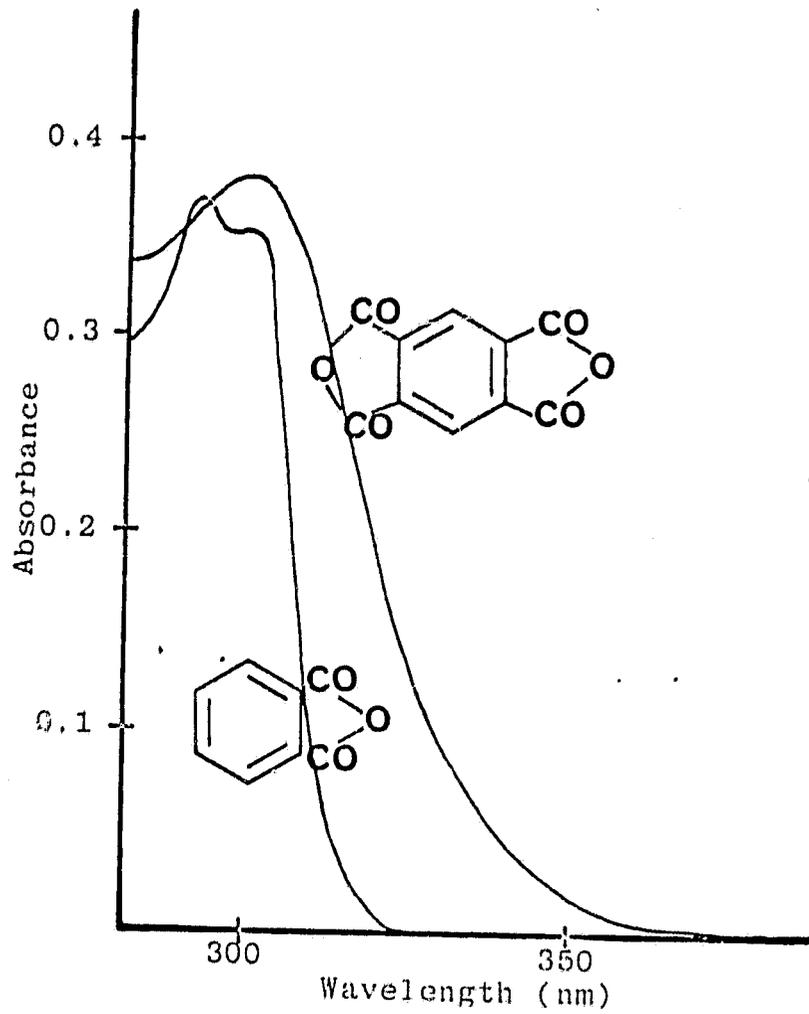
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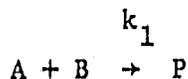
Figure 12: Absorption spectra for phthalic anhydride and pyromellitic dianhydride in DMA.

measured absorbance in the region in which the amines were examined. An isobestic is well preserved throughout the course of the reaction between 2-AFO and PA (Figure 8). The dotted line in Figures 9 and 10 represents the infinite absorption spectra taken after a sufficient time had elapsed for completion of the first stage of the reaction (ten half-lives). At this point, the isobestics for the 2,5-diaminofluorenone (2,5-DAFO) (Figure 9) and 2,6-diaminofluorenone (2,6-DAFO) (Figure 10) were no longer maintained. The absorbance peaks for the monoamic acid derivatives of these two compounds could not be determined experimentally.

The 2,7-diaminofluorenone (2,7-DAFO) presented a more difficult problem (Figure 11). An isobestic point developed only in the latter stages of the reaction, suggesting that the amine was reacting with PA to form the monoamic acid which proceeded to form the diamic acid via a consecutive first-order process. The data which formed the isobestic represented the stage of the reaction sequence after all of the amine had been converted to the monoamic acid. These data could thus be treated as a first-order process to determine the terminal absorbance value for the monoacid product and the pseudo first-order rate constant,  $k'_2$ , for the second stage of the reaction ( $k_2 = 1.93 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$ ). With this information, it was possible to determine the rate constant for the first stage of the reaction. (See Calculations, section c.)

4. Calculations(a) Determination of pseudo first-order rate constants

For the bimolecular reaction,



the rate is defined as:

$$\text{rate} = \frac{-dA}{dt} = k_1 [A][B].$$

The use of a large excess of one of the reactants allows the simplification of this rate equation to that of a first-order kinetic equation

$$[B] \gg [A]$$

$$k_1 [B] = k'_1$$

$$\text{rate} = -\frac{d[A]}{dt} = k'_1 [A].$$

In terms of absorbance data, the standard plot for a first order reaction is the following,<sup>38</sup>

$$\ln (A_\infty - A_t) = \ln (A_\infty - A_0) - k_1 t \quad (1)$$

where  $A_\infty$  is the terminal absorbance value for the reaction obtained after ten half-lives have elapsed,  $A_0$  is the initial absorbance for the reaction mixture, and  $A_t$  is the absorbance value at time,  $t$ . The slope of this line would yield the pseudo first-order rate constant which, upon correction for the concentration of phthalic anhydride used, gives the second-order rate constant for the reaction.

(b) Mangelsdorf-Swinbourne equation

For those reactions which did proceed beyond the first stage,

it was necessary to utilize the Mangelsdorf-Swinbourne plot<sup>39</sup> to determine the correct terminal absorbance value,  $\Lambda_{\infty}$ , for the first stage of the reaction. This plot was readily derived by solving the standard first-order kinetic equation (1) for a series of data points  $\Lambda_1, \Lambda_2, \dots, \Lambda_n$ , taken at times  $t_1, t_2, \dots, t_n$ , (2) and a second series of data points  $\Lambda'_1, \Lambda'_2, \dots, \Lambda'_n$  taken at the corresponding times  $t_1 + \Delta, t_2 + \Delta, \dots, t_n + \Delta$ , (3) where  $\Delta$  is a constant.

$$(\Lambda_{\infty} - \Lambda_t) = (\Lambda_{\infty} - \Lambda_0)e^{-kt} \quad (2)$$

$$(\Lambda_{\infty} - \Lambda'_t) = (\Lambda_{\infty} - \Lambda_0)e^{-k(t + \Delta)} \quad (3)$$

The ratio of equations (2) and (3) is the Mangelsdorf-Swinbourne equation.

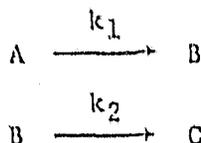
$$\Lambda_t = \Lambda'_t e^{k\Delta} + \Lambda_{\infty}(1 - e^{k\Delta}) \quad (4)$$

The intercept of this line would yield the correct infinite value for the reaction.

This plot was tested on the reaction of 2-AFO with PA (Figure 13) to assure that it gave the correct value for  $\Lambda_{\infty}$  and indeed the calculated and experimental values agreed within a three-percent error margin ( $\Lambda_{\infty \text{ calc}} = 0.649, \Lambda_{\infty \text{ exp}} = 0.633$ ).

