

SPECTROMETRIC STUDIES OF 4-SUBSTITUTED
PHTHALIC ANHYDRIDES AND PHTHALIMIDES

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We hereby recommend that the Dissertation prepared under
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I. INTRODUCTION

When a molecule absorbs radiation its energy increases in proportion to the frequency of the photon as expressed by

$$\Delta E = E_2 - E_1 = h\nu = \frac{hc}{\lambda}$$

where h is the Planck's constant, ν and λ the frequency and the wavelength of the radiation, and c the velocity of the light. The molecule is promoted from the normal or ground state E_1 to a higher energy excited state E_2 . The difference between E_2 and E_1 corresponds to the frequency at which the absorption occurs. Any effect, such as that of a substituent, which changes the energy of the highest occupied orbital and/or the lowest unoccupied orbital will therefore shift the frequency of the absorption. A comprehensive study of the ultraviolet and infrared spectra of a series of compounds will furnish valuable information on the effects of substituents on the electronic configurations of the molecules.

There are various correlations reported between the quantitative extents of shifts in ultraviolet absorption maxima and of infrared group frequency shifts and other physical and chemical properties, such as reactivities, acid and base strengths, etc. for numerous compounds. However, no

systematic investigations of the ultraviolet and infrared spectra of the phthalic anhydrides and phthalimides mono-substituted on the benzene ring have been reported. It is the objective of this study to investigate the ultraviolet and infrared spectra of the 4-substituted phthalic anhydrides and phthalimides to demonstrate their substituent effects and to correlate their absorption spectra with other physical properties of the substituents.

Such effects of substituents on electronic configurations will also be examined by dipole moment measurements of some representative compounds of these series.

Solvent effects on the ultraviolet spectrum of phthalimide, as a model compound, were also studied in order to obtain a better understanding of the nature of the excited state of these molecules.

II. THEORY AND HISTORICAL

A. Ultraviolet Spectra

1. Theory

a. Electronic Excitation

The electronic transitions that are involved in the ultraviolet and visible regions are $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$, in the order of increasing energy. The frequency at which excitation occurs is determined by the energy difference between the initial and final states between which a quantum transition can be brought about by an external electromagnetic field, and the intensity depends upon the probability of occurrence of such a transition. Compounds that contain non-bonding electrons on oxygen, nitrogen, sulfur, or halogen atoms are capable of showing $n \rightarrow \sigma^*$ absorptions. Transitions to π^* ($n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$) are associated only with unsaturated centers in the molecule. With only a few exceptions, $\pi \rightarrow \pi^*$ transitions are very intense.

All carbonyl compounds have an $n \rightarrow \pi^*$ transition. The low molar absorptivities of such bands indicate a low probability of excitation. This transition is normally (in aldehydes and ketones) at a comparatively long wavelength, but is shifted to shorter wavelength by an adjacent heteroatom. This hypsochromic, or blue, shift results from the greater electronegativity of the adjacent halogen, nitrogen

or oxygen in comparison to carbon. The highly electronegative atoms cause electron withdrawal from the chromophoric carbonyl groups, and the energy gap between the ground state and the π^* state is widened. As a general rule, shifts in the position of λ_{\max} are bathochromic, or red shifts, when a chromophore is placed in conjugation with an unsaturated center. The conjugation effect decreases the energy gap between the ground state and π^* state. Both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions are shifted toward longer wavelengths by an increase in the number of unsaturated linkages in conjugation with the chromophore undergoing the transition.

b. Solvent effects on electronic transitions

The position of the absorption peaks of a compound may be shifted somewhat if different solvents are used. Electronic transitions result in a redistribution of electrons within the molecule. The position of an absorption that involves non-bonding electrons is particularly sensitive to the polarity of the solvent. If the group is more polar in the ground state than in the excited state the non-bonding electrons in the ground state are stabilized by hydrogen bonding, or electrostatic interaction with a polar solvent, and the absorption is shifted to shorter wavelength with increasing solvent polarity. If the group is more polar in the excited state, the non-bonding electrons of the excited state are stabilized by interaction with a polar solvent, and the absorption is shifted to longer wavelength with increasing solvent polarity. Polar solvents usually shift the $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ bands to shorter wavelength and the $\pi \rightarrow \pi^*$ band to longer wavelength. However, there are exceptions.

c. Substitution effect on electronic transitions

Substitution affects the transitions by both inductive and resonance effects. Induction affects the ground state and excited states about equally and in the same direction, and produces little change in the position or intensity of the absorption bands. On the other hand, resonance raises substantially the energy of the highest occupied orbital and affects the lowest unoccupied orbital to only a small extent or not at all, thus shifting the position of the band to red.

2. Review of Studies with Relevant Compounds

a. Ultraviolet Absorption of Benzene

Benzene exhibits three principal transitions: the symmetry-forbidden ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition, giving rise to the weak, long wavelength band centered around 254 nm ($\epsilon_{\max} \sim 200$); the forbidden ${}^1B_{1u} \leftarrow {}^1A_{1g}$ transition, which is responsible for the band at about 204 nm ($\epsilon_{\max} \sim 7000$); and the intense, allowed ${}^1E_{2u} \leftarrow {}^1A_{1g}$ transition, associated with the far ultraviolet band at 180 nm.

Extensive studies of the spectra of benzene derivatives have been made by Doub and Vandenbelt¹. In their papers, these authors proposed a nomenclature which has gained considerable acceptance. In general, benzene and its derivatives have three major $\pi \rightarrow \pi^*$ excitations. The short-wavelength, high-intensity band of benzene at 204 nm. is called the primary band, and the long-wavelength, lower-intensity band at 254 nm is called the secondary band. Appropriately substituted benzenes give rise to spectra in which displacements of all the benzene

bands occur, and frequently the 180 nm band is shifted to the quartz ultraviolet, in which case this high-intensity band is called the second primary band. For substituted benzenes, all three bands may arise from allowed transitions.

b. Substituted Benzenes

In spite of large changes in symmetry, the spectroscopic behavior of substituted benzenes is largely uniform and greatly resembles that of the parent compound. Thus substitution in benzene does not usually produce great changes or new bands in the spectra, but only modifies the spectrum of the parent compound. It is thus convenient to describe the effect of substitution as a perturbation². Substitution perturbs the benzene ring both by resonance and inductive effects.

Systematic structure-spectra correlations have been successful with monosubstituted and disubstituted benzenes¹. It has been suggested¹ that the displacement of the primary band of benzene is due to an electronic interaction of various substituents with the parent nucleus which results in a lessening of the constraint or force holding the electrons responsible for the absorption of light. Displacement is greatest for compounds capable of greatest electronic interaction. This enhanced effect has been ascribed to resonance.

Stevenson³ found that the frequency shift associated with the secondary bands are predictable on the basis of quantum mechanical calculations.

Rao^{4,5} has correlated the position of the 200 nm band in monosubstituted and para-disubstituted benzene derivatives with Hammett reactivity constants and resonance parameters of the groups. For para-complementary disubstituted benzenes, his relationship with σ -constants is of the following form:

$$\lambda = \lambda_0 + \rho\sigma$$

The sign of the slope is positive or negative depending on whether the varying substituents are electron attracting or withdrawing in nature.

For disubstituted benzenes in general, Rao⁵ found that the total resonance effect of the two groups, measured by the absolute value of the difference of the σ_R values of Taft, correlates well with the wavelength shifts:

$$\Delta\lambda = A|\sigma_R(1) - \sigma_R(2)| + C$$

where $\sigma_R(1)$ and $\sigma_R(2)$ are the σ_R values for two substituents and A and C are constants.

c. Substituted phthalic anhydrides and phthalimides

Studies of ultraviolet spectra of monosubstituted phthalic anhydrides are scattered. Some of the reported data are listed in Table 1. Such measurements of phthalimides monosubstituted in the benzene ring also were not done systematically, until Arcoria et al.^{6,7,8} and Caswell⁹ studied several such compounds in alcoholic and aqueous basic solutions. F. Lee¹⁰ also found that the spectra of the isoelectronic monoaza-analogs of phthalimides and their derivatives in various solvents show a similar spectral

behavior to that of phthalimide.

Previous investigations¹¹ at this laboratory has included studies on the spectra of phthalimidoacetic acids.

Cheng¹² studied tetrahydrophthalimides in both ethanol and aqueous basic solutions.

Previously reported data for compounds relevant to the present study are summarized in Table 2.

B. Infrared Spectra

I. Theory

a. Origin of infrared spectrum

Infrared spectra have their origin in the transitions between vibrational and rotational levels which belong to the ground electronic state of the molecule.

According to classical electrodynamics any motion of an atomic system that produces a change in dipole moment leads to emission or absorption of radiation. During the vibrational motion connected with a normal vibration the charge distribution undergoes a periodic change; this may or may not result in a change in the molecular dipole moment. If a change does occur, the vibration is said to be infrared active. The frequencies of the absorptions are determined essentially by the mechanical motions of the molecule. If a diatomic molecule is considered to be two weights connected by a helical spring, the vibrational frequency $\tilde{\nu}$, will be expressed as following:

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{k \left(\frac{1}{m_1} + \frac{1}{m_2} \right)} \text{ cm}^{-1}$$

TABLE 1
 Reported Ultraviolet Spectrum
 of Some Substituted Phthalic Anhydrides

Compound	Solvent	λ_{\max} , nm (log ϵ)	Reference
Phthalic anhydride	95% Ethanol	288 (2.90)	13
	95% Ethanol	225 (3.9)	14
		274 (3.1)	
		280 (3.0)	
	Dioxane	251 (3.6)	14
		288 (3.3)	
		297 (3.2)	
	CCl ₄	287 (3.2)	15
		295 (3.3)	
Heptane	211 (4.58)	16	
	245 (3.74)		
	286 (3.38)		
	295 (3.44)		
Ether	249 (3.7)	17	
	279 _s (3.2)		
	288 _s (3.3)		
	297 (3.3)		
4-Methylphthalic Anhydride	Pentane	254 (3.80)	18
		288 (3.37)	
		298 (3.43)	
	Heptane	217 (4.63)	16
		255 (3.72)	
	289 (3.29)		
	299 (3.38)		

TABLE 2

Reported Ultraviolet Spectra of Some Monosubstituted
Phthalimides and Related Compounds

Compound	Solvent	λ_{\max} , nm (log ϵ)	Reference
Phthalimide	95% Ethanol	237.8 (4.20) 290 (3.50)	9
	0.1 N NaOH	271 (3.03)	
	0.1 N HCl	237.5 (4.06) 297 (3.44)	
4-Acetamido- phthalimide	95% Ethanol	238 (4.40)	19
		247 (4.47)	
		253 (4.41)	
		289 (3.56)	
	Methanol	325 (3.67)	
		275 (4.10) 283 (4.11) 310 (4.17)	20
CH ₃ OH KOH	311 (4.17)		
4-Aminophthalimide	95% Ethanol	242 (4.50)	9
		252 (4.51)	
		308 (3.93)	
		372.5 (3.70)	
	0.1 N NaOH	267 (4.03)	
	0.1 N HCl	216 (4.57) (230) (4.22) 238 (4.03) 260 (3.03) 295 (3.18)	7
4-Hydroxyphthalimide	95% Ethanol	234 (4.50)	8
		262-6 _s (3.44)	
		280 _s (3.31)	
		324 (3.46)	
4-Methoxyphthalimide	95% Ethanol	234 (4.54)	8
		280 (3.35)	
		321 (3.47)	

Table 2 continued

Table 2 Continued

Compound	Solvent	λ_{\max} , nm (log ϵ)	Reference
4-Nitrophthalimide	95% Ethanol	231 (4.25)	
4-Azaphthalimide (cinchomeronimide)	95% Ethanol	223.5 (4.09)	10
		231.5 (3.90)	
		271.5 (3.48)	
	Water	224 (4.08)	10
		231.5 (3.93)	
		279 (3.44)	
	0.1 M HCl	224 (3.99)	10
		231 (3.82)	
		272 (3.65)	
	2.0 M HCl	225 (3.87)	10
		232 (3.83)	
		272 (3.74)	
0.1 M NaOH	265 (3.42)	10	
Cinchomeronimide- l-oxide	95% Ethanol	241 (4.23)	10
		257 (4.04)	
		311 (3.85)	
		311 _(i) (3.67)	
	Water	239 (4.02)	10
		266 (4.02)	
		330 _(i) (2.7)	
	0.1 M HCl	239 (4.32)	10
		256.5 (4.11)	
		304 (3.74)	
	2.0 M HCl	239 (4.27)	10
		256 (4.10)	
304 (3.71)			
329 _(i) (3.48)			
0.1 M NaOH	272 (4.12)	10	
3,4,5,6-Tetrahydro-	95% Ethanol	280 (2.51)	12
	0.1 N NaOH	featureless	12
<u>cis</u> -1,2,3,6-Tetra- hydrophthalimide	95% Ethanol	248 (2.09)	12
	0.1 N NaOH	214 ----	12

where k is the force constant in dynes/cm,
 m_1 and m_2 are masses in grams and
 c is the velocity of light.

The intensities of the absorption bands are connected essentially with electrical properties, such as the dipole moments, polarizability and interactions of electrical and magnetic moments. The integrated intensity of an infrared band A , corresponding to the i^{th} fundamental vibrational transition, is expressed as

$$A_i = \frac{N\pi}{3c^2} \left(\frac{2\mu}{2Q_i} \right)^2$$

where N is a number which depends upon the units in which A_i is expressed, c is the velocity of light, μ is the molecular dipole moment, and Q_i is the normal coordinate for the i^{th} vibration.

The experimentally observed intensity, A , is related to the absorption coefficient, α_ν by

$$A = \int \alpha_\nu d\nu = \frac{1}{Cl} \log_e \frac{I_0}{I} d\nu$$

where C is a unit of concentration, l is the path length, I_0 is the incident intensity of radiation of frequency ν and I is the transmitted intensity²¹.

b. Specific group frequencies

As vibrational analysis was extended to an increasing number of molecules, it became apparent that certain groups of atoms gave rise to vibration bands at or near the same frequency, irrespective of the particular molecule in which

the group occurred. Such a band can be used to characterize the absorbing group, and bears a formal resemblance to the specific chromophoric groups in electronic spectra.

c. Factors that influence band frequencies

Although band elasticity (force constant, k) and relative masses in the bound atoms constitute the two most important factors determining frequency, there are a host of other effects, both internal and external with respect to the molecule, which influence the absorption frequency. Nature, size and electronegativity of neighboring atoms, electronic and steric effects, phase changes and hydrogen bonding may all cause shifts in frequency.

The carbonyl group stretching vibration of interest in this work is affected by the following factors:^{22,23}

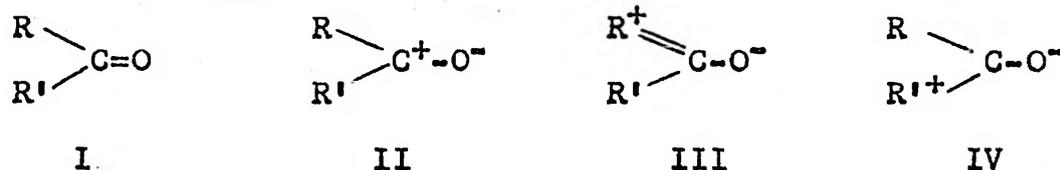
(1) External factors: The carbonyl stretching band is somewhat sensitive to changes in physical state. Generally, the highest recorded frequency is observed in the vapor state. For the liquid state, dilute solutions in non polar solvents give the highest recorded carbonyl stretching band frequency values. In more polar solvents molecules capable of ready distortion of the π -electron cloud still show appreciable shifts in the carbonyl band. In the solid state a similar situation might be expected. In crystalline solids the carbonyl frequencies are further lowered due to lattice field effects and possible association.

(2) Internal factors:

(a) Electronic and steric nature of the substituents: three factors might be considered as affecting

the carbonyl stretching frequency:

(i) Distribution of electrons in and neighboring to the carbonyl group. In terms of the organic structure involved, the force constant (or electron distribution) of a carbonyl group is a composite of the following resonance structures:



The actual contribution of any particular structure will depend on the ability of groups R and R' to attract or repel electrons. If the contribution of II is significantly greater than III and IV, the position of the carbonyl frequency should be at a higher value than for a carbonyl in which I is the major contributing structure. On the other hand, if structure III and IV are significant factors in the electron distribution within the carbonyl group, then the band position should shift to lower frequencies as a result of the increased single bond character of the C=O bond system.

Although useful in many instances, subtle differences in molecular structures, tend to limit the application of correlations of this type, particularly those involving steric phenomena.

(ii) Conjugation with multiple bonds: conjugation of the carbonyl group with an ethylenic double bond decreases the frequency by 20-40 cm^{-1} while the intensity of the bond increases²³. Aryl group conjugation also shifts the

band to a lower frequency, but to a lesser degree than double-bond conjugation. The influence of conjugation is additive to other effects which can influence the C=O frequency.

(iii) Steric distortion of the bond angles: the effect of steric strain is most clearly demonstrated in small ring carbonyl compounds²²:

<u>ring size</u>	<u>ketones</u>
4	1780 cm ⁻¹
5	1745
6	1715
7	1705

The intensity of the C=O band also decreases with increasing ring size.

(b) Hydrogen bonding: The carbonyl stretchings are affected by hydrogen bonding with a hydroxylic substance. The association of a hydrogen with the carbonyl group tends to decrease the double-bond character of the carbonyl, as shown below, thereby shifting the absorption to a lower frequency value.



(c) Vibrational coupling: The interaction of two vibrating units suitably located can split a band into two components, one above and the other below a common frequency. The mean of the two frequencies has been considered to be close to the unperturbed frequency and the separation is a measure of the degree of coupling²³. The coupling is very strong if the two oscillators have a common atom, as in the

case of carbon dioxide. There will be two stretching vibrations, the first where one C=O stretches while the other contracts. This vibration appears at 2350 cm^{-1} . The other vibration involving both C=O bonds stretching together, appears in the region near 1340 cm^{-1} . In acid anhydrides, the two carbonyl absorption bands are separated always approximately the same distance apart (about 60 cm^{-1})²⁴.

(d) Accidental degeneracy (Fermi Resonance)

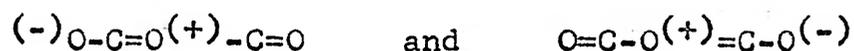
Anomalous splittings of the carbonyl stretching bands which cannot be explained by conformational, equilibrium or association effects are found in several molecules. The splitting is caused by coupling between the carbonyl stretching mode and the overtone or combination band of another low-lying vibration mode²³. A detailed study of the infrared spectra of substituted benzoyl chlorides has clearly shown that the magnitude of the band splitting (Fermi resonance) depends greatly on the substitution²⁵.

2. Review of Studies with Relevant Compounds

a. The infrared spectrum of an acid anhydride

The infrared spectrum of an acid anhydride is characterized by a doublet separated about 60 cm^{-1} apart in the $1750\text{-}1850\text{ cm}^{-1}$ region. It was originally suggested that this doublet arises from a mechanical coupling between the carbonyl vibrations as mentioned above²⁶. However, according to Popov *et al.*²⁷ and Mirone and Chiorboli²⁸, the large separation of the two carbonyl bands of anhydrides cannot be due to a pure mechanical coupling between the carbonyl

vibrators alone, but is mainly due to an interaction of electronic nature. They argued that the asymmetrical vibration of the O=C-O-C=O group supports stabilization by two alternative resonance structures

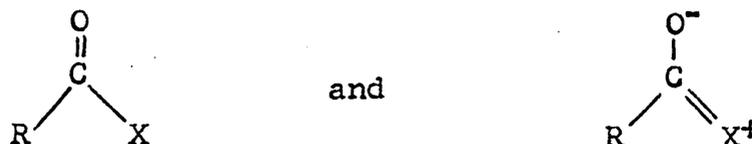


These give an important contribution to the actual structure of anhydrides, as shown by the high value of the resonance energy (about 30 kcal/mole)²⁹. This does not occur, however, for the symmetrical vibration. Consequently, the potential function includes a positive coupling constant between the carbonyl stretching coordinates, whose effect is the raising of the symmetrical frequency and the lowering of the anti-symmetrical one.