(c) Treatment of the consecutive first-order reaction

For the reaction,



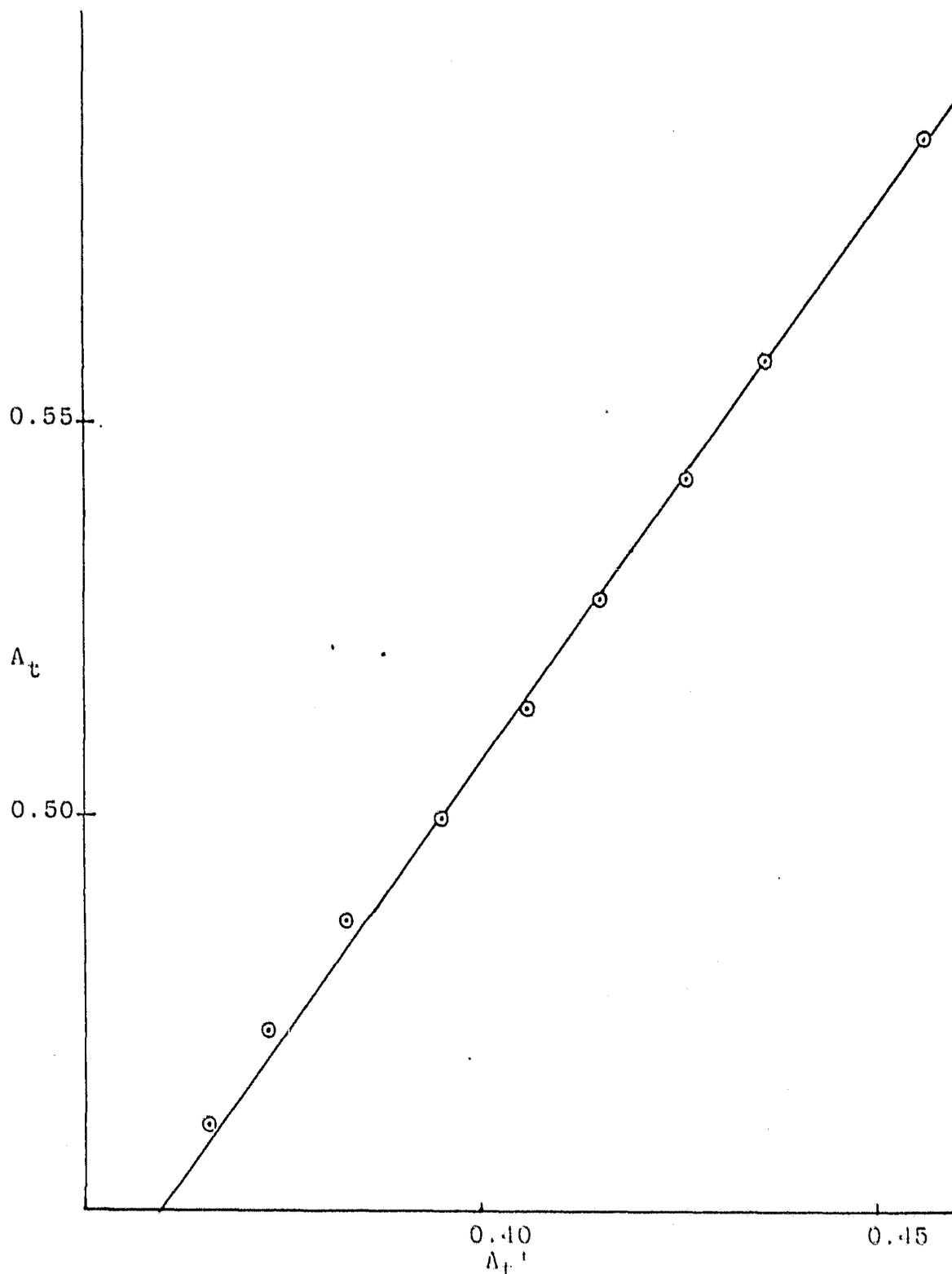
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Figure 13: Mangelsdorf-Swinbourne plot for the reaction between 2-aminofluorenone and excess (0.1M) phthalic anhydride in N,N-dimethylacetamide.

the concentrations of reacting species are defined by the following equations,

$$[A] = A_0 e^{-kt} \quad (5)$$

$$[B] = A_0 k_1 (e^{-k_1 t} - e^{-k_2 t}) / (k_1 - k_2) \quad (6)$$

$$[C] = A_0 \{1 - (k_1 e^{-k_2 t} - k_2 e^{-k_1 t}) / (k_2 - k_1)\}. \quad (7)$$

The absorption data could be related to the concentrations of the various species present at time,  $t$ , through the following equation:

$$A_{\text{obs}} = \epsilon_{\text{obs}} [A] = \epsilon_a [A] + \epsilon_b [B] + \epsilon_c [C]. \quad (8)$$

The absorbance values for the amine (A) and the diacid product (C) could be directly determined from the data. The values for  $k_2$  and the absorbance value for the monoacid product (B) were derived from a standard first-order plot of the data which formed an isobestic. With this information, it was possible to determine the correct value for  $k_1$ . A plot of the calculated absorbance values for the amine (5), the monoamic acid (6), and the diamic acid (7) is presented in Figure 14. The total absorbance was calculated according to equation (8) and a comparison was made of the calculated and experimental values for  $A_{\text{obs}}$  (Figure 15).

#### Reaction with pyromellitic dianhydride

Pyromellitic dianhydride (PMDA) was sublimed and reacted with 2-AFO following the previously described procedure. The Cary 14 spectra for the second stage of this reaction is reproduced in Figure 16.

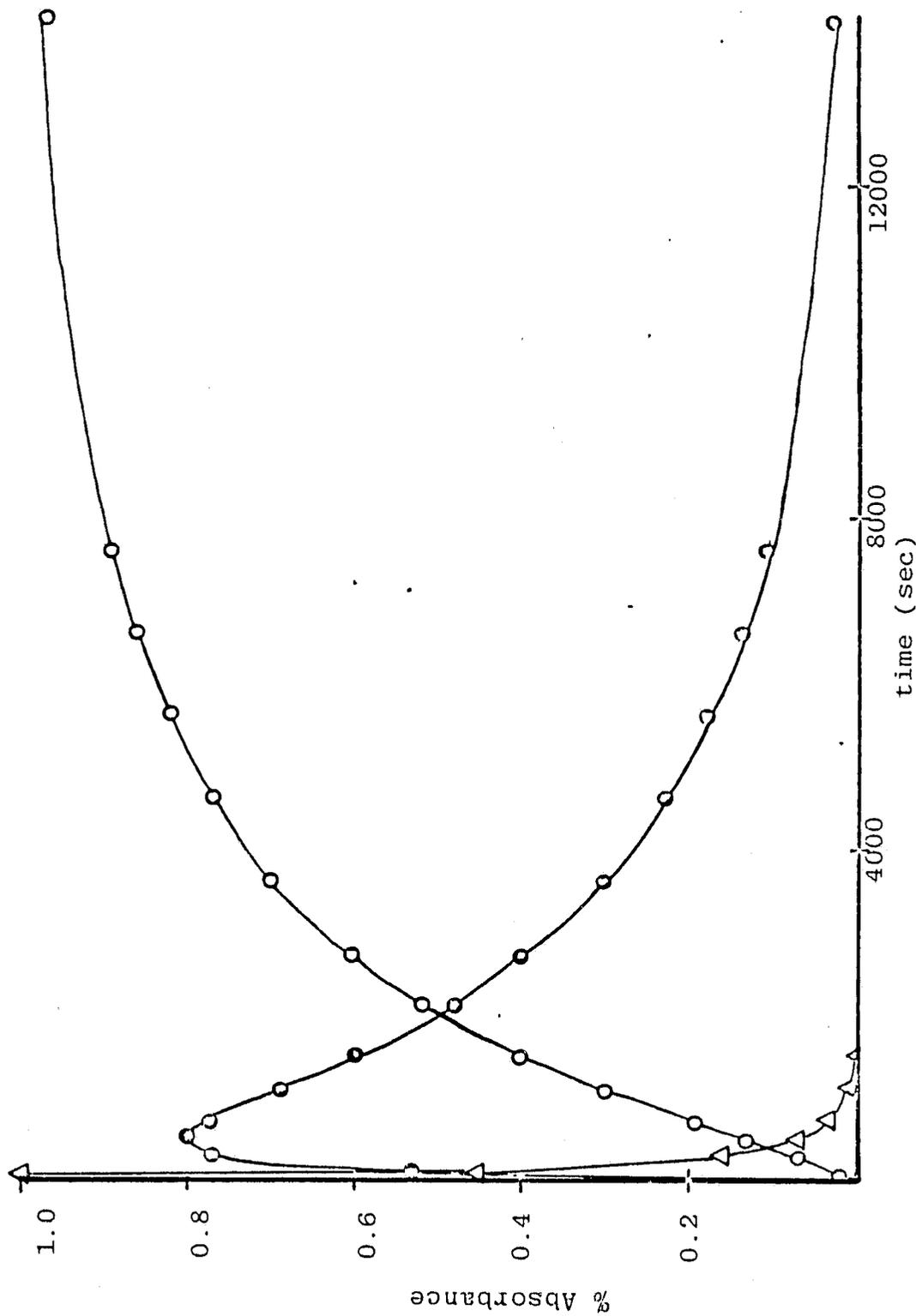


Figure 14: Consecutive first-order reaction plot of absorbance data for the reaction between 2,7-diaminofluorenone and 0.1 M phthalic anhydride.