The symmetrical (in phase) stretching mode gives rise to the high frequency band and the asymmetric (out of phase) mode to the low frequency band. This assignment³⁰ explains why the relative intensities of the two carbonyl bands depend upon the geometric arrangement of the carbonyl groups. In cyclic anhydrides the higher frequency band is relatively weaker. In open-chain anhydrides the two bands are nearly of the same intensity, the high-frequency band being slightly more intense. The almost colinear arrangement of the two carbonyl groups in cyclic anhydrides results in a symmetric mode with very low infrared activity, due to the cancellation of dipole moments.

The intensities of the carbonyl absorption bands of compounds containing conjugated carbonyl groups increase

with conjugation³¹. This increase in carbonyl intensity with conjugation can be considered in terms of resonating forms. For a carbonyl conjugated with an electron donating group the most important resonating forms are, in addition to the ionic form inherent in the carbonyl group itself, of the types:

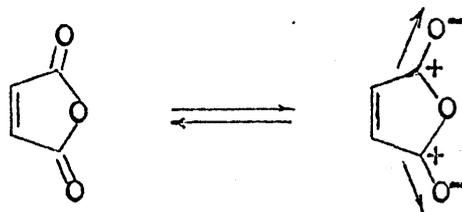


The stretching of the carbonyl band will therefore lead to an electronic structure of the molecule with a larger contribution of the charge-separated canonical form than in the molecule with equilibrium bond lengths. This increase will depend on the availability of such a charge separated electronic configuration. This also explains the phenomenon that among the 5-membered cyclic anhydrides, the value of the ratio of optical densities of low-frequency carbonyl band to that of high frequency band, D_L/D_H , is much higher for derivatives of maleic and succinic anhydride than that for phthalic anhydride and its derivatives. Marguardt³² argued that in unsaturated 5-membered cyclic anhydrides, like maleic or phthalic anhydride, the carbonyl groups can conjugate with the ether-oxygen (the only possibility in saturated compounds) and with the unsaturated function of the molecule as shown below for maleic anhydride. Intensification of the asymmetric stretching

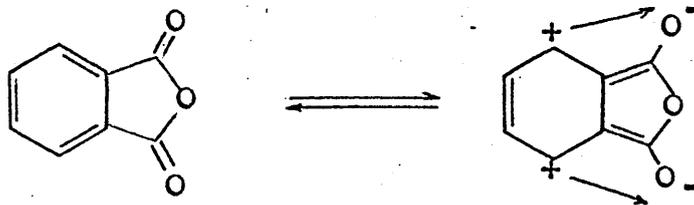


band can therefore be expected due to increase of the moment of the carbonyl group which is stretched.

Quite different is the situation in the case of the symmetric stretching mode, since here at any time both carbonyl groups are identically stretched or contracted, that is, identically polarized. It may therefore be expected that for a case like maleic anhydride the opposing identical influence of both carbonyls on the olefinic function and on the ether-oxygen should make simultaneous conjugation with both carbonyls almost impossible (shown in figure below). The intensity and the direction of the carbonyl bond moments related to this vibration will therefore be those of independent (non-conjugated) carbonyl groups. These will give rise to a mode which is, for geometric reasons, almost inactive in the infrared region.



Simultaneous conjugation of the unsaturated function with both carbonyl groups might nevertheless be possible in phthalic anhydride, due to the presence of a large pool of π -electrons. As a result, even in the symmetric mode, the magnitude of the moments related to the stretched two carbonyl groups will be increased and the angle between them decreased, resulting in rather large molecular moment for the stretched extreme structure



This could explain the high intensity of the symmetric carbonyl stretching band of phthalic anhydride as compared with that of maleic anhydride.

b. The infrared spectrum of a cyclic $\begin{array}{c} \text{O} \\ \parallel \\ \text{-C-NH-C-} \\ \parallel \\ \text{O} \end{array}$ group.

There has been some controversy³³ on the number of the C=O bands observed for compounds containing the group $\begin{array}{c} \text{O} \\ \parallel \\ \text{-C-NH-C-} \\ \parallel \\ \text{O} \end{array}$ in a ring system. In some cases one band is reported for diacyl-amino-compounds, in others two. The two bands observed in succinimides were assigned, one each to the cyclic carbonyl groups³⁴. On the other hand, N-bromosuccinimide has only one band^{33a}. In their studies on N,N-diacetylanilines and dibenzoylamino compounds, Grove et al.^{33b} and Orr³⁵ reported that the number of carbonyl bands observed depends upon the symmetry of the substitution. Abramovitch³⁶ re-examined a series of compounds including symmetrically and unsymmetrically monosubstituted N,N-diacetylanilines. He found that all the compounds have at least two bands that appear in the 6μ region. Both of these bands were attributed to amide carbonyl stretching vibrations. In many cases one of these bands appears only as a shoulder. Some of these compounds exhibited a single sharp peak in solution spectra, though this can sometimes be resolved into its component bands

by using a narrower slit. The possible symmetry effect mentioned above does not, in fact, exist and it seems that all N,N-diacylamino compounds exhibit doublets for the amide absorption if examined at sufficiently low scanning speeds and narrow enough slit widths. Also there seems to be no reason to attribute either of the bands to a specific carbonyl group as has been done in the cases of the succinimides³⁴. Abramovitch³⁵ attributes this multiplicity of bands as an example of vibrational coupling of the two carbonyl groups. However, Matsuo³⁷ suggested that the splitting of the carbonyl absorptions in cyclic imides is mainly due to the electronic stabilization of the out-of-phase vibration though a contribution of the ionic structures $^{\ominus}\text{O}-\text{C}=\text{N}^{\oplus}-\text{C}=\text{O}$ and $\text{O}=\text{C}-\text{N}^{\oplus}=\text{C}-\text{O}^{\ominus}$ just as in the case of anhydrides.

c. Correlations of substituent effects on infrared frequency and intensity

There are many possible correlations of infrared band frequency and intensity for various systems of compounds³⁸. For aromatic carbonyl compounds Thompson et al.³⁹ found a linear Hammett relation of the carbonyl frequencies of the type of $\text{C}_6\text{H}_5-\text{CO}-\text{R}$ substituted in the aromatic ring. The relation may be expressed by equation:

$$\nu = \nu_0 + \rho\sigma$$

where ν is the observed group frequency in the substituted derivative, ν_0 is the group frequency in unsubstituted compound and ρ and σ are the usual Hammett functions.

Thompson et al. also have considered the possibility of

plotting ν^2 versus σ on the ground that the substitution will affect the vibration frequency by alternation of a linkage force constant. Similar relations have also been found for other systems^{40,41}. Rao and Silverman⁴² proposed the correlation of frequency with the electrophilic substituent constant, σ^+ , thus:

$$\nu = \nu_0 + \rho \sigma^+$$

However, a statistical study⁴³ showed that both substituent constants, σ and σ^+ , correlate the frequencies equally well.

The intensity of the carbonyl vibration of these compounds also depends linearly on Hammett substituent constants in the following forms:

$$\log A = \log A_0 + \rho \sigma, \text{ and}$$

$$\log A = \log A_0 + \rho^+ \sigma^+$$

although the dependence is very small^{39,42}.

d. Reported infrared data

The reported infrared carbonyl absorptions for cyclic anhydride and cyclic imides are listed in Table 3 and 4 respectively.

C. Dipole Moments

1. General Considerations

When a bond is formed between two atoms that differ in electronegativity, there is a separation of negative charge from the positive charge. The bond then constitutes an electric dipole moment which is defined by the relation:

$$\vec{\mu} = q\vec{l}$$

TABLE 3
Reported Infrared Carbonyl Absorption
on Cyclic Anhydrides

Compounds	Phase	$\nu_{C=O}, \text{ cm}^{-1}$		Reference
Succinic anhydride	KBr	1866	1767	44
	CCl ₄ soln.	1866	1792	30
	CHCl ₃ soln.	1872	1790	45
Maleic anhydride	cyclohexane	1856	1796, 1784	28
	CCl ₄	1858	1795, 1784	
	benzene	1855	1795, 1785	
	CHCl ₃	1858	1796, 1785	
	n-butanol	1856	1796, 1786	
	CCl ₄	1835	1770	
2-Methylmaleic anhydride	CCl ₄	1832	1764	30
2,3-Dimethyl maleic anhydride	CCl ₄	1812	1757	30
2-methyl-3-hexadecylmaleic anhydride	CCl ₄	1802	1757	30
Phthalic anhydride	mineral oil	1835	1748	46
	KBr	1850	1757	47
<u>cis-Endomethylene tetrahydro-phthalic anhydride</u>	CCl ₄	1855	1783	30
4-Nitrophthalic anhydride	KBr	1876	1786	48
3-Nitrophthalic anhydride	KBr	1866	1786	49

TABLE 4
Reported Infrared Carbonyl Absorption
on Cyclic Imides

Compound	Phase	$\nu_{C=O}$, cm^{-1}		Reference
Succinimide	KBr	1770	1698	50
	acetonitrile	1769	1728	37
	CHCl_3	1786	1764, 1730	37
	Nujol	1786	1727, 1715	
Maleimide	KBr	1770	1702	50
	acetonitrile	1770	1737	37
Glutarimide	KBr	1769	1702	50
Phthalimide	benzene	1781	1747	37
	CHCl_3	1775	1735	51
	CHCl_3	1778	1739	52
4-Nitrophthalimide	CHCl_3	1780	1736 _s	51
	KBr	1786	1712 _s	53
4-Acetamido-phthalimide	KBr	1767	1712	54

where \vec{l} is the radius vector directed from the center of gravity of the negative electric charge to the center of gravity of the positive electric charge, the absolute magnitude of each charge being q .

Functional groups are distinguished by a characteristic group moment which expresses the charge distribution in the group itself.

The molecular dipole moment is the vectorial sum of the individual bond dipole moments. The dipole moment of a molecule is a direct characteristic of its electronic configuration and indirectly of the atomic constituents. Any perturbation under the influence of certain structural factors such as the introduction of substituent groups into the molecule is reflected in the magnitude of the dipole moment. The substituents affect the dipole moments by a redistribution of the electron density by both inductive and resonance effects. Therefore, it is not surprising that relationships between the dipole moment and other molecular properties, such as the reciprocal solubility exist⁵⁵. There also exist relationships between the dipole moments and Hammett's reactivity constants⁵⁶.

The practical determination of a dipole moment is based on the existence of an orientation effect of polar molecules in an applied electric field. One of the most used method for measuring dipole moments is based on combining dielectric constant and refractive index measurements.

A complete literature review of all dipole moments measured prior to 1961 has been compiled by McClellan⁵⁷.

Some of the reported dipole moments for compounds relevant to this study are summarized in Table 5.

TABLE 5
Reported Dipole Moments

<u>Compound</u>	<u>Dipole Moment (solvent, temp.) Debye</u>	<u>Reference</u>
Maleic anhydride	3.94 (dioxane, 35°)	58
Phthalic anhydride	5.25 (benzene, 20°)	59
Succinic anhydride	4.20 (dioxane, 10°) 3.80 (benzene, 25°)	59 60
Succinimide	1.47 ± 0.01 (dioxane, 30°)	61
Cyclohexane-1,2-imide	1.74 ± 0.02 (dioxane, 30°)	61
Phthalimide	2.14 ± 0.02 (dioxane, 20°)	62
4-Chlorophthalimide	1.43 ± 0.03 (dioxane, 20°)	62
4-Nitrophthalimide	2.60 ± 0.03 (dioxane, 20°)	62

2. Method used in present study for estimating dipole moments of phthalic anhydrides and of phthalimides

It was assumed that:

1. The structures of phthalic anhydride and of phthalimide are planar, and this planarity is not distorted by substituents on the benzene ring.

2. The dipole vector of the substituent X lies along the C-X bond and is in the plane of the molecule.

3. The dipole vectors of the cyclic imide and anhydride groups bisect these groups and that these groups are electron-withdrawing.

The dipole moments of monosubstituted phthalic anhydrides and phthalimides may then be estimated from the moments of C_6H_5-X and of the imide or anhydride by vector addition:

$$\mu^2 = \mu_0^2 + \mu_x^2 + 2\mu_0\mu_x \cos \theta$$

where μ is the dipole moment of the substituted compound, μ_0 is the dipole moment of the unsubstituted anhydride or imide, μ_x is the dipole moment of C_6H_5-X and θ is the angle between the vectors.

The dipole moments calculated by this method and using the values of 5.29 ± 0.03 and 2.14 ± 0.02 Debyes for phthalic anhydride and phthalimide are summarized in Table 6 and the details for this calculation is illustrated in Appendix II.

TABLE 6
Calculated Dipole Moments

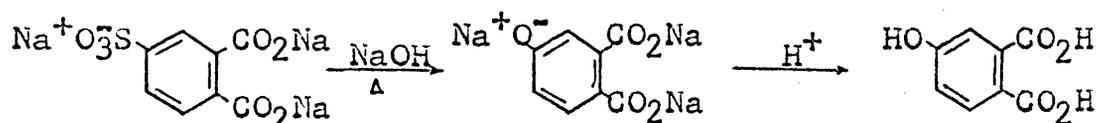
<u>Compound</u>	<u>μ, Debyes</u>
4-Chlorophthalic anhydride	3.95 ± 0.05
4-Methylphthalic anhydride	5.67 ± 0.03
4-Nitrophthalic anhydride	2.70 ± 0.03
4-Azaphthalimide	1.13 ± 0.01
4-Chlorophthalimide	1.09 ± 0.02
4-Methylphthalimide	2.52 ± 0.02
4-Nitrophthalimide	2.47 ± 0.03

III. EXPERIMENTAL

A. Synthesis

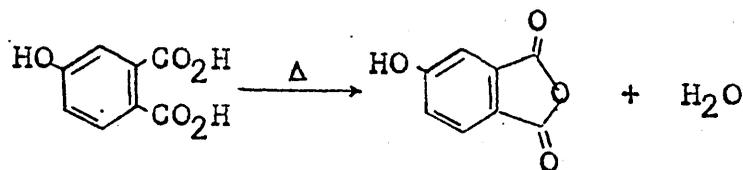
All the melting points were determined with an Eleetrothermal melting point apparatus. Microanalysis was by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Preparation of 4-Hydroxyphthalic Acid



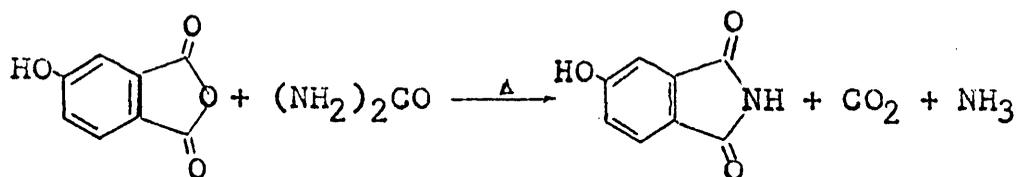
The procedure used by Caswell and Atkinson⁸ was followed. In a 250 ml. pressure flask was placed 16.6 g. (0.05 mole) of sodium 4-sulfophthalate and 30 g. of powdered sodium hydroxide. The materials were thoroughly mixed and then heated to 175-180° for three hours. The greenish fused mass was poured into 200 ml. of water. The resulting solution was acidified with 1 N hydrochloric acid to a pH of about 2. The mixture was filtered to remove *m*-hydroxybenzoic acid, and the filtrate was extracted continuously with ether for 24 hours. The ethereal extract was dried with anhydrous magnesium sulfate and the solvent was removed in a rotary evaporator, giving 9.1 g. (97.5%) of 4-hydroxyphthalic acid, m.p. 195-197° (reported⁶³ 204-5°). The acid was used without further purification.

Preparation of 4-Hydroxyphthalic Anhydride



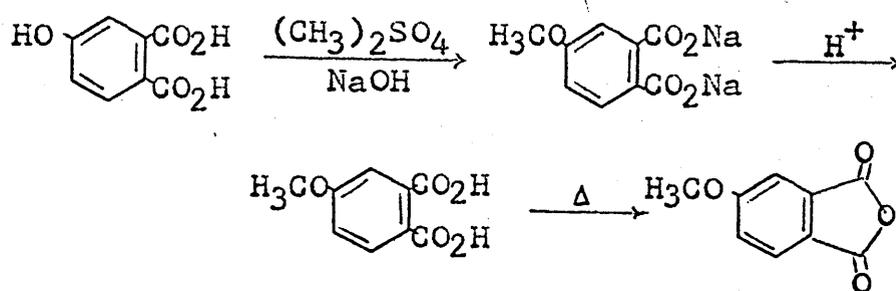
The procedure described by Bentley and Weizmann⁶³ was used. Thus, 7 g. (0.39 mole) of 4-hydroxyphthalic acid was heated to about 210° until all effervescence had ceased, giving 5.6 g. (88.7%) of 4-hydroxyphthalic anhydride, m.p. 161-165°. Two recrystallizations from glacial acetic acid raised the melting point to 174-174.5° (reported⁶³ 171-173°).

Preparation of 4-Hydroxyphthalimide



One and six-tenths grams of 4-hydroxyphthalic anhydride was heated with 0.6 g. of urea at 160-170°. The mixture melted at first and after some gas evolved, it solidified to give 1.5 g. of 4-hydroxyphthalimide, m.p. 286-288°. Recrystallization from 95% ethanol, raised the melting point to 297° (reported⁶³ 290°).

Preparation of 4-Methoxyphthalic Acid and Its Anhydride

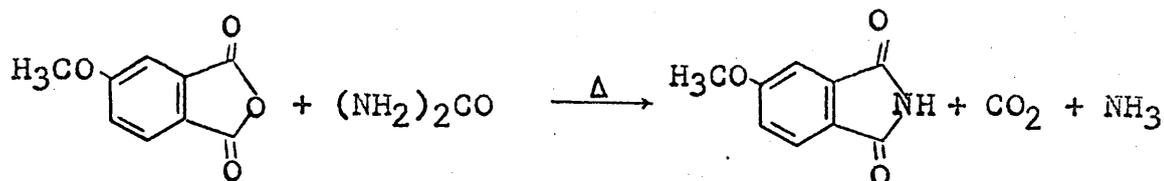


The synthesis of the acid was carried out by the procedure described by Caswell and Atkinson⁸. Thus, into a three-necked flask fitted with a reflux condenser, a magnetic stirrer, and a dropping funnel, was placed 7 g. (0.04 mole) of 4-hydroxyphthalic acid in a solution of 4.5 g. of sodium hydroxide in 15 ml. of water. To this solution, 4.9 g. of dimethyl sulfate was added dropwise. Then 5 ml. of 20% sodium hydroxide was added and the mixture was refluxed for 30 minutes to hydrolyze any ester formed. The solution was then cooled to room temperature and acidified with concentrated hydrochloric acid to $\text{pH} = 1$. After standing overnight, a yield of 4.5 g. (75%) of 4-methoxyphthalic acid, m.p. 163-164° (decompn.) was obtained. Recrystallization from water gave glittering crystals, m.p. 166-167.5° with effervescence. (Reported⁶³ slowly heated: 170°; rapidly heated: 178°).

4-Methoxyphthalic anhydride was obtained by heating the acid in an oil bath at 180-190° until no more effervescence occurred. The residual melt was diluted with glacial acetic acid, and the precipitate was recrystallized from acetic anhydride, followed by washing with absolute

ether. The product melted at 94.5-95° (reported⁶³ 98-99° and 93°⁶⁴).

Preparation of 4-Methoxyphthalimide



The same procedure as was used for 4-hydroxyphthalimide was followed. Thus, 4-methoxyphthalimide was obtained by heating 4-methoxyphthalic anhydride with urea at 160-170° until all effervescence had ceased. The crude product was recrystallized from toluene, giving material which melted at 219-220°. Further recrystallization from 95% ethanol raised the melting point to 220-222° (reported⁶³ 224-225°).