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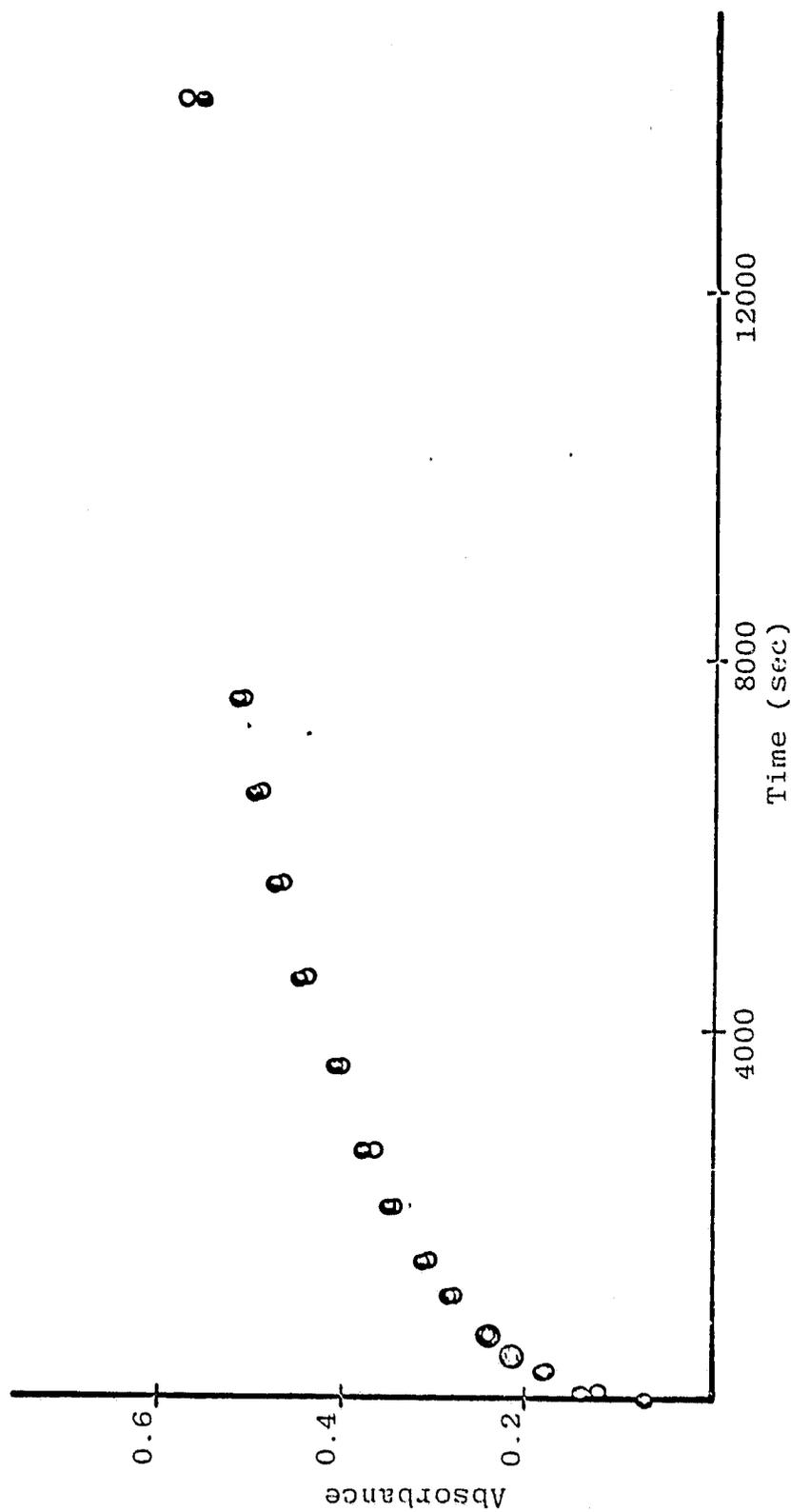


Figure 15: Change in absorbance versus time for (O) observed values and (O) calculated values for the reaction between 2,7-diaminofluorenone and 0.1 M phthalic anhydride in DMA.

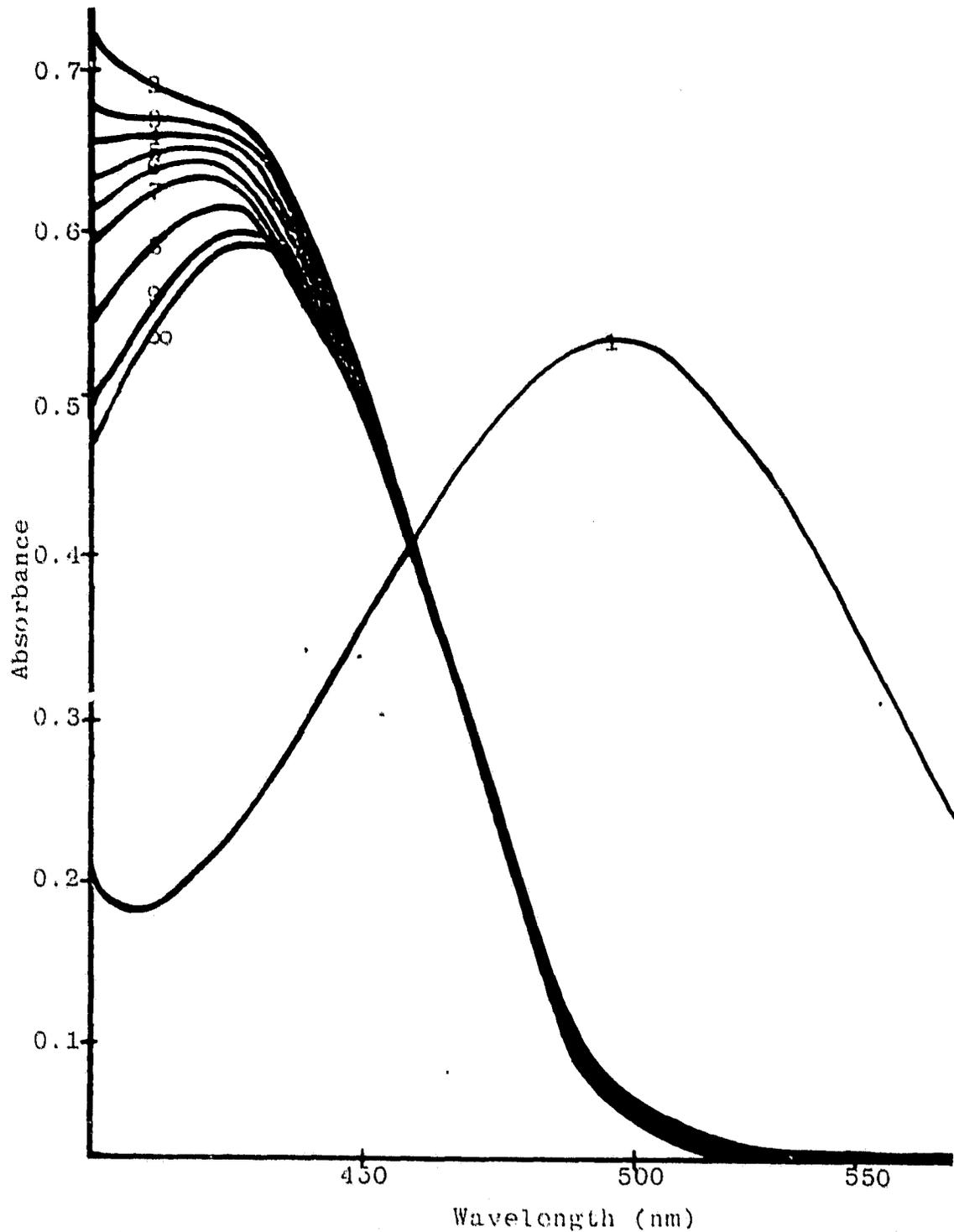


Figure 16: Absorption spectra versus time for the reaction of 2-aminofluorenone with 0.1 M prymellitic dianhydride in DMA. (Second stage.)