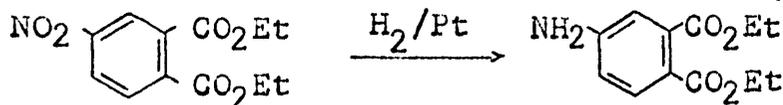
Preparation of Diethyl 4-Nitrophthalate



This synthesis was carried out by the same procedure as described by Blicke and Smith⁶⁵. A suspension of 25.1 g. (0.12 mole) of 4-nitrophthalic acid in 50 ml. of absolute ethanol was partially saturated with hydrogen

chloride and refluxed for 24 hours. The greater part of ethanol was removed in a rotary evaporator, and the residue was poured into 80 ml. of water. The oily layer was washed with 5% sodium bicarbonate solution, and then with water. It was dried over fused sodium sulfate and distilled under diminished pressure furnished by a water aspirator. The portion which boiled at 210-214° (ca. 21 mm.) was collected, and diluted with absolute ethanol and cooled in an ice bath. The pale greenish yellow crystals were filtered with a Büchner funnel which had been cooled previously to 0°C. Unless the mixture of ester and alcohol was kept cold, the ester redissolved in the solvent. The crystalline ester was suspended in a small amount of absolute ethanol, cooled to 0° for a short time and filtered again. The yield was 27.9 g. (89%) of diethyl 4-nitrophthalate, m.p. 31-32° (reported⁶⁶ 33-34°). The ester was used without further purification.

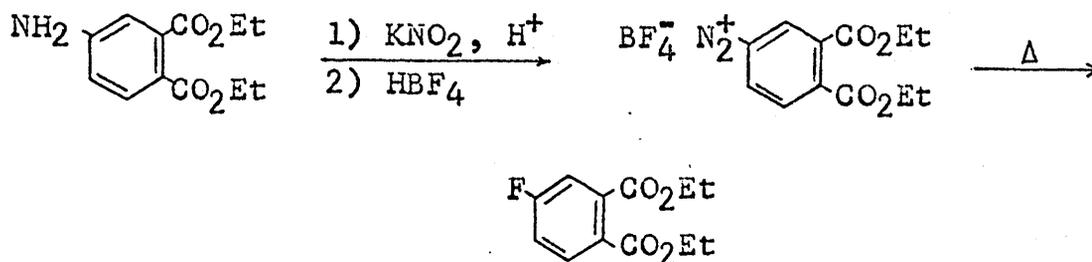
Preparation of Diethyl 4-Aminophthalate



The procedure of Blicke and Smith⁶⁵ was followed. Thus, 23 g. (0.08 mole) of diethyl 4-nitrophthalate was dissolved in 90 ml. of absolute ethanol and reduced with hydrogen, in the presence of 0.1 g. of platinum oxide catalyst, under an initial pressure of 59.8 psi. The reaction

was completed in 20 minutes. Heat was evolved during the reaction. The mixture was allowed to cool at room temperature and to stand for about one hour before filtering with suction. The filtrate was concentrated in a rotary evaporator, giving 13.5 g. of colorless crystals, m.p. 95-96° (reported⁶⁵ 95°). An additional 4.0 g. was obtained as pale yellow crystals. The overall yield was 17.5 g. (85.3%).

Preparation of Diethyl 4-Fluorophthalate

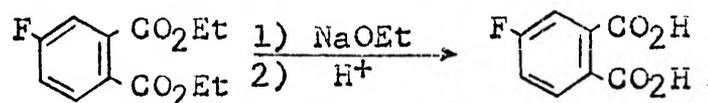


The procedure used by Blicke and Smith⁶⁵ was followed. Thus, 11.8 g. (0.05 mole) of diethyl 4-amino-phthalate was dissolved in a mixture of 20 ml. of concentrated hydrochloric acid and 10 ml. of water. The solution was cooled to 0° and then diazotized with 4.3 g. of potassium nitrite in 15 ml. of water by adding dropwise and stirring. To the cold, diazotized solution was added 26 ml. of 48% fluoroboric acid slowly. The mixture was stirred rapidly, whereupon the diazonium fluoroborate of diethyl phthalate precipitated. The precipitate was filtered through a sintered glass funnel and washed with absolute ethanol and then twice with absolute ether. The diazonium salt was dried in a vacuum desiccator over sulfuric acid for 24 hours. The yield was 21.2 g.

Ten grams of the dry diazonium salt was placed in a 500 ml. round-bottomed flask connected to a wash bottle which contained a 10% solution of sodium hydroxide. The flask was heated slowly to 125° in an oil bath and when the evolution of gases had ceased the temperature of the bath was raised to 140° and maintained there for one hour. The oily residue was dissolved in carbon tetrachloride, and the solution was washed with 10% aqueous sodium hydroxide and then with water. The carbon tetrachloride layer was separated and dried overnight over fused sodium sulfate. The solvent was removed in a rotary evaporator and the residue was distilled under reduced pressure furnished by water aspirator. The fraction boiling at 167-175° (Ca. 22 mm. Hg) (reported⁶⁵ 165-170° at 25 mm. Hg) was collected. Its weight was 2.5 g. (36%).

Preparation of 4-Fluorophthalic Acid

a. From diethyl 4-fluorophthalate



A mixture of 13.8 g. of diethyl 4-fluorophthalate and 13 g. of sodium hydroxide in 30 ml. of 50% ethanol was refluxed for 4 hours. Some solid formed during the refluxing. After cooling the solid was collected and acidified with 12 N sulfuric acid. The acidified solution was extracted with ether, and the solvent was removed in a rotary evaporator. The residue was allowed to crystallize, giving 4.3 g. (41%)

of crystals, m.p. 138-140° (reported⁶⁵ 147-148° in a sealed tube). Some decomposition was observed when the melt was heated to 160-170°. A small portion was sublimed under vacuum. The sublimate melted at 149-151° and decomposed at about 190°.

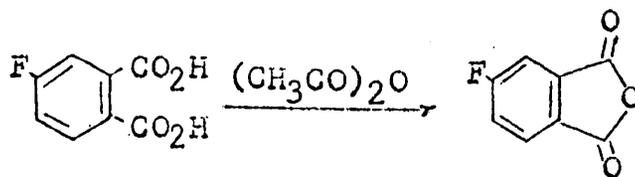
b. From 4-aminophthalimide



The method described by Martinez^{10a} was followed with some modification for this preparation. Thus, 16.15 g. (0.1 mole) of 4-aminophthalimide was dissolved in 80 ml. of 48% fluoroboric acid and placed in a one-liter beaker equipped with an efficient mechanical stirrer and cooled in an ice-salt bath. At 0°C, a chilled solution of 10.2 g. (0.12 mole) of potassium nitrite dissolved in 17 ml. of water was added dropwise to the reaction mixture while the mixture was kept cold and stirring. After the addition, the mixture was stirred for another 10 minutes, and was then filtered through a sintered glass funnel by suction. The ivory colored precipitate was then washed once with 15 ml. of chilled fluoroboric acid, twice with absolute methanol, eight times with ether. The precipitate was thoroughly dried after each wash. The diazonium salt was then dried in a hood on a piece of filter paper for 48 hours. The yield was 38.2 g. The dried salt was then transferred to a one-liter, one-neck round-bottomed flask connected by a wide-bore bent glass tubing to a one-liter filter flask. The

flask was heated in an oil bath slowly to 135°, where voluminous heavy, white fumes of boron trifluoride and nitrogen were evolved. The heating was continued until no more fumes were evolved. The solid residue was extracted with boiling water. The extract was cooled overnight, giving 9.2 g. of brownish precipitate which had a melting range of 162-283° with decomposition. Attempts at purification of this product, labelled as "intermediate" in the equation were unsuccessful. This intermediate was refluxed with 100 ml. of 2 N sodium hydroxide for 3 hours. The solution was allowed to cool, then acidified with concentrated hydrochloric acid, and extracted with ether. The ether was removed in a rotary evaporator, and the residue was diluted with benzene, giving 4.1 g. (25%) of 4-fluorophthalic acid, m.p. 141-143° (reported⁶⁵ 147-148° in a sealed tube) with a great deal of bubbling. No melting point depression was observed when mixed with the acid prepared by hydrolysis of the corresponding ester.

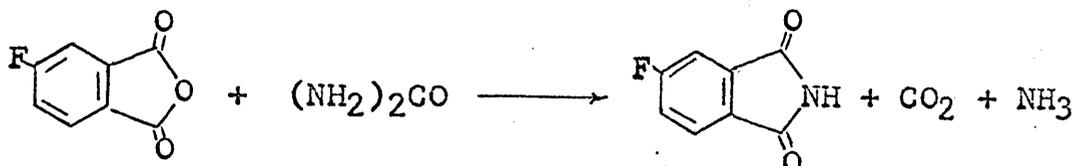
Preparation of 4-Fluorophthalic Anhydride



Four grams (0.22 mole) of 4-fluorophthalic acid was refluxed with 6 ml. of acetic anhydride for 3 hours. Most of the solvent was removed in a rotary evaporator by dilution with benzene and repetition of the procedure several times.

The yield was 2.5 g. (68.5%) of 4-fluorophthalic anhydride, m.p., 75.5-76.5° (reported⁶⁵ 76-78°).

Preparation of 4-Fluorophthalimide



a. By direct heating with urea

A mixture of 0.88 g. (0.005 mole) of 4-fluorophthalic anhydride and 0.3 g. (0.005 mole) of urea was heated over an oil bath. The mixture melted at about 90° (bath temperature), and started bubbling at 130-140°. After the bubbling ceased, the melt resolidified. The solid was recrystallized from a toluene-carbon tetrachloride mixture, giving 0.4 g. (45.5%) of colorless crystals, m.p. 177-178°.

b. By refluxing in nitrobenzene

Three grams of 4-fluorophthalic anhydride was refluxed with 0.9 g. of urea in 10 ml. of nitrobenzene for one hour. The mixture was allowed to stand and solidify. The yellow solid was collected, weight 1.73 g. (57.7%) and recrystallized from benzene to give a product melting at 150-164°. Recrystallization from toluene-carbon tetrachloride raised the melting point to 178-180°.

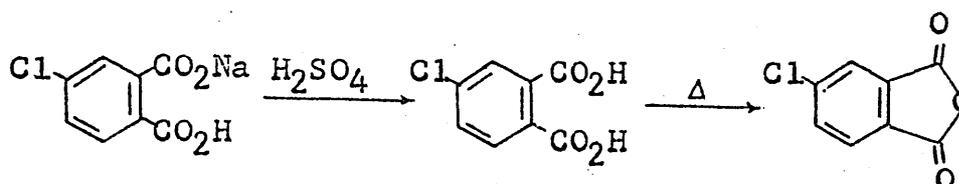
For analysis, a sample was recrystallized from toluene two more times, m.p. 181.5-182.5°.

Calculated for $\text{C}_8\text{H}_4\text{O}_2\text{NF}$: C, 58.18; H, 2.45;

N, 8.48; F, 11.51.

Found: C, 58.13; H, 2.22; N, 8.39; F, 11.52.

Preparation of 4-Chlorophthalic Acid and Its Anhydride



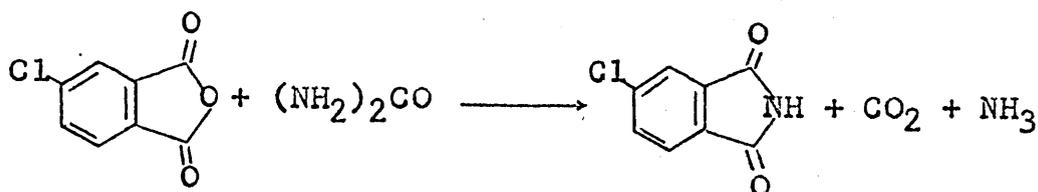
This synthesis was carried out by the procedure described by Martinez^{10a} with some modification. A saturated solution of 100 g. (0.45 mole) of 4-chlorophthalic acid monosodium salt in water was acidified with concentrated sulfuric acid to pH about 2. The mixture was filtered by gravity, and the filtrate was extracted continuously with ether for 60 hours. The ethereal extract was distilled to remove most of the solvent. The residue was diluted with a benzene-petroleum ether mixture, and the acid crystallized out. The air-dried yield was 47 g., m.p. 134-137°. Concentration of the mother liquor gave an additional 18.2 g., m.p. 136-154°. The overall yield was 65.2 g. (72%). Recrystallization from acetic acid raised the melting point to 147.5-149°C (reported⁶⁷ 150° in a sealed tube).

The anhydride was obtained by procedure of Blicke and Smith⁶⁵. Ten grams of 4-chlorophthalic acid was heated. After the water formed through the conversion of the acid into the anhydride had been removed, the residue was then distilled. The distillate solidified immediately, b.p. 283° (reported⁶⁵

284° at 750 mm.); m.p. 82.5-89°, weight 7.5 g. (83%).

It was recrystallized from acetic acid, washed with absolute ether three times, giving m.p. 94-95.5° (reported⁶⁵ 98°).

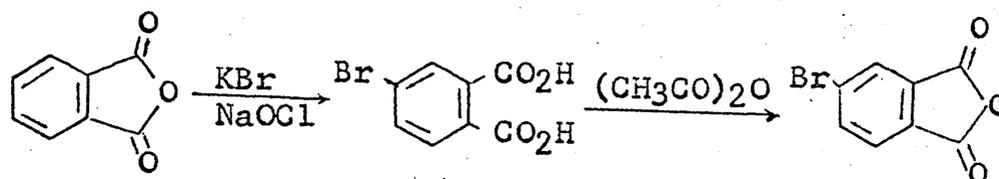
Preparation of 4-Chlorophthalimide



a. A mixture of 0.9 g. (0.005 mole) of 4-chlorophthalic anhydride and 0.3 g. of urea was heated over an oil bath to 150-160°. The mixture melted, effervesced and solidified to yield 0.6 g. (66%) of 4-chlorophthalimide, m.p. 194-203°. Recrystallization from 95% ethanol gave a melting point of 209.5-210.5°. (reported⁶⁸ 210-211°).

b. A mixture of 4.6 g. (0.3 mole) of 4-chlorophthalic anhydride and 1.8 g. of urea (0.3 mole) in 25 ml. of nitrobenzene was refluxed for one hour. The temperature was kept between 150-160°C. The mixture was then allowed to cool and crystallize. After filtering, the crystals were washed twice with absolute ethanol, recrystallized from a 1:1 (volume) benzene-alcohol mixture giving 3.2 g. (70%), m.p. 210-212° (reported⁶⁸ 210-211°).

Preparation of 4-Bromophthalic Anhydride



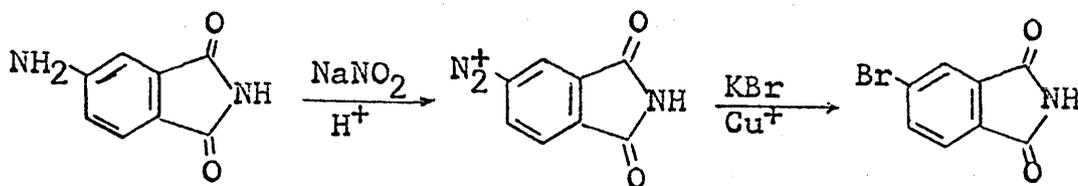
4-Bromophthalic acid was prepared by the procedure used by Martinez^{10a}. In a one-liter beaker, a magnetically stirred solution of 37 g. (0.25 mole) of phthalic anhydride and 30 g. of potassium bromide crystals in 355 ml. of 5.25 % sodium hypochlorite solution was heated slowly while gradually acidifying with 3 N sulfuric acid. The mixture changed color from brown to yellow to colorless. The mixture was then heated to about 90-100° to complete the reaction. It was then cooled to room temperature, made alkaline with 16% sodium hydroxide solution, and filtered. The filtrate was reacidified with 1 N sulfuric acid and extracted with about 400 ml. of ether in four portions. The combined ethereal extracts were dried over anhydrous magnesium sulfate overnight. Removal of solvent in a rotary evaporator gave 6.8 g. (11%) of 4-bromophthalic acid, m.p. 171.5-180°, with decomposition (reported⁶⁹ 170.5°).

Six grams of the crude 4-bromophthalic acid was refluxed with 12 g. of acetic anhydride for half an hour. The solvent was removed in a rotary evaporator, and the liquid residue was diluted with petroleum ether. The crystals were collected and washed with carbon tetrachloride giving 4.1 g.

(75.3%) of pale yellow crystals, m.p. 98-101°.

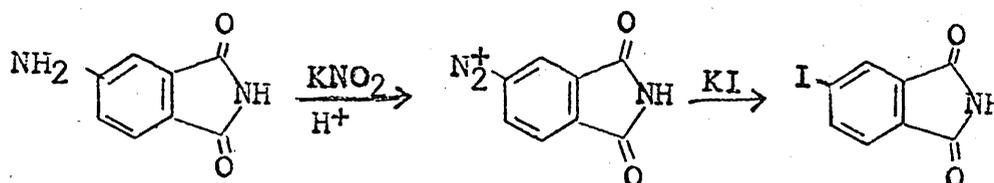
Recrystallization from glacial acetic acid and drying in a drying pistol at 56° for 4 hours gave a product melting at 102-105° (reported⁶⁵ 108-109°; reported⁶⁹ 104-106°).

Preparation of 4-Bromophthalimide



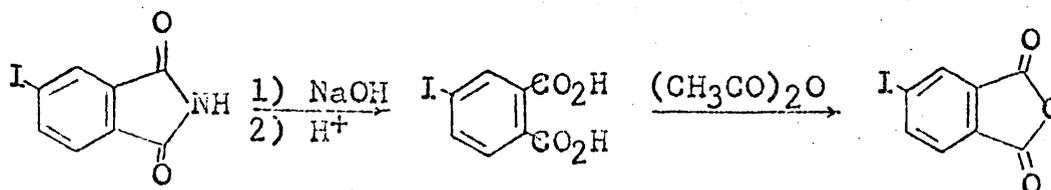
The procedure described by Elvidge et al.⁷⁰ was used. A solution of 5.4 g. (0.033 mole) of 4-aminophthalimide in 15 ml. of concentrated sulfuric acid was cooled in an ice-salt bath, and 2.6 g. powdered sodium nitrite was stirred into the mixture. Thirteen grams of potassium bromide was added to the greenish solution. Then 8 g. of copper powder was added in portions. The mixture was stirred for another 15 minutes while it warmed up to room temperature. It was then poured into 200 ml. of ice-water and filtered. The filtrate was extracted continuously with benzene for 24 hours. The extract was concentrated in a rotary evaporator, giving 1.2 g. (18%) of 4-bromophthalimide, m.p. 182-205°, which after recrystallization from glacial acetic acid melted at 218° with decomposition. Further recrystallization from glacial acetic acid raised the melting point to 230-233° (reported⁷¹ 229.5°).

Preparation of 4-Iodophthalimide



This synthesis was carried out by Martinez^{10a} modification of the procedure of Katz⁷². A mixture of 7.1 g. (0.044 mole) of 4-aminophthalimide and 25 ml. of concentrated sulfuric acid in 155 ml. of water was placed in a 1500 ml. beaker and cooled in an ice-salt bath to 0°C with stirring. A solution of 3.74 g. (0.044 mole) of potassium nitrite in 14 ml. of water was added in small portions until a positive nitrous acid test was obtained with starch-potassium iodide paper. Stirring was continued for another 15 minutes, then 20 ml. of a 65% potassium iodide solution was added, while the reaction temperature was still kept at 0°C. After an additional hour of stirring, the beaker was heated on a steam cone for 45 minutes to decompose the diazonium salt. After cooling, 11.7 g. (97.5%) of brown-colored 4-iodophthalimide was obtained by suction filtration. It melted at 205-212° with decomposition. Recrystallization from methanol raised the melting point to 226-228° with decomposition (reported⁷² 222-224°).