Preparation and characterization of products1. Amic acid derivatives of diaminobenzophenones

Preparation<sup>40</sup> of the monoamic acid was accomplished by dissolving the phthalic anhydride in anhydrous ether and excess diamine in a minimum amount of tetrahydrofuran. The phthalic anhydride was then added dropwise with stirring to the amine. If there was no immediate precipitation of product, the volume of the reaction mixture was reduced to one-half the original volume and anhydrous ether was then added until the product precipitated from solution (Table 2).

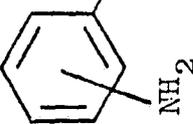
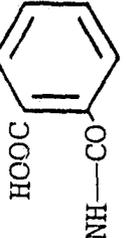
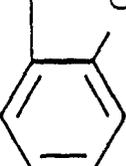
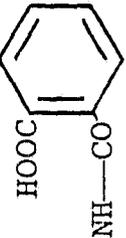
The same solvents were used for the preparation of the second product. The amine was added to excess phthalic anhydride with stirring and precipitation of the product was again accomplished by reducing the volume of the reaction mixture and adding ether (Table 2).

2. Amic acid derivative of 2-amino-9-fluorenone

2-Amino-9-fluorenone and phthalic anhydride were reacted in glacial acetic acid according to the method of Fletcher et al<sup>42</sup> (Table 2). It was hoped that the rest of the compounds in this series could be synthesized according to this procedure. Several attempts with the 2,7-DAFO and 2,6-DAFO yielded product mixtures which were inseparable through solvent extraction and column chromatography.

Purification of any of the products was greatly inhibited by the dehydration of the amic acid which would occur with heating. Recrystallization was therefore excluded. Further, at approximately

Table 2: Properties of the monoamic acid derivatives of some of the aminobenzophenones and of 2-aminofluorenone.

| Compound  | m.p. °C (literature)           | Equivalent Weight<br>Calc. | Equivalent Weight<br>Found |
|---|--------------------------------|----------------------------|----------------------------|
|    |                                |                            |                            |
|    | 3, 4'-                         |                            |                            |
|    | 70-71                          |                            |                            |
|  | 4, 4'-                         | 345                        | 375                        |
|  | 310-316(305-310) <sup>42</sup> | 343                        | 348                        |
| 2   |                                |                            |                            |

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stoichiometric concentrations, it appeared the reaction was no longer the simple reaction which was seen at much lower concentrations.

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## RESULTS

### Basicity Measurements

The method utilized for standardization of the pH meter yielded concentration pKa values rather than hybrid activity-concentration values. Many determinations of pK values for organic acids or bases in organic solvent-water mixtures have utilized the standardization of the meter with a purely aqueous buffer of known pH. To determine if there were a difference between the two methods for this solvent system, pyridine was titrated as a typical amine base. The results found were 3.57 and 5.22 for the pKa values by external buffer standardization and calibration curve respectively. The value for the pKa found for pyridine using the calibration curve technique is virtually the same as that found for pure water alone. Therefore, this method was used to obtain data that would resemble and could be compared to that obtained from other media such as alcohol-water mixtures and other methods such as spectrophotometry.

Prior to utilizing the calibration curve method of standardization, a large number of titration curves had been correctly obtained but incorrectly evaluated. These data included many diamines for which kinetic studies were not performed. Extensive re-evaluation of these data as detailed by Appendix 1 was performed. The results of all titrations are presented in Table 3. The calibration curve pK determinations as well as the kinetic results were obtained by E. Sugg (S); the other pKa measurements were obtained by Charles Potter (P).

Examination of the data reveals that where there are common values the agreement is excellent. It is even more reassuring when it is realized that entirely different electrodes and reagents were used for each series and that the sets of determinations were separated by over eighteen months.

Table 3: Summary of pKa values determined potentiometrically in AN/water.

| <u>Amine</u>                 | <u>P (computer)</u>  | <u>S (Calibration Curve)</u>  |
|------------------------------|--|-------------------------------|
| 2-Aminodiphenylmethane       |  | pK <sub>A</sub> = 3.41 ± 0.06 |
| 3-Aminodiphenylmethane       |  | pK <sub>A</sub> = 4.29 ± 0.03 |
| 2,2'-Diaminodiphenylmethane  | pK <sub>1</sub> = 2.24 ± 0.03<br>pK <sub>2</sub> = 4.03 ± 0.02 |                               |
| 2,4'-Diaminodiphenylmethane  | pK <sub>1</sub> = 3.00 ± 0.01<br>pK <sub>2</sub> = 4.57 ± 0.04 |                               |
| 3,3'-Diaminodiphenylmethane  | pK <sub>1</sub> = 3.73 ± 0.02<br>pK <sub>2</sub> = 4.57 ± 0.03 |                               |
| 3,4'-Diaminodiphenylmethane  | pK <sub>1</sub> = 3.68 ± 0.07<br>pK <sub>2</sub> = 4.79 ± 0.07 |                               |
| 4,4'-Diaminodiphenylmethane  | pK <sub>1</sub> = 4.08 ± 0.03<br>pK <sub>2</sub> = 4.99 ± 0.06 |                               |
| 3,3'-Diaminodiphenylcarbinol | pK <sub>1</sub> = 3.51 ± 0.02<br>pK <sub>2</sub> = 4.49 ± 0.07 |                               |
| 4,4'-Diaminodiphenylether    | pK <sub>1</sub> = 3.82 ± 0.04<br>pK <sub>2</sub> = 5.14 ± 0.03 |                               |
| <u>Aminobenzophenones</u>    |  |                               |
| 2-Aminobenzophenone          | N.M.   | N.M.                          |
| 4-Aminobenzophenone          | N.M.   | N.M.                          |

S (Calibration Curve)

P (computer)

Amine

Aminobenzophenones

|                          |   |  |
|--------------------------|---|--|
| 2-Aminobenzophenone      | $pK_A = 3.12 \pm 0.04$                          | $pK_A = 3.03 \pm 0.07$                                   |
| 3,3'-Diaminobenzophenone | $pK_1 = 2.1 \pm 0.02$<br>$pK_2 = 3.29 \pm 0.01$ | $pK_1 = 2.10 \pm 0.02$<br>$pK_2 = 3.37 \pm 0.01$         |
| 3,4'-Diaminobenzophenone | $pK_A = 3.36 \pm 0.01$                          | $pK_A = 3.38 \pm 0.01$                                   |
| 3,5'-Diaminobenzophenone | $pK = 4.02 \pm 0.03$                            |  |
| 2,4'-Diaminobenzophenone | $pK = 2.40 \pm 0.01$                            | $pK = 2.57 \pm 0.01$<br>$pK(\text{rec}) = 2.45 \pm 0.01$ |
| 4,4'-Diaminobenzophenone | $pK = 2.55 \pm 0.02$                            | $pK = 2.65 \pm 0.01$<br>$pK(\text{rec}) = 2.60 \pm 0.55$ |