Preparation of 4-Iodophthalic Anhydride



The method of Martinez^{10a} was used with some modification for the preparation of 4-iodophthalic acid. A mixture of 8 g. (0.03 mole) of 4-iodophthalimide in 100 ml. of 3. N sodium hydroxide was refluxed for one hour. The mixture was filtered while hot and the filtrate was acidified with concentrated hydrochloric acid. The acid solution was extracted three times with 50 ml. of ether. The combined ethereal extract was dried, and the solvent removed in a rotary evaporator. The yield was 2.5 g. (32%) of brown 4-iodophthalic acid, m.p. 174-176°.

The crude acid was then heated with 7 ml. of acetic anhydride for 15 minutes. Cooling precipitated 4-iodophthalic anhydride, m.p. 121.5-124°. Two washings with absolute ether raised the melting point to 124.5-126° (reported⁶⁵ 125-126°). The yield was 1.7 g. (73.9%).

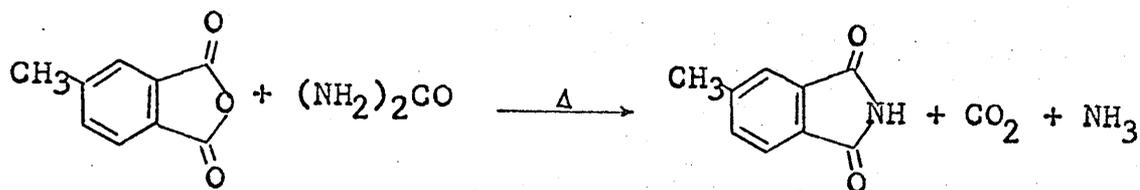
Purification of 4-Methylphthalic Anhydride

The 4-methylphthalic anhydride from City Chemical Co., New York, had a melting point range at 109-131°, presumably mostly acid (m.p. 150.5°). Following the procedure of Morgan and Coulson⁷⁴, 15 g. of this material was distilled at atmospheric pressure. The fraction which boiled at 298-301° was collected as it solidified during distillation. The yield was 12.1 g. (89.6% based on acid) of colorless crystals, m.p. 88-94°.

Recrystallization from acetic anhydride followed by drying at 56° (boiling acetone) in a drying pistol over phosphorus pentoxide for 8 hours, raised the melting point to 91.5-92.5°

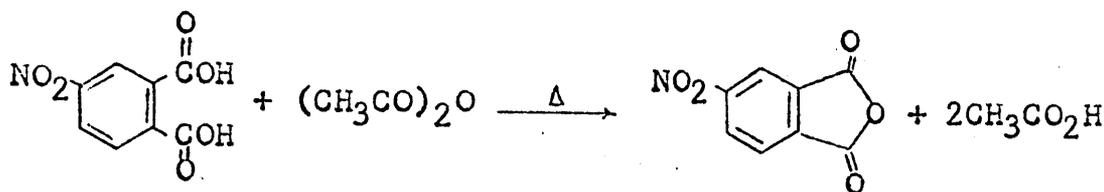
(reported⁷⁴ 93°).

Preparation of 4-Methylphthalimide



A mixture of 1.6 g. (0.01 mole) of 4-methylphthalic anhydride and 0.6 g. (0.01 mole) of urea was heated at 150-160°. The mixture melted, effervesced and finally solidified. The yield was 1.2 g. (75%) of crude 4-methylphthalimide. Recrystallization from 95% ethanol gave a product melting at 195-195.5° (reported⁷⁵ 194.5-195°).

Preparation of 4-Nitrophthalic Anhydride



The method of Wiseman et al.⁷⁶ was used with some modifications. Thus 4-nitrophthalic acid was converted quantitatively into anhydride by refluxing a mixture of 4-nitrophthalic acid and an equal weight of acetic anhydride for one hour. The solvent was removed in a rotary evaporator. The residue was recrystallized from acetic anhydride, followed by washing with absolute ether. The melting point was 108-120°C. Drying in a drying pistol over phosphorus pentoxide

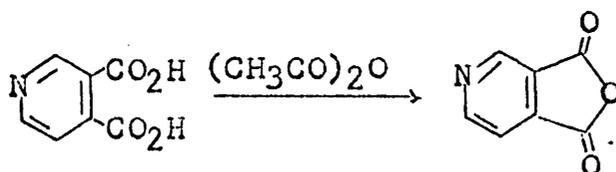
at 56° (boiling acetone) for 12 hours raised the melting point to 117.5-119° (reported⁷⁶ 117-119°).

Purification of 4-Carboxyphthalic Anhydride

"Trimellitic anhydride" from Amoco Chemical Company melted at 239° with decomposition. Trimellitic acid melts⁷⁴ at 238°.

Fifty grams (0.23 mole) of this acid was heated under reduced pressure furnished by a water aspirator. After it had refluxed for about 1.5 hour, the residue was cooled and solidified. It was dissolved in acetone, and benzene was added, forming 33.3 g. of a colorless precipitate, m.p. 166.5-169° (reported⁷⁷ 157-158°). An additional 1.8 g. was obtained from the mother liquor, m.p. 167-169°. The overall yield was 35.3 g. (77.3%).

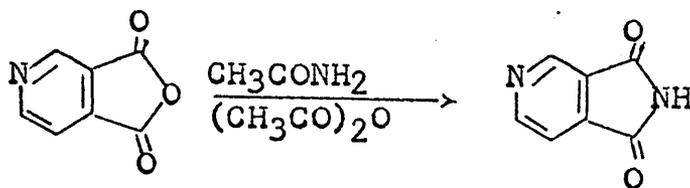
Preparation of 4-Azaphthalic Anhydride



The procedure used by F. Lee¹⁰ was followed. A mixture of 45 g. (0.27 mole) 3,4-pyridinedicarboxylic acid and 22 ml. of acetic anhydride was refluxed for one hour. The mixture was cooled and the solvent was removed in a rotary evaporator. The residue was diluted with 2 ml. of carbon tetrachloride and cooled. The purple colored crystals were

collected and recrystallized from carbon tetrachloride (with charcoal) to give 1.5 g. of colorless crystals, m.p. 75.5-76° (reported⁷⁸ 73°). An additional 0.5 g. was obtained from the mother liquor, giving an overall yield of 2.0 g. (50%).

Preparation of 4-Azaphthalimide



The procedure used by F. Lee¹⁰ was followed. A mixture of 5.5 g. (0.037 mole) of 4-azaphthalic anhydride, 5.1 g. (0.089 mole) of acetamide and 1.5 ml. of acetic anhydride was refluxed for three hours. The reaction mixture was cooled and the imide which separated was collected by filtration and washed with ice-cold water to give 3.7 g. (68.5%) of 4-azaphthalimide. Recrystallization from ethanol (decolorizing charcoal) resulted in pure 4-azaphthalimide, m.p. 231-232°, (reported⁷⁹ 231°).

B. Determination of Spectra

1. Ultraviolet Spectra

The ultraviolet absorption spectra were determined by using a Cary Model 15 Recording Spectrophotometer. All spectra were determined using 1-cm. cells. The molar absorptivities at each wavelength were calculated from the equation

$$\epsilon = A/Cl$$

where A is the observed absorbance, C is the concentration in moles per liter, and l is the cell thickness in centimeters. The concentrations of the samples were in the range 10^{-2} to 10^{-5} M . In the case of phthalimides, the stock solutions in ethanol were prepared by dissolving the solid organic compounds in 95% ethanol. The basic solutions were prepared by diluting stock solution in ethanol with 0.1 N sodium hydroxide, and the spectra were determined after 24 hours of standing to ensure the completion of ring opening.

The solutions of phthalic anhydrides were prepared by dissolving the solid compounds in spectrophotometric grade *p*-dioxane.

The ultraviolet data are listed in Table 7 and Table 8.

2. Infrared Spectra

The infrared spectra were measured with a Perkin-Elmer Model 225 Grating Infrared Spectrophotometer. The KBr pellets were prepared by mixing 5-8 mg. of the sample with 250-270 mg. of spectrograde KBr in a Wig-L-Bug amalgamator (Crescent Dental Manufacturing Co., Chicago, Ill.) for one minute and then pressed with a Carver Laboratory Press Model C at 15,000 psi for 3 minutes. The solution spectra were measured in chloroform solution with concentrations ranging from 10^{-2} to 10^{-3} M in a pair of matched NaCl cells of the path length indicated in Tables 9 - 12.

The resulting infrared spectra data are summarized in Tables 9 and 10 and Tables 11 and 12 for the 4-substituted phthalic anhydrides and phthalimides respectively.

TABLE 7
Ultraviolet Spectra of 4-Substituted
Phthalic Anhydrides

Compound	Solvent	λ_{\max} , nm	$\log \epsilon_{\max}$
Phthalic anhydride	Dioxane	249-50	3.60
		289	3.24
		297.5	3.24
	CHCl ₃	252-3	3.62
		290-1	3.32
		299	3.33
	CCl ₄	287.5	3.25
		296	3.30
	4-Hydroxyphthalic anhydride	Dioxane	232-3
273-4			3.69
310-3			3.45
4-Methoxyphthalic anhydride	Dioxane	233	4.48
		274-5	3.71
		309-11	3.62
4-Methylphthalic anhydride	Dioxane	291	4.51
		259	3.66
		292	3.32
		301.5	3.32
4-Fluorophthalic anhydride	Dioxane	212	4.49
		251	3.61
		286-8	3.20
		296	3.17
4-Chlorophthalic anhydride	Dioxane	220.5	4.48
		225	4.46
		259	3.76
		293	3.28
		302	3.24

Table 7 continued.

Table 7 Continued.

<u>Compound</u>	<u>Solvent</u>	<u>λ_{\max}, nm</u>	<u>$\log \epsilon_{\max}$</u>
4-Bromophthalic anhydride	Dioxane	229	4.45
		262-4	3.84
		297	3.38
		304	3.34
4-Iodophthalic anhydride	Dioxane	213	4.19
		239	4.21
		280	3.80
		309-11 _s	3.40
4-Carboxyl phthalic anhydride	Dioxane	218	4.50
		252	3.76
		296	3.24
		305.5	3.24
4-Nitrophthalic anhydride	Dioxane	214	4.30
		250-6	3.96
		298 _s	3.40
4-Azaphthalic anhydride	Dioxane	211	4.11
		284	3.50

TABLE 8

Ultraviolet Spectra of 4-Substituted Phthalimides

Compound	In 95% EtOH		In 0.1 N NaOH	
	λ_{\max} , nm	$\log \epsilon_{\max}$	λ_{\max} , nm	$\log \epsilon_{\max}$
Phthalimide	215	4.58	271	3.03
	229.5	4.21		
	237.5	4.02		
	291	3.26		
	297 _s	3.24		
4-Hydroxy-phthalimide	234	4.46	216.5	4.16
	279	3.23	282.5	3.07
	3.25	3.36		
4-Amino-phthalimide	252	4.25	260-264	3.94
	306	3.67		
	366-370	3.62		
4-Methyl-phthalimide	222.5	4.62	272 _s	2.92
	240	4.03		
	299	3.31		
4-Methoxy-phthalimide	232	4.51	215-6	4.23
	246 _s	4.24	232 _s	3.90
	278-9	3.24	244-6	3.89
	320	3.40		
4-Fluoro-phthalimide	218	4.53	266-8	3.99
	230.5 _s	4.18		
	235-8 _s	3.97		
	284-8 _s	3.06		
4-Chloro-phthalimide	224	4.64	273-6 _s	2.92
	243	4.14		
	297	3.26		
4-Bromo-phthalimide	226.5	4.65	273 _s	3.33
	242-4 _s	4.25		
	267-72 _s	3.21		
	298	3.31		
4-Iodo-phthalimide	236	4.40	216.5	4.25
	279-284 _s	3.43	234-42	3.99
	306.5	3.48		
	410 _s			
4-Nitro-phthalimide	229	4.31	216	4.31
	278 _s	3.57	273-5	3.91

TABLE 9

Infrared Absorption Bands for 4-Substituted Phthalic Anhydrides in KBr Pellets (a)

Substi- tuent	Carbonyl Stretching(C=O)		C-O- Vibration cm ⁻¹	Others cm ⁻¹
	Symmet- rical cm ⁻¹	Asymmet- rical cm ⁻¹		
H	1840	1760	1240(s)	
OH	1833	1757	1295(s)(anhy.) 1239(s)(phenol)	1376 C-O str. and 1197 OH ipd.
OCH ₃	1840	1770	1283(s)	1255 =C-O- of ether
CH ₃	1845	1769	1249 m	
F	1843	1760	1243 m	
Cl	1846	1775	1240(s)	
Br	1840	1768	1238(s)	
I	1836	1775	1235(s)	
CO ₂ H	1850	1778	1235 _s (anhy.) 1283 _m (CO ₂ H)	1696 _s C=O from CO ₂ H 1433 Combination and/or of C=O stret. 1408 and OH ipd. also from CO ₂ H
NO ₂	1868	1782	1256 ^m or 1243	1533(m) asym. NO ₂ stret. 1343(s) sym. NO ₂ stret.

(a) The spectra were measured in the range of 2500 cm⁻¹ to 1000 cm⁻¹.

TABLE 10

Infrared Absorption bands of 4-Substituted
Phthalic Anhydrides in CHCl_3 Solutions (a)

Substi- tuent	Carbonyl Stretching(C=O)		C-O- Vibration cm^{-1}	Others cm^{-1}
	Symmet- rical cm^{-1}	Asymmet- rical cm^{-1}		
H	1850	1770	1252(m)	
OH	1840	1768	1272 m	
OCH ₃	1834	1765	1251	1251 =C-O- of ether
CH ₃	1851	1765	1257(s)	
F	1850	1775		
Cl	1855	1780	1256(s)	
Br	1850	1775	1246	
I	1850	1774	1239(m)	
CO ₂ H	1855	1780	1255-1195(broad)	1705 C=O from CO ₂ H
NO ₂	1860	1780	1252(m)	1540(m) asym. NO ₂ str. 1355(m) sym. NO ₂ str.
Aza	1855	1783	1268(m)	

(a) Spectra were measured in a pair of 0.1 mm path length cells except aza-compound which was measured in 0.625 mm cells.

TABLE 11

Infrared Absorption Bands of 4-Substituted
Phthalimides in KBr Pellets^(a)

Substi- tuent	Carbonyl Stretching (C=O) (b)		Aromatic C-H Str.	Amide III Band	Others, cm ⁻¹
	Symm., cm ⁻¹	Asymm., cm ⁻¹			
H	1769	1470, 1730	3055 w		
NH ₂	1754	1707	3048 w		3360 m, NH ₂ str. 3423 m 1640 m, NH ₂ def. 1340 O-N
OH	1750	1702, 1688	3040 w		1390 s phenol C-O str. 1210 s and OH ipd. 3260, 3280 OH
OCH ₃	1755	1717, 1710	3061	1305	1230 =C-O- str. 1480 CH ₃ def.
CH ₃	1760	1735, 1721	3050		
F	1760	1700	3068	1310	
Cl	1772	1712, 1702	3068	1293	
Br	1764	1705	measured in the range of 2500-1000 cm ⁻¹		
I	1763	1715, 1708			
NO ₂	1785	1731, 1701	3100, 3052	1300	1540(s) NO ₂ asym. 1343(s) NO ₂ sym.
Aza	1765	1710			

(a) N-H str. were not included due to the possible presents of moisture.

(b) Average of 3-4 independent measurements.

TABLE 12
Infrared Absorption Bands of 4-Substituted
Phthalimides in CHCl₃ Solutions (a)

<u>Substituent</u>	<u>Carbonyl</u> <u>Sym., cm⁻¹</u>	<u>Stretching</u> <u>Asym., cm⁻¹</u>	<u>NH Stretching</u> <u>cm⁻¹</u>
H	1700	1730	3610, 3420
NH ₂	b		
OH	b		
OCH ₃	1767	1723	3660-80, 3420
CH ₃	1770	1722	3425
F	1775	1734	3680-3700, 3420
Cl	1772	1728	3420
Br	1779	1729	3675-3680, 3420
I	1776	1728	3670-3680, 3420
NO ₂	1781	1738	3600, 3410

a. Spectra were measured in a pair of cells with 0.625 mm path length. Due to the low concentrations of solutions, the assignments of amide III, and C-N-H bands were not possible, the aromatic C-H str. and bending were not visible in the spectra.

b. Not determined due to low solubility.

C. Determination of Dipole Moments

Dipole moments were determined by the method of Hedestrand⁸⁶. This procedure involves determinations of the dielectric constants at a constant temperature for a series of solutions of different concentrations of a substance, and the refractive indices of the same solutions at the same temperature.

The dielectric constants were measured with Wissenschaftliche Technische Werkstätten-type DM 01 Dipolmeter at 20°C. Refractometric measurements were done with a Bausch and Lomb Abbé refractometer at 20°C.

Calibration of DFL 1 type sample holding cell was done with four spectrometric grade liquids, namely, cyclohexane, benzene, carbon tetrachloride and *n*-butyl ether stored over Type 5A molecular sieve. Measurements were done on switch position D2. This calibration was carried out at the start of each set of measurements.

After the cell was filled with the liquid (or solution) the cell contents was allowed to stand for at least ten minutes to assure the constant measuring temperature. Three to five readings were taken for each solution and the average was corrected with correction diagram furnished with the instrument to obtain the corrected dipolemeter reading, *S*.

After each measurement, the cell was rinsed thoroughly with acetone or methanol and dried by flushing with dry nitrogen.

A set of data thus obtained are listed, and the

method used to obtain the calibration curve were shown in Appendix II.

Each compound was measured in three to five different concentrations in dioxane. The weight fractions of solute ranged from 1.5×10^{-3} to 40×10^{-3} . The refractive index of each solution was measured just before the solution was placed in the cell.

The dipole moments μ were then calculated from the equation:⁸⁷

$$\mu^2 = \frac{27 KT}{4 N} \cdot \frac{M_2}{d_1(\epsilon_1 + 2)^2} (a_\epsilon - a_n)$$

where K = Boltzmann Constant = 1.381×10^{-16} erg. deg.⁻¹

N = Avogadro's Number = 6.023×10^{23} mol.⁻¹

d_1 = density of the solvent used

ϵ_1 = dielectric constant of the solvent

a_ϵ = slope of the curve $(\epsilon_{12} - \epsilon_1) = f(\omega_2)$

a_n = slope of the curve $(n_{12}^2 - n_1^2) = f'(\omega_2)$

ω_2 = weight fraction of the solute

M_2 = molecular weight of the solute

ϵ_{12} = dielectric constant of the solution

n_1, n_{12} = refractive indexes of solvent and solution

The measured dipole moments of some representative compounds are listed in Table 13. The calculations involved are illustrated in Appendix II with an example.

TABLE 13

Experimental Dipole Moments in Dioxane at 20°C

<u>Compounds</u>	<u>Dipole Moment, Debves</u>
4-Chlorophthalic anhydride	3.76 ± 0.16
4-Methylphthalic anhydride	5.72 ± 0.08
4-Nitrophthalic anhydride	2.95 ± 0.16
4-Methylphthalimide	2.53 ± 0.17
4-Chlorophthalimide	1.43 ± 0.03
4-Nitrophthalimide	2.60 ± 0.03
1-Thiophthalic anhydride	4.02 ± 0.10

IV. DISCUSSION

A. Ultraviolet Spectra

1. 4-Substituted phthalic anhydrides

The ultraviolet spectrum of phthalic anhydride in dioxane solution shows a broad band at 249-250 nm, presumably a benzenoid band, and two equally intense bands at 289 and 297.5 nm, due to the cyclic anhydride ring. The two long-wavelength bands were shifted slightly to the red and slightly intensified in chloroform solution, but slightly shifted to the blue and intensified to a smaller extent in carbon tetrachloride solution. The absorption maxima in these three solvents are listed in Table 14.

TABLE 14
Absorption Maxima of Phthalic Anhydride

<u>Dioxane</u> λ_{\max} , (log ϵ)	<u>Chloroform</u> λ_{\max} , (log ϵ)	<u>Carbon tetrachloride</u> λ_{\max} , (log ϵ)
249-50 (3.60)	252-3 (3.62)	-----
289 (3.24)	290-1 (3.32)	287.5 (3.25)
297.5 (3.24)	299 (3.33)	296 (3.30)

However, these two bands overlapped considerably, making the exact positions of the absorption maxima difficult to determine.

Substitution at 4-position brings one or two additional intense bands into the region of 210-230 nm, presumably

shifted benzenoid bands, and shifts other bands toward the red. The bathochromic shift of the 249 nm band is in the order of $H < F < CH_3 < Cl < Br < OH < OCH_3$ for electron donating substituents and $H < CO_2H < NO_2$ for electron withdrawing substituents, as shown in Table 15. This order shows a correlation with the ability of a group to donate electrons to the ring or withdraw electrons from the ring.

TABLE 15

The Shifts of the 249 nm. Band of Phthalic Anhydride Due to Substituents at 4-Position in Dioxane

<u>Substituent</u>	<u>Band Shift, λ_{max}, nm.</u>
H	0
F	+1
CH ₃	+9
Cl	+9
Br	+13
OH	+23.5
OCH ₃	+24.5
CO ₂ H	+2
NO ₂	+5

As for the doublets in the long wavelength region, it appears that in the cases of 4-hydroxy-, 4-methoxy-, 4-iodo-, 4-nitro- and 4-azaphthalic anhydrides, this doublet merges into a broad band. In the cases of methyl- and halogen- (other than iodo) substituted phthalic anhydrides, the wavelengths of both

bands increase in the order of $F < H < CH_3 < Cl < Br < CO_2H$ with intensities increasing in the same order. These shifts were listed in Table 16.

TABLE 16

The Shifts of the Doublet of Phthalic Anhydride
in 290-300 nm. Region Due to Substituents
at 4-Position in Dioxane Solutions

<u>Substituent</u>	Band Shift, λ_{max}	
	<u>289 nm. band</u>	<u>297.5 nm. band</u>
H	0	0
F	-2	-1.5
CH ₃	+3	+4
Cl	+4	+4.5
Br	+8	+6.5
CO ₂ H	+7	+8

2. 4-Substituted phthalimides

The spectra of phthalimides in alcohol show intense peaks at about 220 nm, and less intense peaks in the region of 290-320 nm. An additional band around 280 nm. is observed for 4-hydroxy- and methoxyphthalimides and a band at 366-370 nm. for 4-aminophthalimide.

The peaks in the region of 290-320 nm. are due to the cyclic imide moiety. In the case of unsubstituted phthalimide, the spectrum shows a doublet of roughly equally intense in this region. Substitutions at 4-position caused this doublet to merge into a broad band. In order to study the nature of these two peaks, the spectrum of phthalimide, as

a model compound, was measured in various solvents with different polarities. The spectral data were summarized in Table 17. It appears that the shorter wavelength band of this doublet shifts to longer wavelength with increasing solvent polarity, and thus is probably a $\pi \rightarrow \pi^*$ excitation. On the other hand, the shift of the longer wavelength band seems, although not so clearly, to shift in the opposite direction, suggesting a $n \rightarrow \pi^*$ transition. As in the case of anhydrides, the overlapping of these two bands make these assignments difficult.

The ultraviolet spectra of 4-substituted phthalimides in basic solution shows a blue shift and also a small decrease in molar absorptivities as compared to those in alcohol solution. These changes are due to the saponification of the cyclic imide rings to form the salts of phthalamic acids⁸¹.

The freshly made basic solution of 4-hydroxyphthalimide gave a yellow color which faded slowly on standing. The spectrum of this freshly made solution shows a band at 309.5 nm. which disappeared in the spectrum taken after standing for 24 hours. This phenomenon can be explained by the following sequence of reactions:

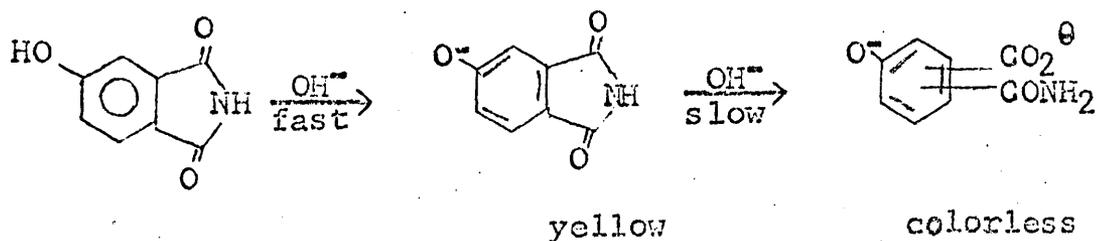
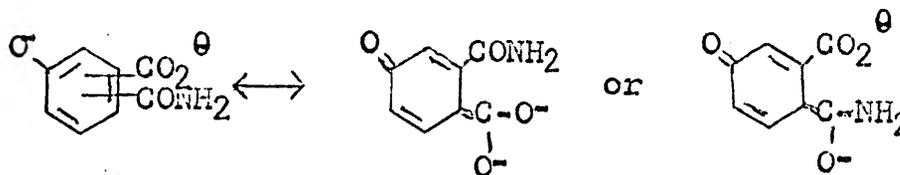


TABLE 17

Solvent Effects on Ultraviolet Spectrum of Phthalimide

<u>Solvent</u>	<u>λ_{\max}(nm)</u>	<u>log ϵ</u>	<u>Solvent</u>	<u>λ_{\max}(nm)</u>	<u>log ϵ</u>
Methanol	215.5	4.58	<u>n</u> -Butanol	230	3.86
	229	4.19		238	3.66
	237	4.02		290	3.02
	291	3.25		295-6	3.00
	295-6	3.23			
95% Ethanol	215	4.58	<u>i</u> -Butanol	214-216.5	4.57
	229.5	4.21		227-230	4.21
	237.5	4.02		238	4.05
	291	3.26		289	3.15
	297 _s	3.24		296-7	3.12
<u>i</u> -Propanol	212.5-215.5	4.54	<u>t</u> -Butanol	215.5	4.55
	229-230	4.15		228-9 _s	4.12
	237.5	3.96		237.5 _s	3.92
	289-290	3.20		288.5-290	3.23
	296	3.17		297-8	3.21
Dioxane	215	4.62	Aceto- nitrile	214-6	4.65
	---	---		225.5	4.12
	---	---		235.5	4.01
	290	3.23		289	3.20
	299	3.19		298	3.17
Chloroform	293	3.31	Carbon tetra- chloride	290	3.13
	300	3.28		299.5	3.14

The spectra of 4-hydroxy- and 4-methoxyphthalimides in alcohol are very similar. The large difference between the absorption maxima of these two compounds in basic solution indicates that a structure change has taken place in one of the substances. The larger bathochromic shift of the hydroxyphthalamate ion may result from the extension of the conjugated system from the phenoxide ions to the group at para position to form the quinoid structure:



The iodo-, nitro-, and aza-compounds have considerably different spectral features from those of other substituted compounds in the same series. These may be due to the charge transfer absorptions and the low-lying d-orbitals of iodine atom must also play a role.

3. Comparison of the spectra of the parent compounds, phthalic anhydride, phthalimide, and thiophthalic anhydride

In the same solvent, dioxane, the spectrum of phthalic anhydride resembles that of phthalimide in the region of 290-300 nm. They both show a doublet of roughly equal intensity. However, the phthalimide absorbs at slightly longer wavelength and its absorption is less intense. In the spectrum of thiophthalic anhydride, this doublet merged into one band and shifted further to the red. However, this doublet does show in cyclohexane solution. These data were summarized

in Table 18.

TABLE 18
Comparison of the Spectra of the Parent Compounds
to Thiophthalic Anhydride

<u>Anhydride in Dioxane</u>	<u>Imide in Dioxane</u>	<u>Thiophthalic Anhydride</u>	
λ_{\max} , (log ϵ)	λ_{\max} , (log ϵ)	<u>Dioxane</u>	<u>Cyclohexane</u>
		λ_{\max} , (log ϵ)	λ_{\max} , (log ϵ)
249-50 (3.60)	----	254 (4.01)	253.5 (4.04)
289 (3.24)	290 (3.23)		299.5 (3.23)
297.5 (3.24)	299 (3.19)	304 (3.28)	307 (3.18)

This increasing in wavelengths with the decreasing in electronegativities may be interpreted that the oxygen atom, being the most electronegative, has the least tendency and the sulfur, being the least electronegative, has the most tendency to release its non-bonding electrons to the carbonyl groups or the π -systems.

B. Infrared Spectra

1. 4-Substituted Phthalic Anhydride

The infrared spectra of 4-substituted phthalic anhydrides show a characteristic doublet for the carbonyl absorption in the region of 1845 and 1770 cm^{-1} , a C-O-C vibration around 1240 cm^{-1} . These bands and some characteristic absorptions due to the substituents were listed in Table 9 and Table 10 for solid and solution spectra respectively. The carbonyl absorption bands are of most interesting to this study. The high-frequency vibrations of the doublets are more

intense as compared with the low frequency vibrations. From the consideration of the geometry of the two carbonyl groups in the molecule, and the possible resonance structures, the symmetrical vibration of these two groups should result in a partial cancellation of change in dipole moment. Thus, the weak, low-frequency absorptions are assigned to the symmetrical mode of vibration and the intense, high-frequency absorptions to the asymmetrical mode of vibration²⁹.

According to Rao²², the mean of the two frequencies has been considered to be close to the unperturbed frequency. In the correlations of the changes in frequency with Hammett sigma values in this study, the average of the symmetrical and asymmetrical frequencies were used.

Table 19 listed the sum of σ_m and σ_p^+ values and $\Delta\nu_{AVE}$ which has been defined as:

$$\Delta\nu_{AVE} = \frac{1}{2}(\nu_{sym.} + \nu_{asym.})_{subst.} - \frac{1}{2}(\nu_{sym.} + \nu_{asym.})_{unsubst.}$$

The plots of $\Delta\nu_{AVE}$ versus $\sigma_m + \sigma_p^+$ are found in Figures 1 and 2 for solution and pellet spectra respectively.

The changes of the frequency of the asymmetrical mode of vibration of carbonyl group due to substituents are plotted versus $\sigma_m + \sigma_p^+$, which is shown in Figure 3.

The equations of the lines by the method of least squares⁸², correlation coefficients⁸² (r), the standard deviations (S. D.)⁸³ and levels of significance⁸⁴ are listed in Table 20.

TABLE 19

Correlation of $\Delta\nu_{\text{AVE}}$ of Carbonyl Absorptions
of 4-Substituted Phthalic Anhydrides with Sigma Values

Substituent	σ_m (a) + σ_p^+ (b)	$\Delta\nu_{\text{AVE}}$	
		CHCl ₃ Solution	KBr Pellets
H	0.000	0	0
OH	-0.825	- 6	-15
OCH ₃	-0.702	-10	+ 5
CH ₃	-0.380	- 2	+ 7
F	+0.264	+ 3	+ 2
Cl	+0.487	+ 7	+10
Br	+0.541	+ 3	+ 4
I	+0.487	+ 3	+ 5
CO ₂ H	+0.771 ^c	+ 8	+14
NO ₂	+1.500	+10	+25

- a. σ^{n} values for meta positions from Van Bekkum, Verkada and Wepster, *Rac. Tsav. Chim.*, 78, 815 (1959).
- b. σ_p^+ values from Brown and Okamoto, *J. Am. Chem. Soc.*, 79, 1913 (1957); 80, 4979 (1958).
- c. σ_m from Wells, "Linear Free Energy Relationships," Academic Press, (1968), p. 14.

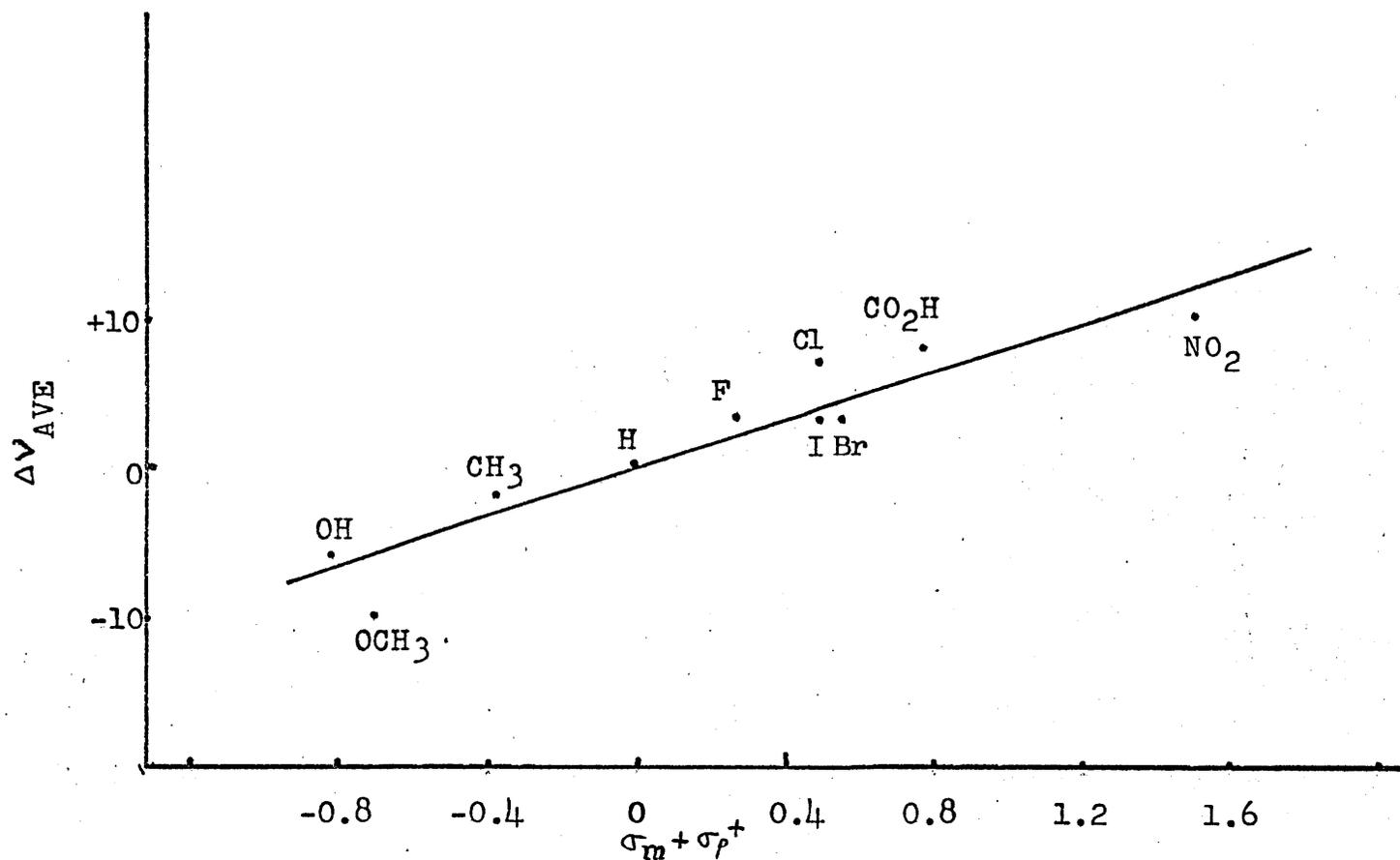


FIGURE 1. $\Delta\nu_{AVE}$ of 4-Substituted Phthalic Anhydrides
in Chloroform Solution Versus $\sigma_m + \sigma_p^+$

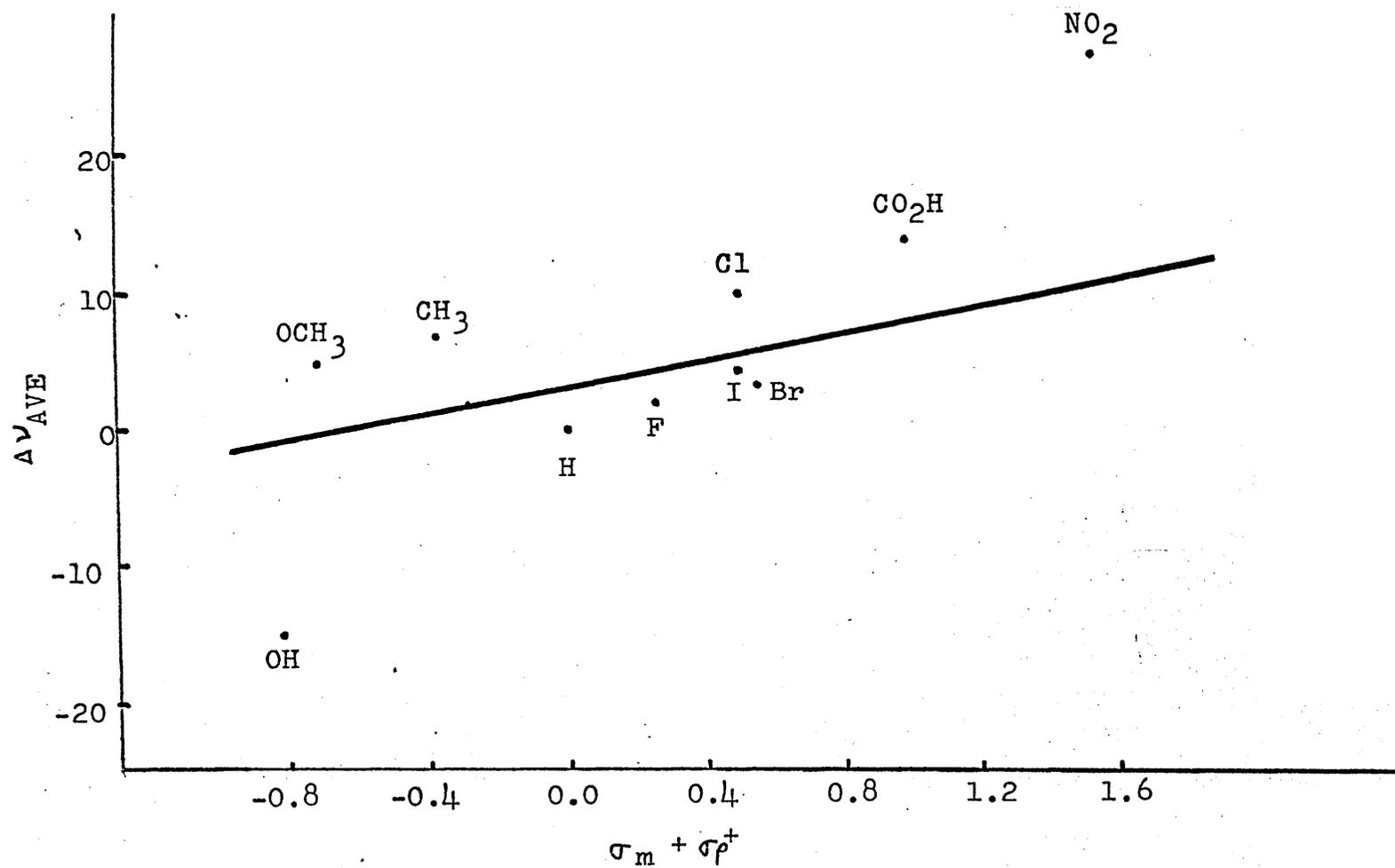


FIGURE 2. ΔV_{AVE} of 4-Substituted Phthalic Anhydrides in Chloroform Solution Versus $\sigma_m + \sigma_p^+$