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Fluorenes

|                       |  |  |
|-----------------------|--|--|
| 2-Aminofluorene       | $pK = 4.43 \pm 0.03$                             |  |
| 2,5-Diaminofluorene   | $pK_1 = 2.49 \pm 0.07$<br>$pK_2 = 4.57 \pm 0.03$ |  |
| 2,7-Diaminofluorene   | $pK_1 = 3.65 \pm 0.02$<br>$pK_2 = 5.13 \pm 0.01$ |  |
| <u>Fluorenes</u>      |  |  |
| 2-Aminofluorenone     | $pK = 2.68 \pm 0.005, (2.70)^a$                  | $pK = 2.71 \pm 0.02 (2.70)^a$                    |
| 2,7-Diaminofluorenone | $pK_1 = 1.68 \pm 0.03$<br>$pK_2 = 3.59 \pm 0.01$ | $pK_1 = 1.73 \pm 0.07$<br>$pK_2 = 3.65 \pm 0.03$ |

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|                                      | <u>P</u>             | <u>S</u>   |
|--------------------------------------|----------------------|--|
| <u>Fluorenones</u>                   |                      |  |
| 2,6-Diaminofluorenone                | $pK_A = 3.0 \pm .02$ | $pK_A = 3.01 \pm 0.01$                           |
| 2,5-Diaminofluorenone                |                      | $pK_A = 3.12 \pm 0.01$                           |
| <u>Other Diamines</u>                |                      |  |
| N,N-dimethyl-pp'-methyl<br>dianiline |                      | $pK_1 = 5.17 \pm 0.01$<br>$pK_2 = 4.05 \pm 0.12$ |
| m,m3-dianiline-p2-TB                 |                      | $pK_1 = 8.23 \pm 0.17$<br>$pK_2 = 4.49 \pm 0.02$ |
| m,m'-dichloromethyldianiline         |                      | NM*  |

\*NM: Not measurable under these conditions.

aDetermined spectrophotometrically.

rec - Titration data calculated using computer program.

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Comparison of the potentiometrically determined value for the pKa of 2-aminofluorenone (2.69) with the spectrophotometrically determined value of 2.70 shows extraordinary agreement.

Additional support for the values reported here is given by the results for amines titrated in 50% aqueous alcohol. (K. A. Allen, J. Cymerman-Craig, and A. A. Diamantis, J. Chem. Soc., 1954, 234). These data are compared below:

| <u>Compound</u>   | <u>Allen</u> | <u>this report</u> |
|-------------------|--------------|--------------------|
| 2-aminofluorene   | 4.36         | 4.43               |
| 2-aminofluorenone | 2.67         | 2.68, 2.71         |

Each pKa tabulated is based upon a minimum of two titrations with each computation utilizing between 16 and 45 data points. The uncertainties indicated are average deviations.

Rates of reaction of aminofluorenones and aminobenzophenones with phthalic anhydride

Standard first-order logarithmic plots of the absorbance data were linear through greater than 90% of the reaction course (Figure 17). Curvature was noted only for those diamines which did proceed beyond the first stage of the reaction. As would be expected, this curvature was downward, suggesting the disappearance of the monoamic acid. The data acquired to the point of deviation from linearity, usually for greater than 50% of the first reaction step, were sufficient to determine the correct pseudo first-order rate constant (Figure 18).

The pseudo first-order, and corrected second-order rate constants are presented in Table 4 for three concentrations of phthalic anhydride. Agreement of three determinations was within six-percent.

The only diamine for which both reaction stages could be evaluated was

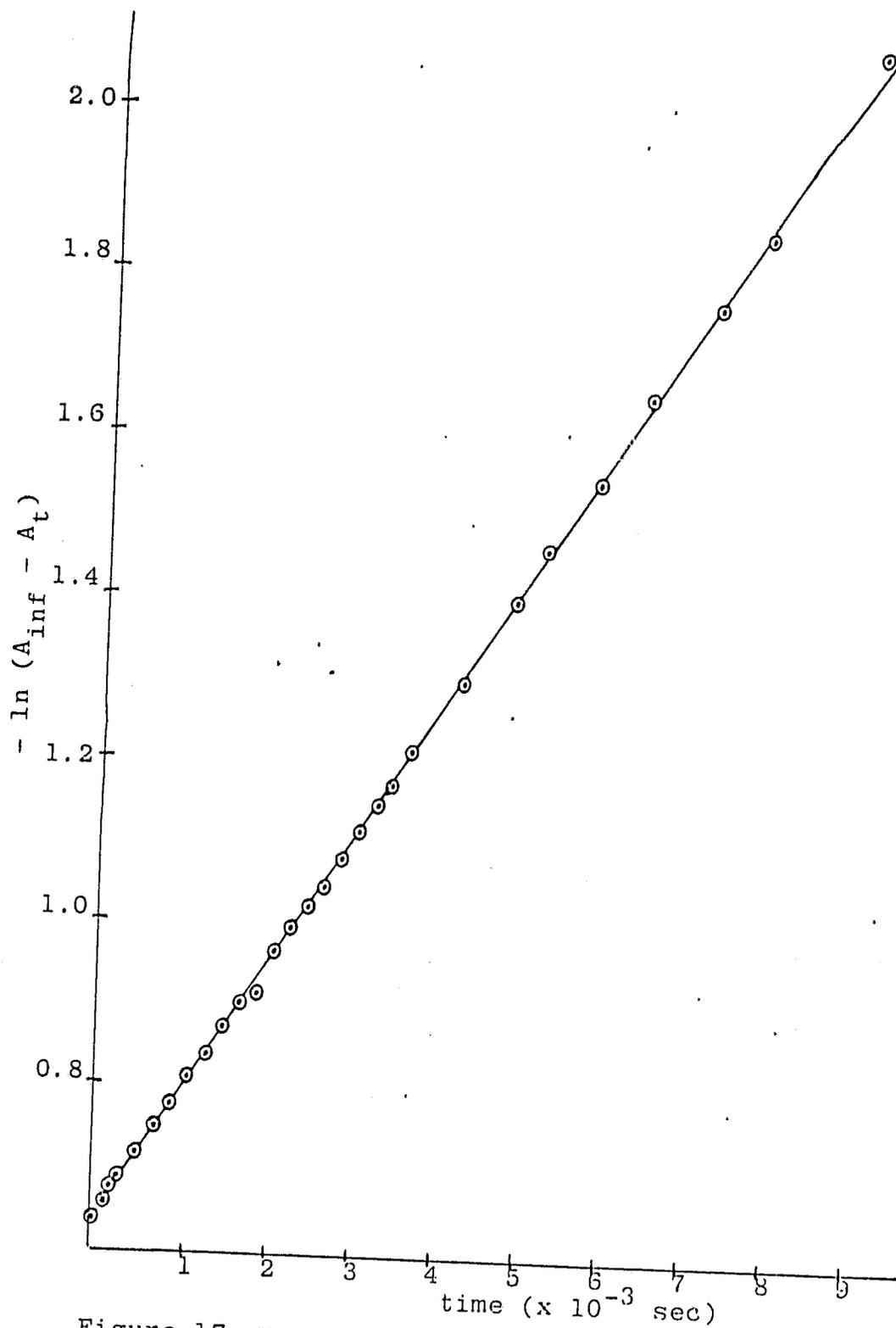
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Figure 17: First-order plot for the reaction of 2-aminofluorenone with excess phthalic anhydride in N,N-dimethylacetamide.