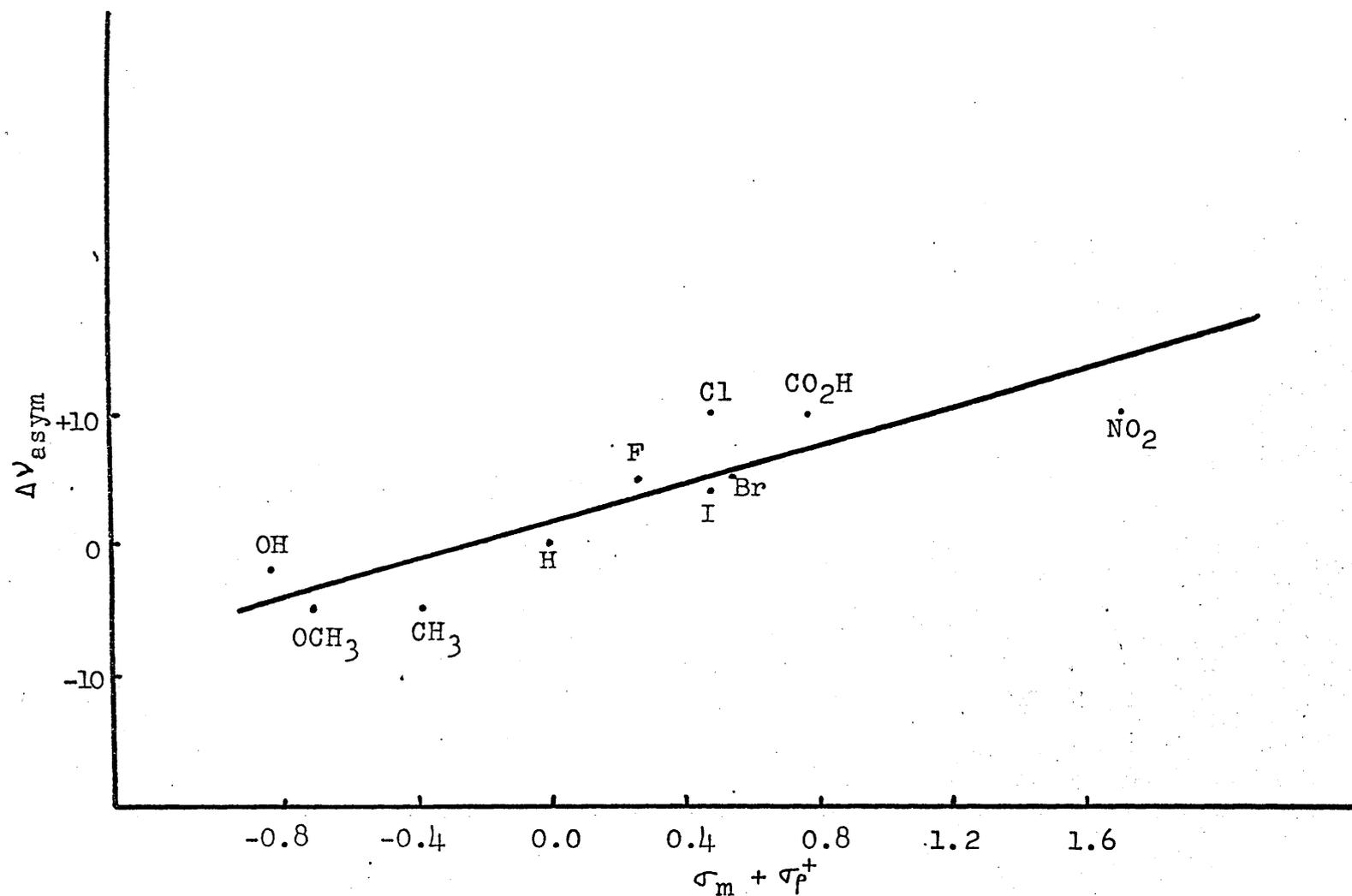


FIGURE 3. $\Delta\nu_{\text{asym}}$ of 4-Substituted Phthalic Anhydride in Chloroform Solution Versus $\sigma_m + \sigma_p^+$

TABLE 20

Hammett Correlation of Carbonyl Bands
4-Substituted Phthalic Anhydrides

<u>Phase</u>	<u>Equation of Line</u>	<u>r</u>	<u>S.D.</u>	<u>Level of Significance</u>
CHCl ₃	$\Delta\nu_{\text{AVE}} = -0.17 + 8.25 (\sigma_m + \sigma_p^+)$	0.933	1.11	1%
KBr	$\Delta\nu_{\text{AVE}} = 3.24 + 11.52 (\sigma_m + \sigma_p^+)$	0.804	3.05	1%
CHCl ₃	$\Delta\nu_{\text{asym}} = 1.61 + 7.44 (\sigma_m + \sigma_p^+)$	0.888	1.36	1%

2. 4-Substituted Phthalimides

The infrared spectra of 4-substituted phthalimides show one or two peaks in the region of 3700-3400 cm^{-1} for N-H stretching, and a broad doublet in the region of 1755-1780 and 1700-1740 cm^{-1} for the carbonyl absorption. These data were summarized in Table 11 and Table 12 for solid and solution spectra respectively.

a. Solid phase spectra

The spectra of 4-substituted phthalimides measured in KBr pellets show a weak, symmetrical vibration peak at higher frequency and a stronger asymmetrical vibration peak at lower frequency for the carbonyl absorptions. In some cases, the asymmetrical mode of vibration resolves into two peaks at a slower scan speed and at a higher resolution. This further splitting may result from the so-called Fermi resonance²³, which is caused by coupling between carbonyl stretching and the overtone or combination band of another low-lying vibration³⁷. In such cases, the average frequency of this doublet is taken as the frequency of the asymmetrical carbonyl stretching vibration for the correlations. The $\Delta\nu_{\text{AVE}}$ is roughly in the same order as that of $\sigma_{\text{m}} + \sigma_{\text{p}}^+$ for the substituents, however the relationship is not linear (rejected at 5% level of significance).

b. Solution phase spectra

The solution spectra of 4-substituted phthalimides measured in chloroform were studied in the regions of 3700-3410 cm^{-1} for the N-H stretching and 1780-1720 cm^{-1} for carbonyl

stretching. A broad, weak peak near 3420 cm^{-1} was observed for all the compounds, which probably was due to the associated N-H stretching. On dilution, another broad peak appears at the region of $3600\text{-}3680 \text{ cm}^{-1}$ for compounds with substituents OCH_3 , F, Br, I, and NO_2 . This indicates that an intermolecular H-bonding does exist in such compounds. However, the degree of association was not studied due to the extremely weak absorption at the concentrations used. The carbonyl stretching show a doublet with the asymmetrical vibration at lower frequency and higher intensity than the symmetrical vibration.

The linear correlation of the differences of the average of the symmetrical and asymmetrical carbonyl stretching of the substituted and the un-substituted phthalimides with $\sigma_m + \sigma_p^+$ are listed in Table 21, and plotted in Figure 4. The least squared line has the following form:

$$\Delta\nu_{\text{AVE}} = 0.04 + 6.208 (\sigma_m + \sigma_p^+)$$

with a correlation coefficient, r , of 0.904, standard derivation of 1.19, and an 1% level of significance.

The fact that excellent correlations between the shift of the carbonyl stretching frequency due to substitution on benzene ring of phthalic anhydrides and phthalimides with $\sigma_m + \sigma_p^+$ indicates that the electrical effects, particularly the resonance effect, play an important role in determining the position of the carbonyl group frequency. The electron-withdrawing groups shift the carbonyl band to higher frequencies and the electron-donating groups shift the carbonyl band to the lower frequencies. The amount of shift correlates linearly

TABLE 21

The $\Delta\nu_{AVE}$ Values of Carbonyl Absorption Bands
of Phthalimides and Hammett Sigma Values

<u>Substituent</u>	$\sigma_m + \sigma_p^+$	$\Delta\nu_{AVE}$	
		<u>CHCl₃</u>	<u>KBr</u>
H	0.000	0	0
OH	-0.825		-39
OCH ₃	-0.702	- 3	-22
NH ₂	-1.338		-24
CH ₃	-0.38	- 4	-11
F	+0.264	+ 5	-11
Cl	+0.487	0	-15
Br	+0.541	+ 4	-19
I	+0.487	+ 2	-17
NO ₂	+1.500	+10	- 3

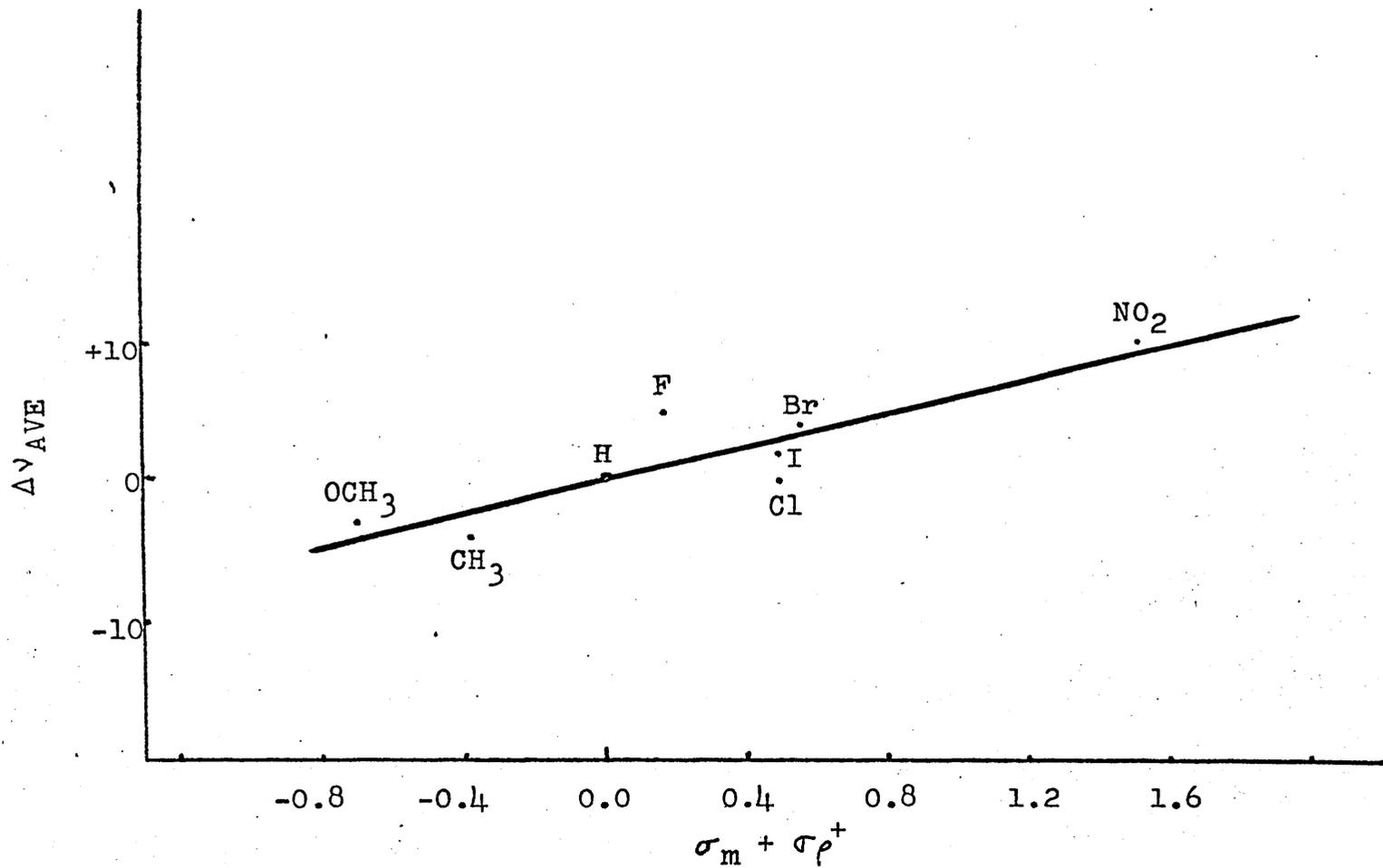


FIGURE 4. $\Delta\nu_{AVE}$ of 4-Substituted Phthalimides in Chloroform Solution Versus $\sigma_m + \sigma_p^+$

with the ability of the substituents to donate electrons to the carbonyl groups through resonance.

The failure of a satisfactory correlation for the phthalimides in solid phase may be attributed to the fact that in some cases, a doublet, caused by Fermi resonance, exists for the low frequency vibration, thus causing uncertainties in the measurements and the assignments.

3. Attempt at measuring relative intensities of carbonyl bands

The intensities of the carbonyl bands for liquid measurements were measured by the procedure described by Brown²¹. The spectra for chloroform solution were measured at two to four different concentrations for the same compound. The value of $\log(I_0/I)_{\max}$ was plotted versus frequency on graph paper which is linear in both frequency and $\log(I_0/I)$. The area under the curve was then determined with the aid of a planimeter. Since only relative values were needed for comparison within a series of compounds, the values thus obtained were used without correction and calibration. The apparent relative intensity values were obtained by formula $B = \frac{1}{Cl}$ $\log(I_0/I)d\nu$ and found to be concentration dependent. According to Ramsay⁸⁰ and Thompson³⁹ if a concentration effect is observed, the intensity B is graphed versus $\log(I_0/I)_{\max}$ for a series of concentrations and the set of points is linearly extrapolated to $\log(I_0/I)_{\max} = 0$, the intercept being taken as the true intensity A. However, the plot of B versus $\log(I_0/I)_{\max}$ failed to show any apparent linearity in this study. No further

attempt was made to obtain the true relative intensities.

The non-linearity of the plot of $B = \frac{1}{cI} \log(I_0/I)$ versus $\log(I_0/I)_{\max}$ may be attributed to the following possibilities:

(1) The solvent-solute dipole-dipole interactions and H-bonding, would cause changes in band intensity. Chloroform used as the solvent in this study is capable of such interactions;

(2) The solvent (CHCl_3) used is very volatile. It is difficult to avoid small losses of the solvent by evaporation during the preparation of the solution and during dilution and transfer to the absorption cell;

(3) The error introduced during the measurement and replotting of the absorption curve, $(\log I_0/I)$ versus ν ;

(4) The shape of the carbonyl band is not a Lorentz curve⁸⁵;

(5) The uncertainty in allowing for overlap by other bands, and the overlap of the two carbonyl bands; and

(6) The low solubilities of the compounds make it impractical to measure at many different concentrations in order to obtain a straight line of high order of confidence.

C. Dipole Moments

The relatively low solubilities of phthalimides and phthalic anhydrides in hydrocarbons have necessitated the determination of the dipole moments of these compounds in dioxane solutions. The "dioxane effect"⁸⁹, which is the effect of dioxane upon the dipole moments of molecules capable

of forming hydrogen bonds, may therefore apply in the cases of the phthalimides. In order to assure the greatest accuracy of prediction, the dipole moments of phthalimide⁶² and of mono-substituted benzenes⁵⁷ used for calculating the predicted values are also for dioxane solutions. The actual dioxane effect is probably small, since the measured dipole moment of phthalimide in benzene⁹⁰ is only 0.02 D less than the value measured in dioxane. The value used for the phthalic anhydride⁵⁹ is for benzene solution, but it should not be subject to the "dioxane effect".

The experimental values obtained in this study are higher than those calculated for the cases of chloro-, nitro- and aza-compounds and within the experimental error for methyl compounds. The experimental values and the corresponding calculated values were listed in Table 22. The experimental procedures and the method of calculations were illustrated in Appendix II.

According to Lumbroso et al.⁶² the difference between the calculated and experimental values for the phthalimides are due to the failure of the groups attached to nitrogen to be coplanar with the ring. If this were true, the experimental value for 4-methylphthalimide should also deviate from the predicted value.

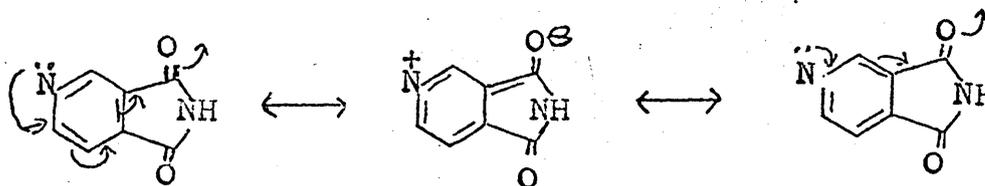
Enolization could result in increased dipole moments, but no evidence for it has been found.

The higher experimental value for 4-azaphthalimide may be a result of electron donation, by resonance to the meta carbonyl:

TABLE 22

Calculated and Experimental Dipole Moments
of Some 4-Substituted Phthalic Systems

Compound	Dipole Moment, Debyes	
	Calculated	Experimental
Phthalic anhydride		5.29 ± 0.03
4-Methylphthalic anhydride	5.67 ± 0.03	5.72 ± 0.08
4-Chlorophthalic anhydride	3.95 ± 0.05	3.76 ± 0.16
4-Nitrophthalic anhydride	2.70 ± 0.03	2.95 ± 0.16
Thiophthalic anhydride		4.02 ± 0.10
Phthalimide		2.14 ± 0.02
4-Methylphthalimide	2.52 ± 0.02	2.53 ± 0.17
4-Chlorophthalimide	1.09 ± 0.02	1.43 ± 0.03
4-Nitrophthalimide	2.47 ± 0.03	2.60 ± 0.03
4-Azaphthalimide	1.13 ± 0.01	2.20 ± 0.18



The dipole moments of the phthalic systems decrease in the order of $O > S > N$ as for the compounds phthalic anhydride, thiophthalic anhydride and phthalimide. The dipole moments of these compounds were compared in Table 23.

TABLE 23
Dipole Moments of Phthalic Systems
in Dioxane Solutions

Compound	Dipole Moments
Phthalic anhydride	5.29 ± 0.03 Debyes
Thiophthalic anhydride	4.02 ± 0.10 Debyes
Phthalimide	2.12 ± 0.02 Debyes

Considering the electronegativities, one would expect the dipole moments decreases as the electronegativity decreases, that is in the order of anhydride $>$ imide $>$ thioanhydride.

This apparent discrepancy may explained on the basis of the following factors:

(1) The back donation of electrons to the empty d-orbital of sulfur.

(2) The larger sulfur atom make the distance between the centers of charges longer and therefore increases the group moment.

(3) There are two pairs of unshared electrons on the sulfur atom compared to only one pair on nitrogen, and thus sulfur pulls more electron cloud toward it.

D. Suggestions for Further Studies

1. In order to make more definite assignments of the nature of the ultraviolet absorption bands, particularly the doublets in the long wavelength region, and to study quantitatively the substituent effects upon the band positions, it is necessary to have the overlapped and submerged bands in ultraviolet spectra deconvoluted. This can be done with a computer program (LFT) developed by Thomson and Metzler to resolve these bands in ultraviolet spectra. Use of this program was not possible for the present study due to the non-availability of such a computer facility at this institution at this time.

2. The extent of the intermolecular hydrogen bonding in phthalimides can be studied by infrared. However, a range of cells of varying path lengths is required to facilitate the measurement of a wide concentration range. It can be studied complementarily in the N-H stretching and the C=O stretching region, for the intermolecular H-bonding will shift the N-H stretching, as well as the C=O stretching to a lower frequency, and also changes the intensities of these bands.

3. It would be of interest to measure the pK_a 's of phthalimides to compare with the dipole moment measurements, as a check of the N-H polarization idea.

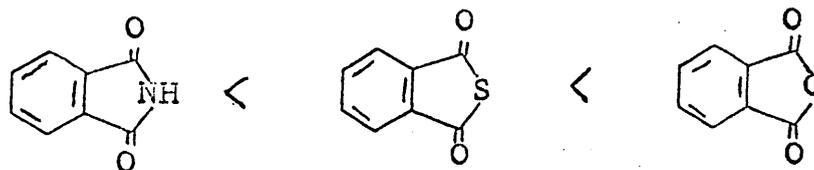
V. SUMMARY

A series of 4-substituted phthalic anhydrides and phthalimides were synthesized. The infrared and ultraviolet spectra of these compounds were studied. Selective ranges of infrared spectra were studied both in KBr pellets and in chloroform solution. The carbonyl stretching frequencies in solutions for both anhydrides and imides correlate linearly with substituent constants, $\sigma_m + \sigma_p^+$, indicating that the electronic effect is important in determining the position of Carbonyl band, and showing influence by para-resonance interaction. The infrared spectra of phthalimides show a peak at around 3400 cm^{-1} for N-H stretching. On dilution an additional band around 3600 cm^{-1} appeared for compounds with OCH_3 , F, Br, I, and NO_2 as substituents, showing that intermolecular hydrogen bonding exists in these compounds.

The ultraviolet spectra of the anhydrides were studied in dioxane solutions and show a band at 249-260 nm. region and two equally intense bands in 290-300 nm. The bands were shifted to the red by substituents at 4-position. The shifts for the former band are in the order of $\text{H} < \text{F} < \text{CH}_3 < \text{Cl} < \text{Br} < \text{OH} < \text{OCH}_3$ for electron-donating substituents and $\text{H} < \text{CO}_2\text{H} < \text{NO}_2$ for electron-withdrawing substituents. The doublet also shifted, and the intensities increased in the order of $\text{F} < \text{H} < \text{CH}_3 < \text{Cl} < \text{Br} < \text{CO}_2\text{H}$.

The ultraviolet spectra of phthalimides were measured in alcoholic and basic solutions. In alcoholic solutions, these spectra show intense peaks at about 220 nm, and less intense peaks in the region of 290-320 nm. This latter peak resolves into a doublet in the spectrum of the parent compound, phthalimide. The solvent effect study indicates the possibility that one may be due to a $\pi \rightarrow \pi^*$ and the other may be due to a $n \rightarrow \pi^*$ transition. The spectra in basic solutions are spectra of phthalamate ions formed by opening the imide rings by attacking of hydroxide ions.

The dipole moments of several of these compounds were measured in dioxane solutions. The dipole moments increase when the substituents at the 4-position are electron-withdrawing in nature. The dipole moments of the phthalic systems increase in the order of