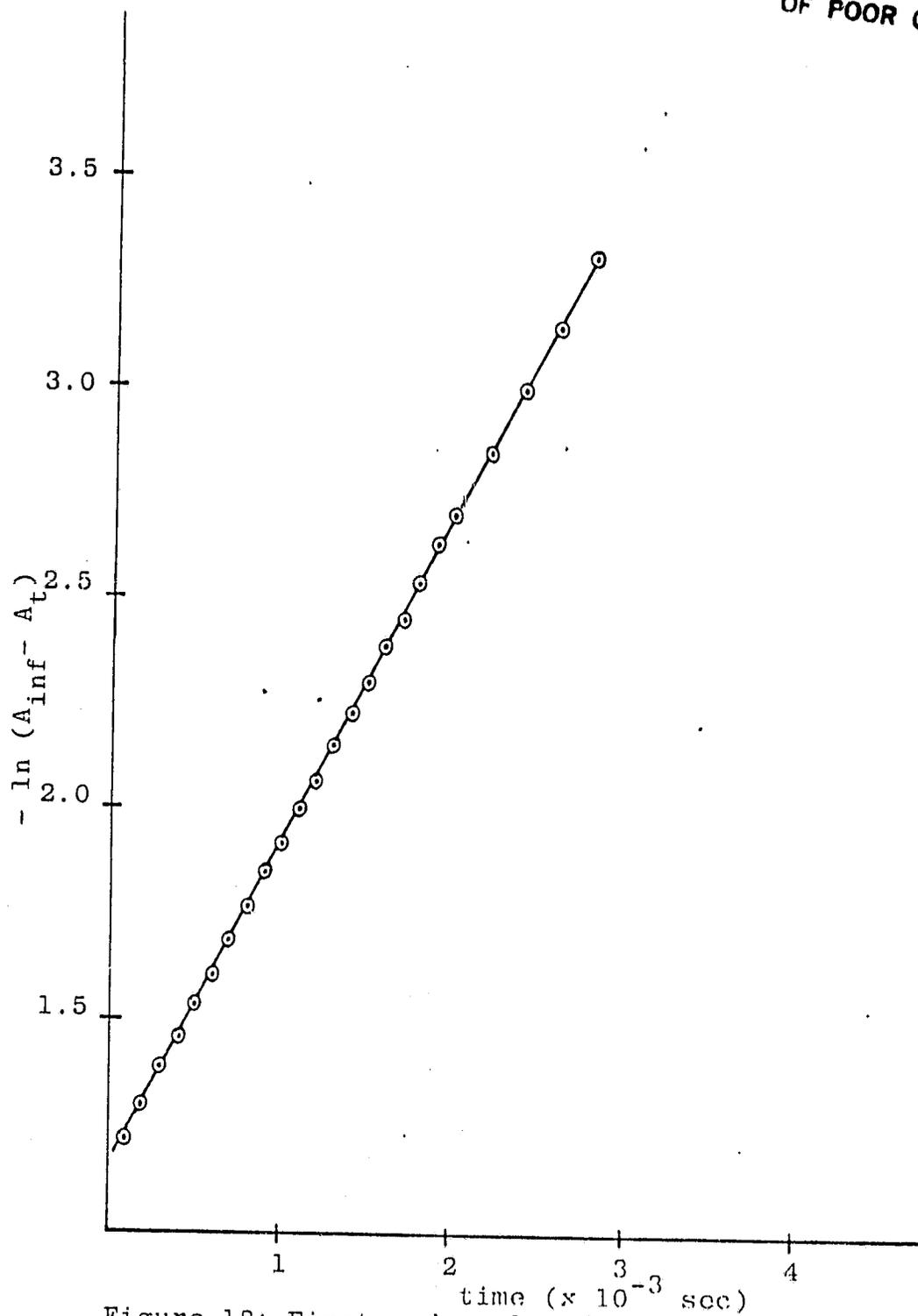
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Figure 18: First order plot for the reaction between 2,5-diaminofluorenone and excess (0.2M) phthalic anhydride in N,N-dimethylacetamide.

Table 4: Pseudo first-order and second-order rate constants for the formation of the monoamic acid derivatives of the fluorenones and benzophenones.

| Compound   | Phthalic Anhydride |        |        |
|--|--------------------|--------|--------|
|  | 0.05 M             | 0.10 M | 0.20 M |
| 2-aminofluorenone<br>k' (10 <sup>5</sup> sec <sup>-1</sup> )<br>k <sub>1</sub> (10 <sup>4</sup> M <sup>-1</sup> sec <sup>-1</sup> )  | 7.53               | 15.6   | 33.8   |
|  | 1.52               | 1.56   | 1.69   |
| 2,6-diaminofluorenone<br>k' (10 <sup>4</sup> sec <sup>-1</sup> )<br>k <sub>1</sub> (10 <sup>3</sup> M <sup>-1</sup> sec <sup>-1</sup> )  | 1.67               | 3.80   | 7.72   |
|  | 3.65               | 3.80   | 3.86   |
| 2,5-diaminofluorenone<br>k' (10 <sup>4</sup> sec <sup>-1</sup> )<br>k <sub>1</sub> (10 <sup>3</sup> M <sup>-1</sup> sec <sup>-1</sup> )  | 1.15               | 2.46   | 5.02   |
|  | 2.298              | 2.46   | 2.51   |
| 2,7-diaminofluorenone<br>k' (10 <sup>3</sup> sec <sup>-1</sup> )<br>k <sub>1</sub> (10 <sup>2</sup> M <sup>-1</sup> sec <sup>-1</sup> )<br>k <sub>2</sub> (10 <sup>3</sup> M <sup>-1</sup> sec <sup>-1</sup> ) | 0.83               | 1.53   | 3.10   |
|  | 1.75               | 1.53   | 1.55   |
|  | 1.82               | 1.93   | 1.91   |
| 3-aminobenzophenone<br>k' (10 <sup>5</sup> sec <sup>-1</sup> )<br>k <sub>1</sub> (10 <sup>3</sup> M <sup>-1</sup> sec <sup>-1</sup> )  | 9.06               | 19.5   | 43.0   |
|  | 1.81               | 1.95   | 2.15   |
| 3,3'-diaminobenzophenone<br>k' (10 <sup>4</sup> sec <sup>-1</sup> )<br>k <sub>1</sub> (10 <sup>3</sup> M <sup>-1</sup> sec <sup>-1</sup> )   | 1.22               | 2.54   | 5.36   |
|  | 2.44               | 2.54   | 2.68   |
| 3,4'-diaminobenzophenone<br>k' (10 <sup>4</sup> sec <sup>-1</sup> )<br>k <sub>1</sub> (10 <sup>3</sup> M <sup>-1</sup> sec <sup>-1</sup> )   | 3.22               | 6.38   | 12.4   |
|  | 6.43               | 6.38   | 6.21   |

Table 4, continued

| Compound   | Phthalic Anhydride |        |        |
|--|--------------------|--------|--------|
|  | 0.05 M             | 0.10 M | 0.20 M |
| 4,4'-diaminobenzophenone                         |                    |        |        |
| $k'$ ( $10^5 \text{ sec}^{-1}$ )                 | 4.29               | 9.1    | 17.6   |
| $k_1$ ( $10^4 \text{ M}^{-1} \text{ sec}^{-1}$ ) | 8.58               | 9.1    | 8.795  |
| 2,4'-diaminobenzophenone                         |                    |        |        |
| $k'$ ( $10^5 \text{ sec}^{-1}$ )                 | 1.09               | 2.63   | 4.83   |
| $k_1$ ( $10^4 \text{ M}^{-1} \text{ sec}^{-1}$ ) | 2.12               | 2.63   | 2.42   |

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2,7-diaminofluorenone. Each stage was first order in amine and first order in anhydride. The two rate constants found are  $k_1 = 1.52 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$  and  $k_2 = 1.93 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$ .

Reaction of 2-aminofluorenone with pyromellitic dianhydride

The reaction of PMDA with 2AFO proceeded in the usual manner seen for this dianhydride.<sup>8</sup> The first step of the reaction was quite rapid ( $k_1 = (4.47 \pm .08) \times 10^{-1} \text{ M}^{-1} \text{ sec}^{-1}$ ) while the second stage was much slower ( $k_2 = (3.98 \pm .07) \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$ ). The second stage of the reaction appeared to go cleanly with maintenance of an isobestic at 458 nm. Evaporation of solvent from one of the cuvettes yielded light-yellow rod-shaped crystals (m.p. 125-126°C). Agreement of the data for two concentrations of PMDA was within four percent.

DISCUSSION

Basicities of the fluorenones and benzophenones

The low basicities of the fluorenones and benzophenones was best explained by the electron-withdrawing effect of the carbonyl function. This effect was found to be somewhat decreased with the addition of a second amino function. The pKa values for the 4-aminofluorene, 2-aminobenzophenone, and the 4-aminobenzophenone could not be measured potentiometrically. The diamino derivatives of these compounds were sufficiently basic for protonation of one of the amino functions to occur.

Reactivities of the benzophenones and the fluorenones

Jencks<sup>43</sup> has suggested that of the acylation of amines by anhydrides would be catalysed by both the amic acid formed and by added acid. Catalysis by the acid product has indeed been seen by others,<sup>18</sup> as has been previously mentioned. In the system under investigation in this present study, the concentration of the acid product was too low for catalysis to occur. The absence of deviation from linearity of the first-order plots verifies this assumption.

Correlation of the dependence of reactivity on basicity

To determine what correlation existed between the basicity of the amines and their reactivity with phthalic anhydride, a plot was devised to show the dependence of the logarithm of the second-order rate constant,  $k_1$ , for the first step of the reaction, on the

logarithm of the formation constant,  $K_H$ , where

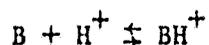
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$$\log K_H = -pK_a$$

for protonation of the first amino function.

When comparing symmetric and unsymmetric diamines, it was necessary to make a correction for the equivalence of the amino functions in the symmetric compounds.

To account for the apparent high basicity of the 2,7-DAFO, the 3,3'-diaminobenzophenone (3,3'-DABP) and the 4,4'-diaminobenzophenone (4,4'-DABP) the formation constant for the reaction



was divided by a factor of two. The true pKa value is then the reciprocal of this value. To account for increased reactivity resulting from equivalent sites, the second-order rate constants were also divided by a factor of two.

There is still the question of comparing monoamines with unsymmetric diamines, for which no corrections were made. The basicity and reactivity of the second amino function in the unsymmetric diamines was too low to be determined, and thus they have been treated as monoamines. The validity of these assumptions remains questionable.

The large slope and good linearity for the plot of log K versus (-log  $k_1$ ) for the diamino fluorenones implied a marked dependence of reactivity on basicity (Figure 19). It would appear that a common reactive site existed for all three of these compounds and that only the basicity of this site contributed to the reactivity of the compounds in this series.

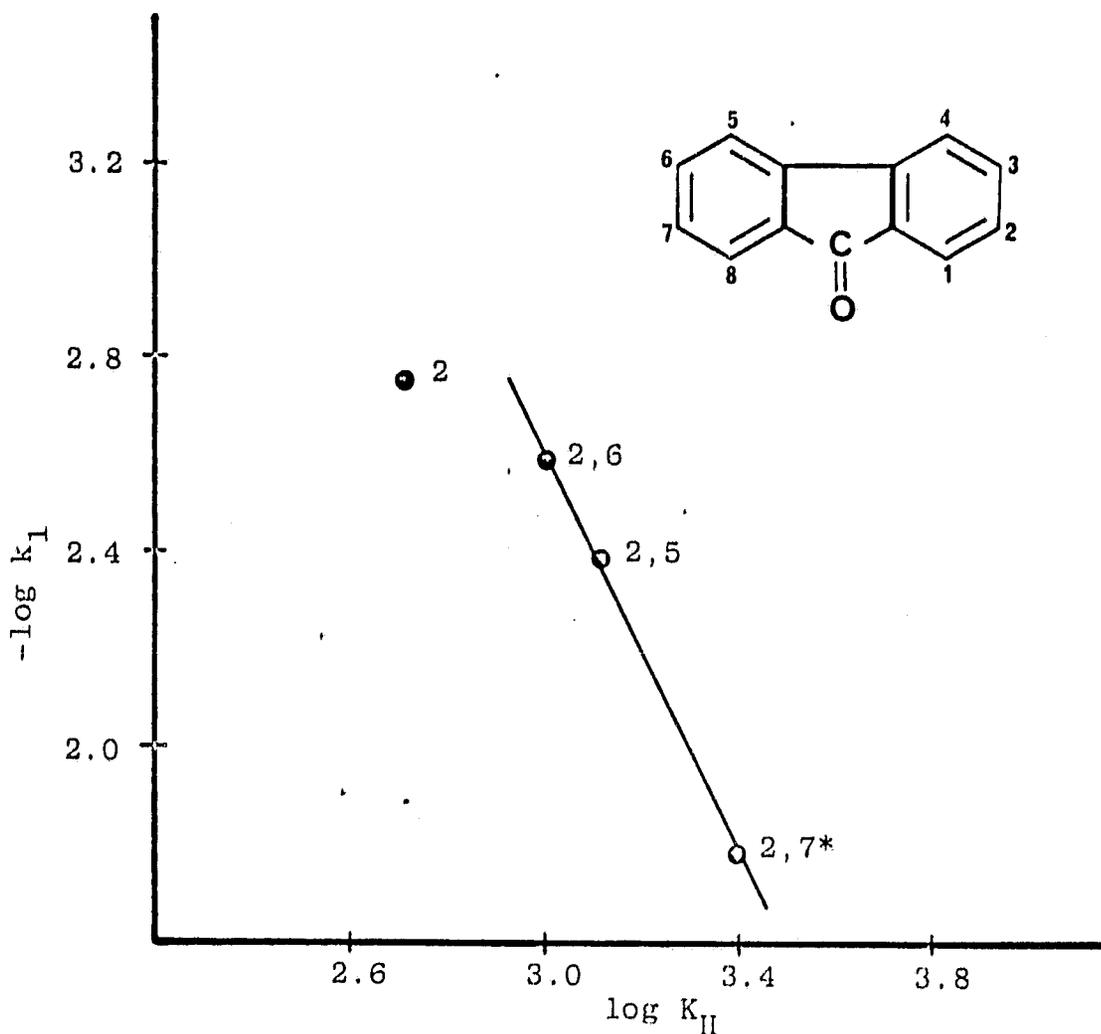
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Figure 19: Correlation of  $\log k_1$  for the formation of the monoamic acid<sup>-</sup> with  $\log K_H$  for fluorenone series.

| Compound | $\log K_H$  | $k_1 (10^3 \text{ M}^{-1} \text{ sec}^{-1})$ |
|----------|-------------|--|
| 2-       | 2.708       | 1.76   |
| 2,6-     | 3.055       | 2.58   |
| 2,5-     | 3.115       | 4.02   |
| 2,7-     | 3.703(3.4)* | 32.3 (16.15)*                                |

\*Statistical correction applied due to symmetry of this molecule.

The deviation of the 2-aminofluorenone may reflect the previously discussed idea that with decreasing basicity, other effects would markedly influence the reactivity of the amine. This was more adequately illustrated by the case of the benzophenones (Figure 20).

Even with symmetry corrections for the 3,3'-DABP and the 4,4'-DABP, a good linear correlation between  $\log K_H$  and  $(-\log k_1)$  was not found. A common reactive site would probably exist for the series of 3-aminobenzophenones as the 3-position is the only position in the molecule which cannot directly interact with the carbonyl function, but the diaminobenzophenones could not really be compared to the monoamine in the series and a line formed only by two points was not much on which to base a discussion. The least basic members in this series the 4,4'-DABP and the 2,4'-DABP deviate sharply from any sort of linear relationship with the other compounds in this series and even though the 2,4'-DABP was more basic than the 4,4'-DABP, the order of reactivity was reversed.

In general, all that could be said of these compounds was that a relationship between basicity and reactivity existed. This relationship was linear for the more basic aminofluorenones while other effects appeared to influence the reactivity of the less basic benzophenones such that a linear relationship between basicity and reactivity could no longer be seen.

Admittedly, more compounds would have to be examined in both of these series before a complete discussion of the electronic and structural effects which determine both the basicity and reactivity of these compounds would be valid.

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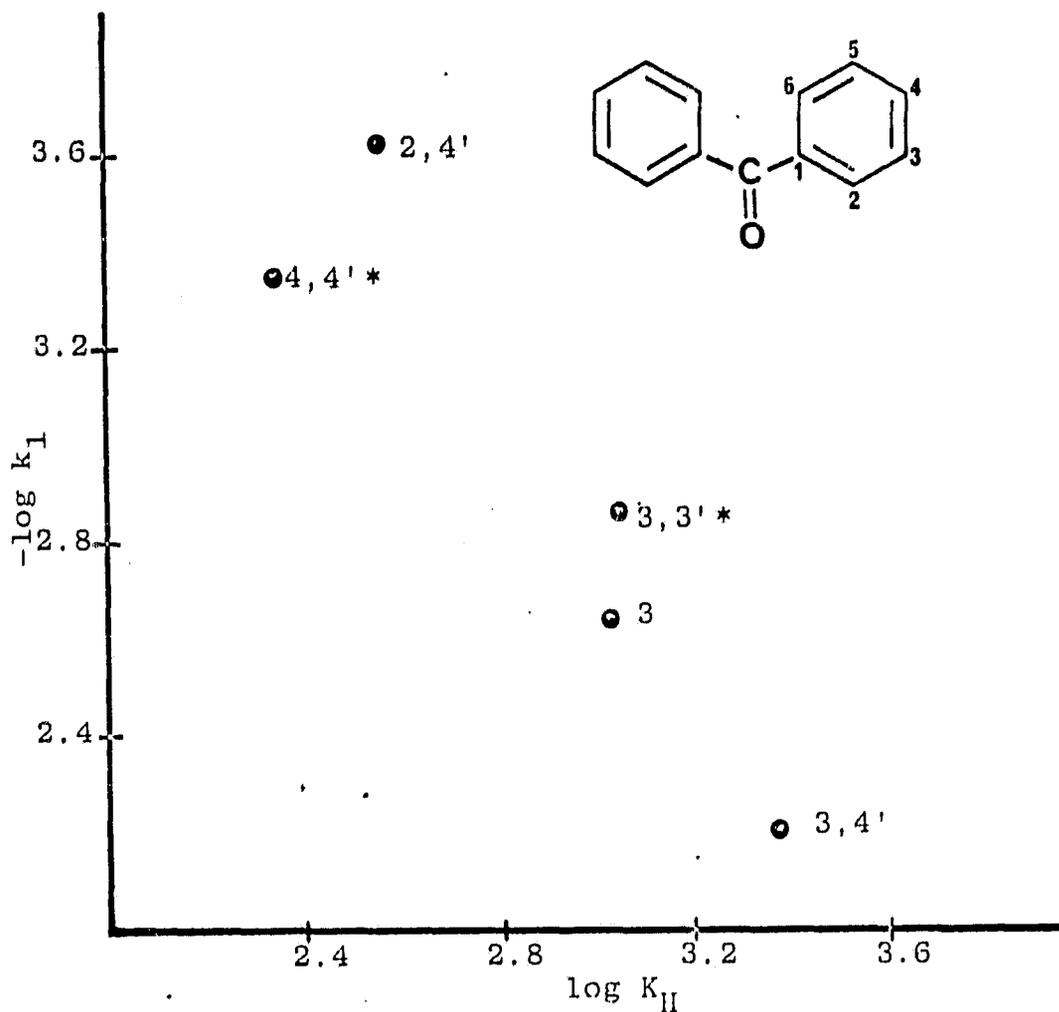


Figure 20: Correlation of  $\log k_1$  for the formation of the monoamic acid with  $\log K_H$  for the benzophenone series.

| Compound | $\log K_H$     | $k_1 (10^4 \text{ M}^{-1} \text{ sec}^{-1})$ |
|----------|----------------|--|
| 2,4'     | 2.566          | 2.452  |
| 4,4'     | 2.645 (2.344)* | 8.812 (4.406)*                               |
| 3,3'     | 3.35 (3.05)*   | 27.69 (13.85)*                               |
| 3,4'     | 3.375          | 61.15  |
| 3        | 3.03           | 22.77  |

\*Statistical correction applied due to symmetry of this molecule.

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## Appendix 1

The Evaluation of  $pK_a$  Basicity Constants

The determination of  $pK_a$  values as originally planned was quite simple. Titration curves for the titration of the amines of interest in the appropriate solvent with the selected titrant would be carried out to well beyond the calculated equivalence point. The Gran method of equivalence point estimation would be used and would produce not only the equivalence point but also the standardization of the pH meter.

The basic equations for the Gran Method are outlined on pp 19-21. Successful application of this technique to titrations in acetonitrile-water mixtures was reported in 1974 (G. Velinov, D. Ivanov, and O. Budevsky, J. Electroanal. Chem. and Interf. Electrochem. 57 (1974) 97).

A computer program was written to process the post equivalence point data and determine both the Nernst coefficient (theoretical value 59 millivolts), the apparent  $E^{\circ'}$  and the equivalence volume. This was and is a desirable feature. For some glass electrodes the response will be somewhat time dependent, i.e., the slope may change. The drifting of the  $E^{\circ'}$  values with time is, of course, well known and is the reason that pH meters must be standardized frequently. For the  $pK_a$  values obtained using calibration curves, such curves were obtained immediately pre- or post-titration. At least two were obtained every 3 hours.

The computer program utilized the equation

$$E^{\circ'} + S \log \frac{(V_H C_H - V_e C_H)}{V_T}$$

where  $E^{\circ'}$  is the formal potential, S the Nernst coefficient,  $C_H$  the volume of

acid added,  $V_e$  the equivalence volume and  $V_T$  the total volume. The theoretical value of  $S$  at  $25^\circ\text{C}$  is 59.2 mV.

The Gran linearization yields

$$V_T 10^{E/S} = 10^{E_0'/S} (V_H - V_e) C_H$$

which was best fit by the computer to give the best value of  $V_e$  when the standard deviation in  $V_e$  was minimal. The minimum was located through variation of the value of  $S$ . Value of  $S$  from 54 to 62 millivolts were measured. The assumption made initially was that the medium was producing changes in the electrode response with time in these reasonably acidic solutions. Since the value of  $S$  seriously affected the calculated hydrogen concentrations for EMF values well negative of  $E_0'$ , the improper selection of  $S$  would lead to very bad estimates of  $\text{pKa}'\text{s}$ . This would become more serious the more basic the amine.

After careful inspection of both calibration curve data and titration data, several regularities emerged. First, where both amine functions were relatively basic, both theoretical values of  $S$  and reliable equivalence points were obtained. Second, where one amine function was relatively basic and one was very weak, theoretical values of  $S$  were obtained for the first protonation but not for the second. Reliable values for the equivalence point could be obtained for the first protonation but not the second. The reliability was measured by agreement with the expected equivalence point as determined from the weight of the amine. This led to a reconsideration of the computational program.

The program used was written in BASIC for use with the Radio Shack TRS-80 computer by Mr. Roger Combs. It was constructed around the equations contained on pp 22-23 for  $\bar{n}$  and  $\beta'$ 's and assumed the theoretical response at

59.2 mV. Estimates of  $E^{\circ'}$ ,  $V_e$ ,  $C_H$  and the initial  $V_T$  were entered and  $\bar{n}$  values calculated to determine the effect on  $\bar{n}$ . For a given point of  $\bar{n}$  values, several calculation options were available which could produce only  $pK$  or both  $pK_1$  and  $pK_2$ . The largest  $\bar{n}$  value calculated determined whether the diamine was showing mono- or di-protonation. The calculation of  $K_1$  and  $K_2$  values was based on linear equations which were evaluated by non linear least squares with the best values of  $K_1$  and  $K_2$  selected for the largest correlation coefficient. This rather elaborate routine worked quite well, was rapid, and appeared reliable. It was necessary to develop this method of data treatment since so many titration curves had been obtained for which no calibration curves were available at all.

The computer treatment of the data made possible the calculation of reliable values for the second protonation constants for several systems such as the 3,3'-diaminobenzophenone and the 2,7-diaminofluorenone which were not clearly resolved utilizing the calibration curve technique.

In Table 3 several values which were discrepant from calibration curve utilization were found to yield comparable  $pK$  values when the computer approach was applied to the raw titration data. These entries are marked (recalc.) in Table 3.