APPENDIX I

Plots of Ultraviolet Spectra

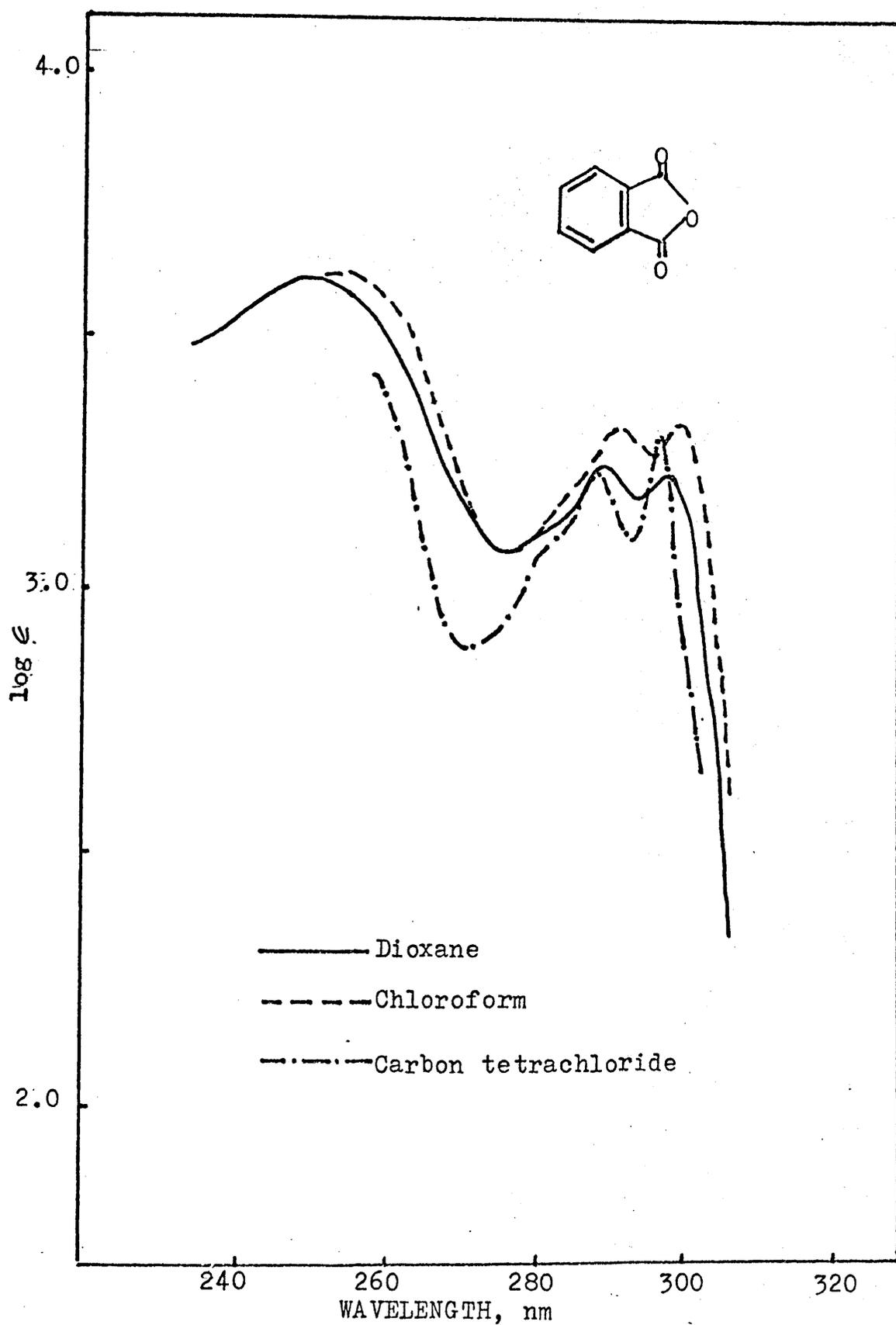


Fig. 5 UV Spectra of Phthalic Anhydride

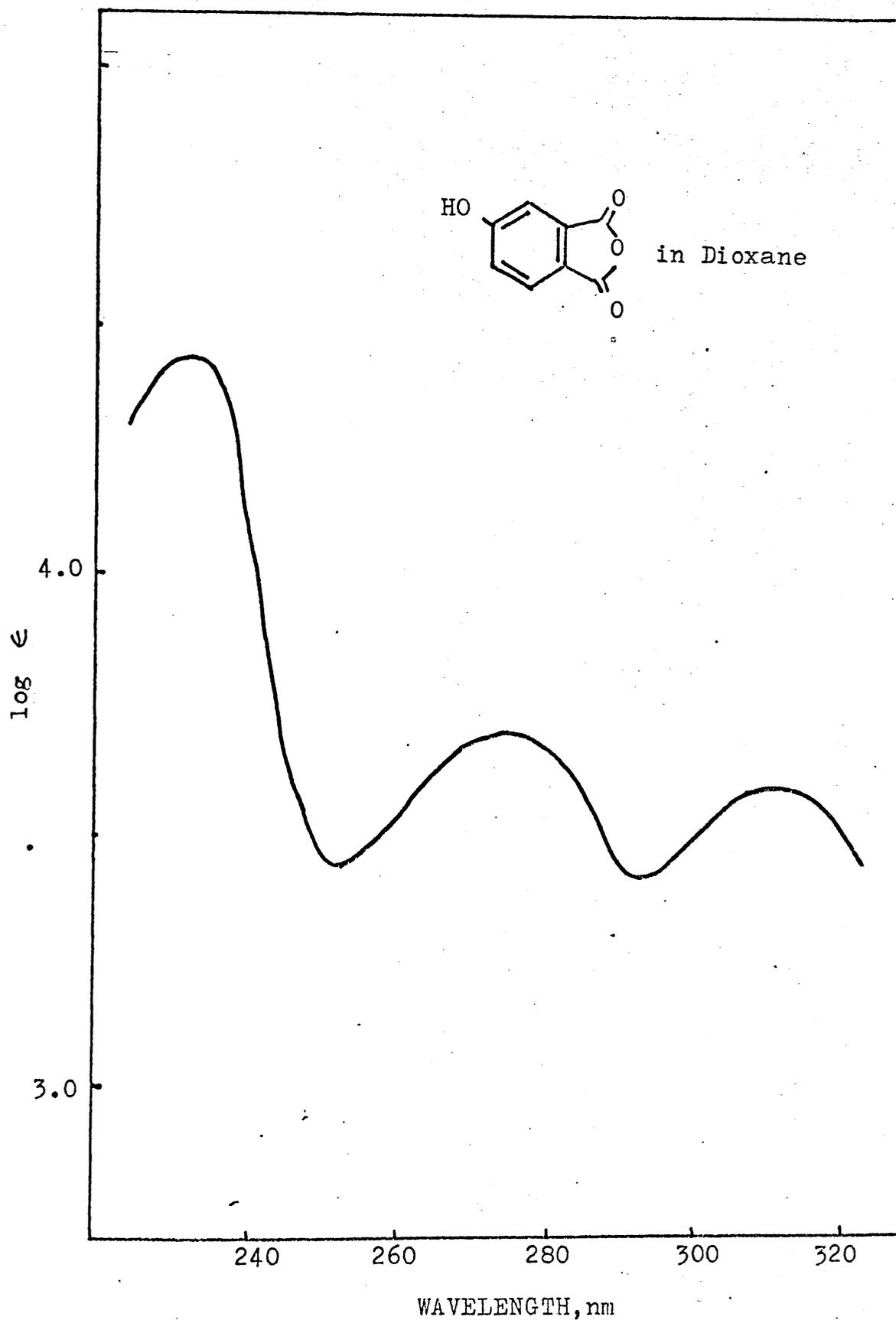


Fig. 6 UV Spectrum of 4-Hydroxyphthalic Anhydride

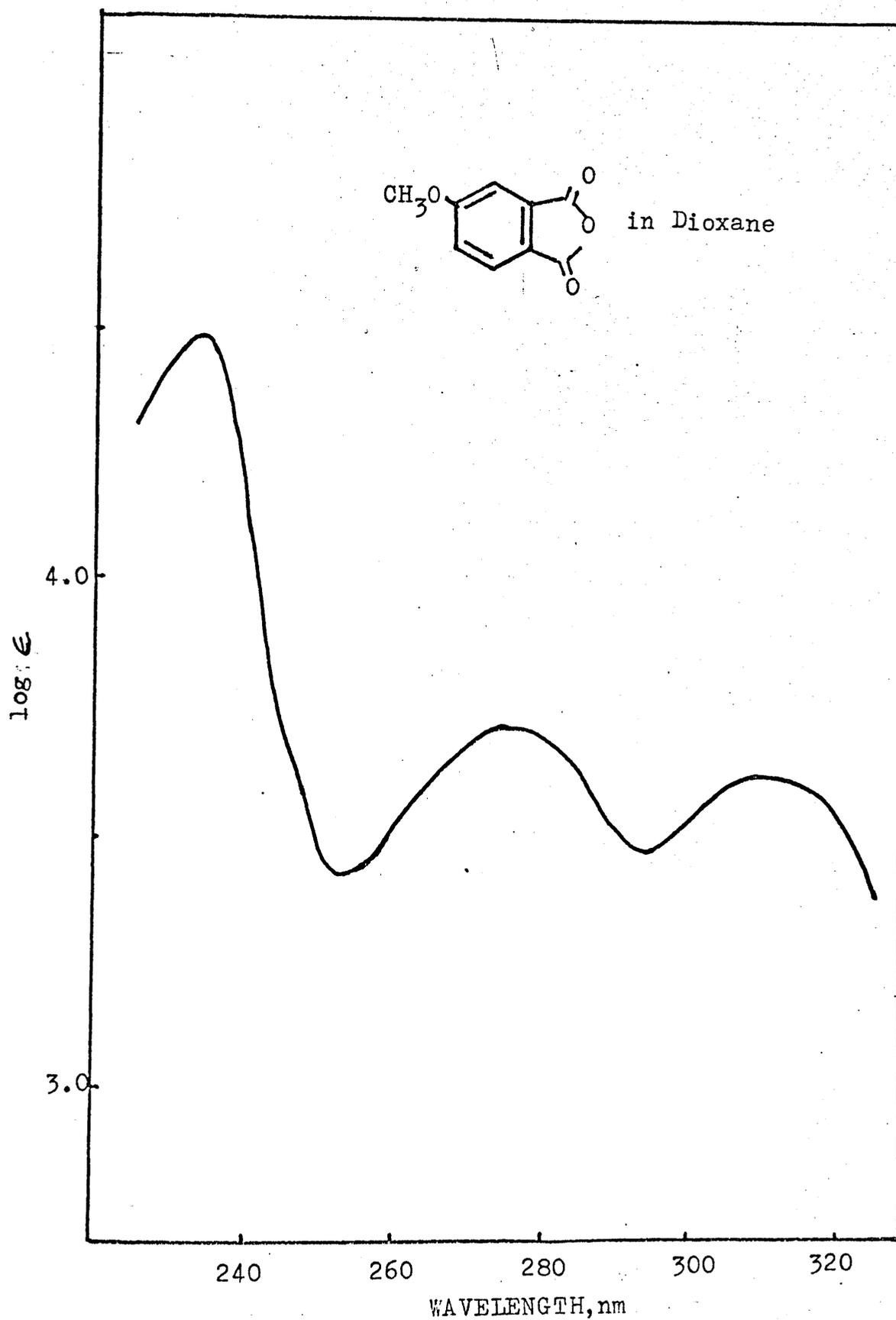


Fig. 7 UV Spectrum of 4-Methoxyphthalic Anhydride

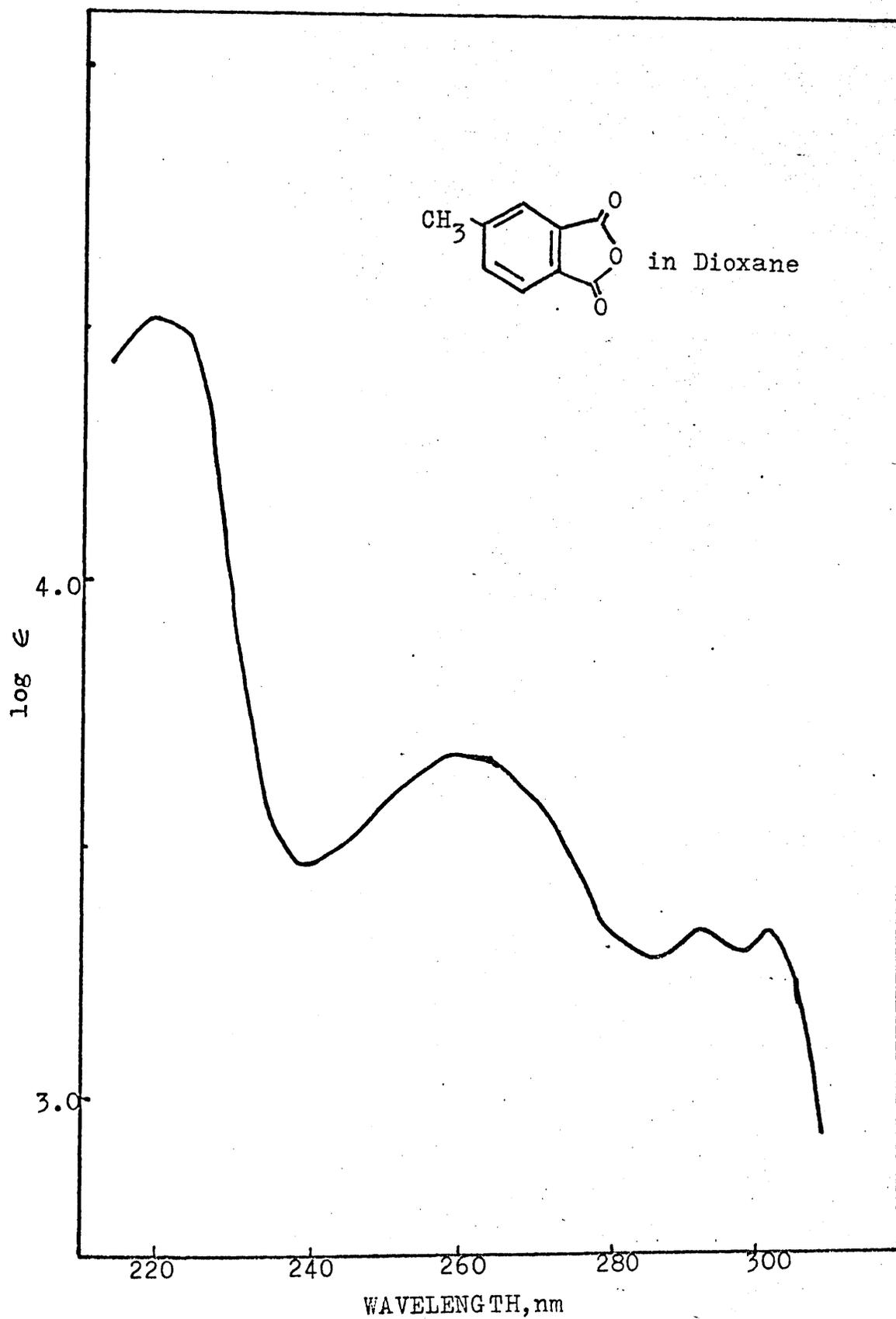


Fig. 8 UV Spectrum of 4-Methylphthalic Anhydride

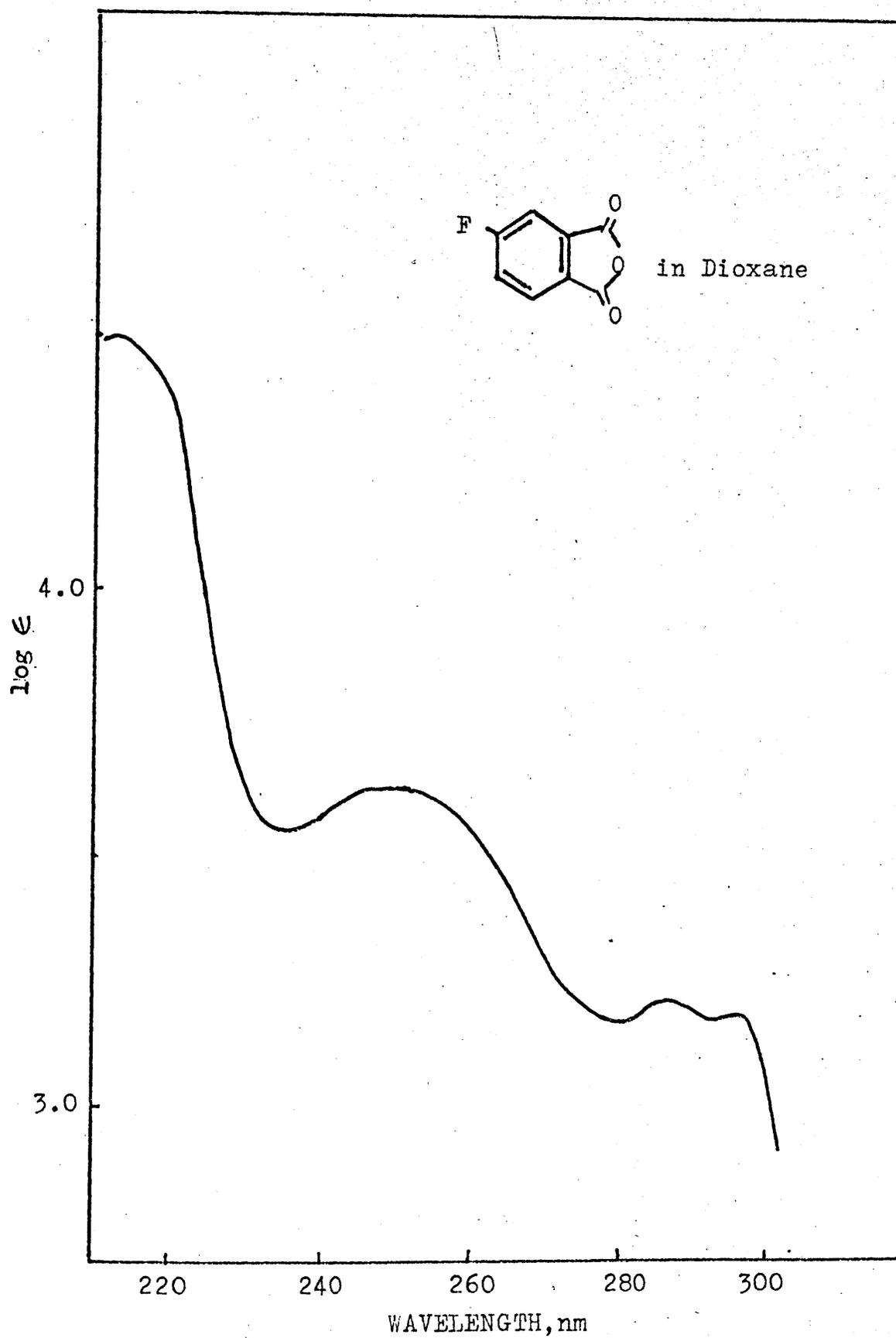


Fig. 9 UV Spectrum of 4-Fluorophthalic Anhydride

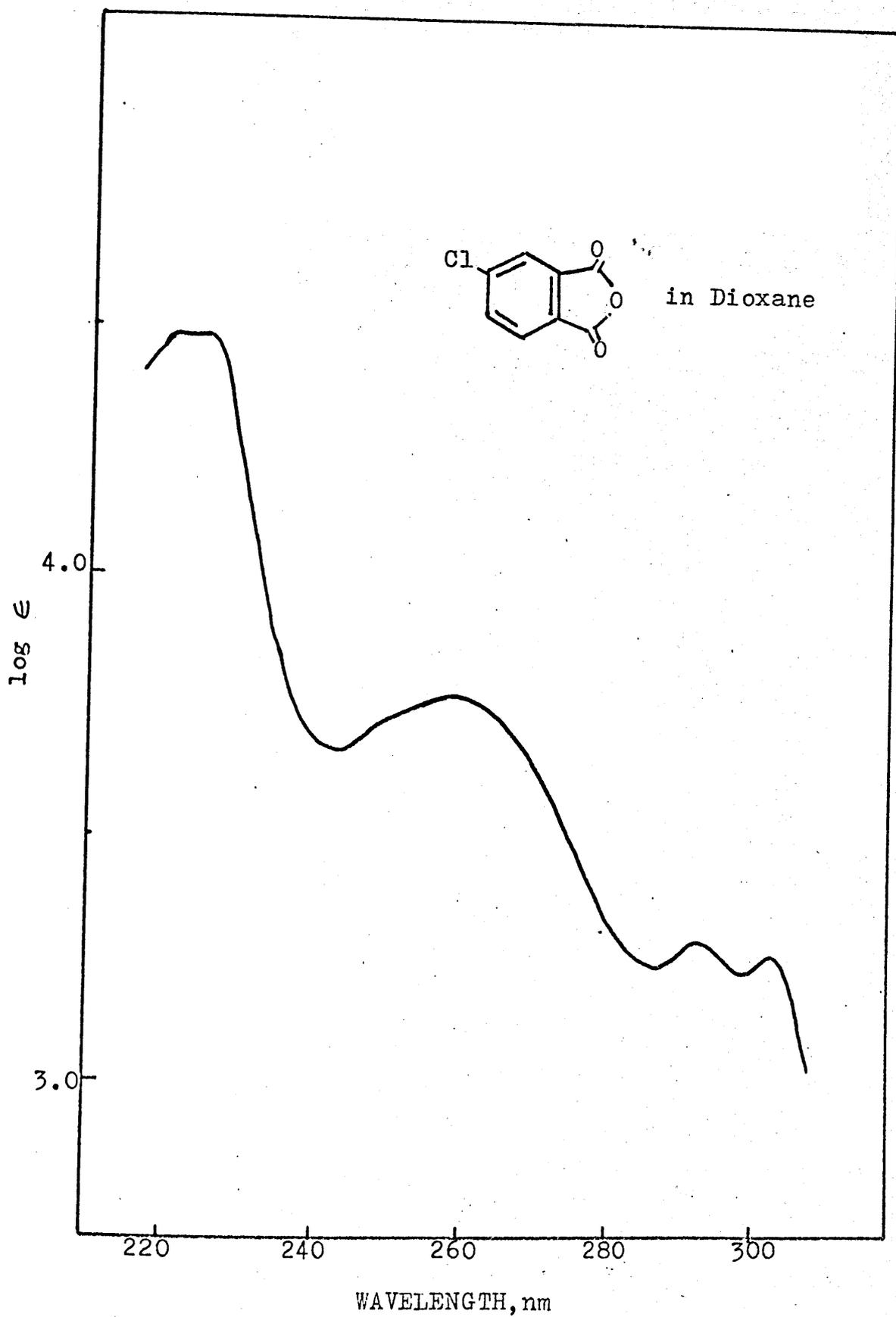


Fig. 10 UV Spectrum of 4-Chlorophthalic Anhydride

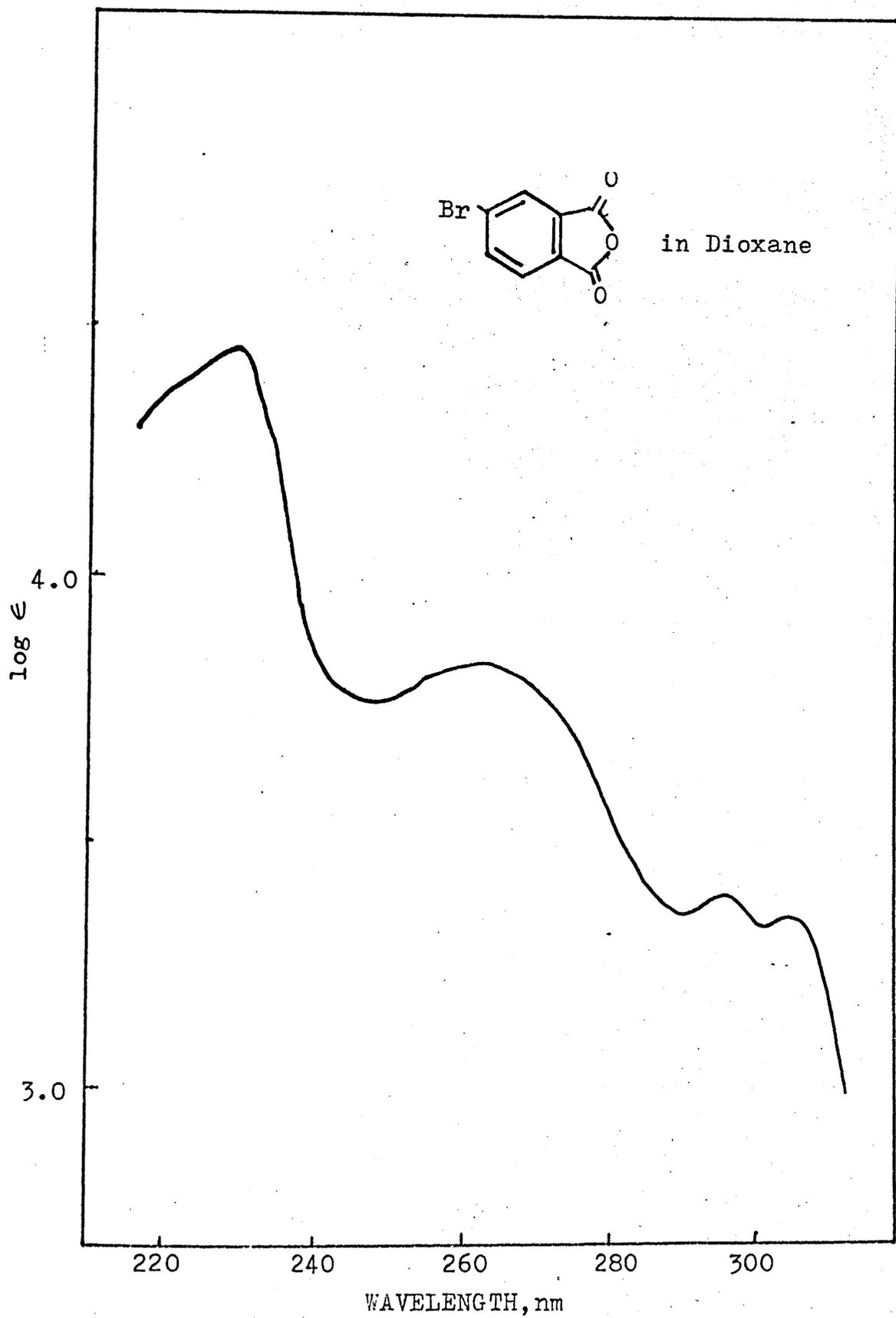


Fig. 11 UV Spectrum of 4-Bromophthalic Anhydride

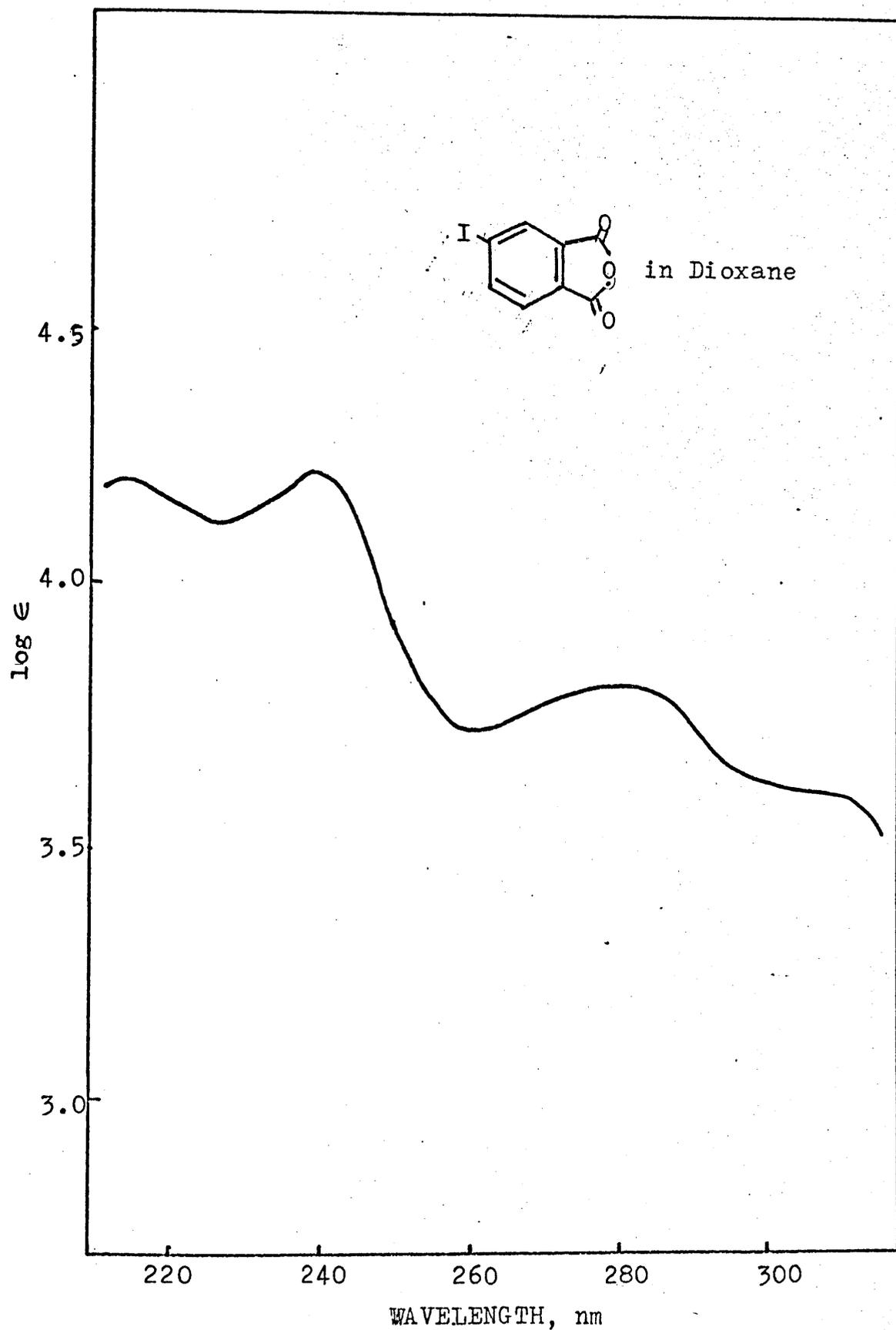


Fig. 12 UV Spectrum of 4-Iodophthalic Anhydride

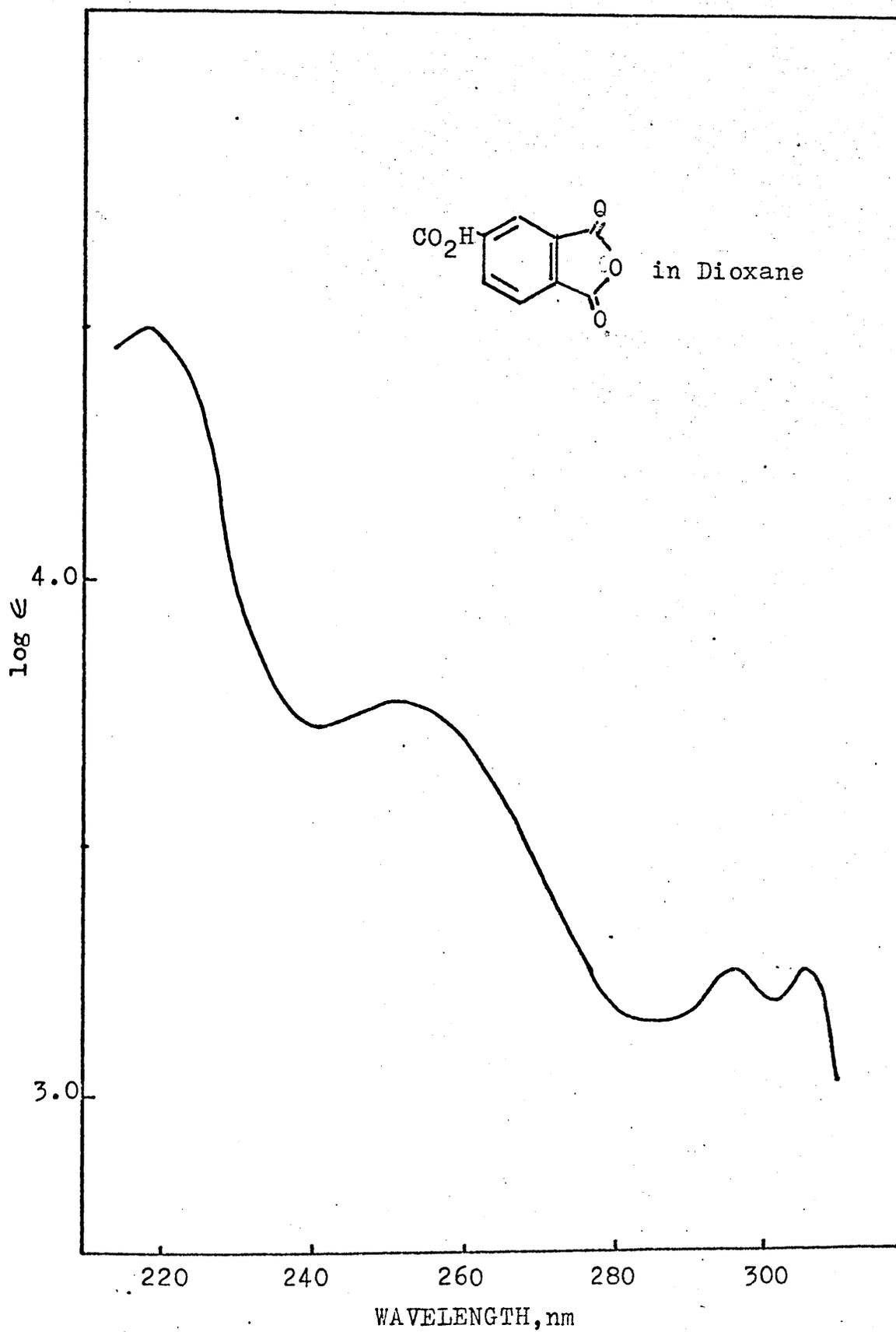


Fig. 13 UV Spectrum of 4-Carboxyphthalic Anhydride

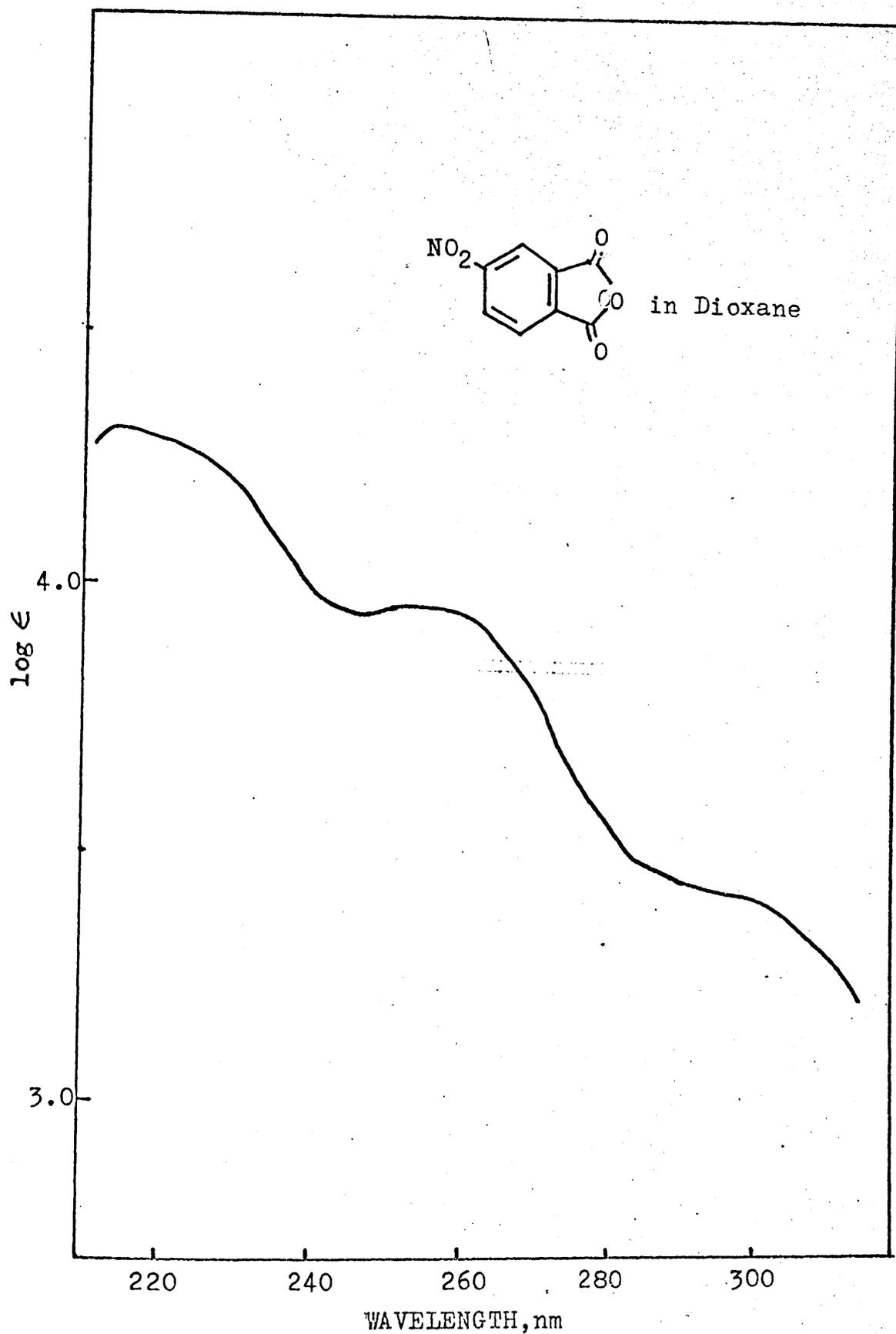


Fig. 14 UV Spectrum of 4-Nitrophthalic Anhydride

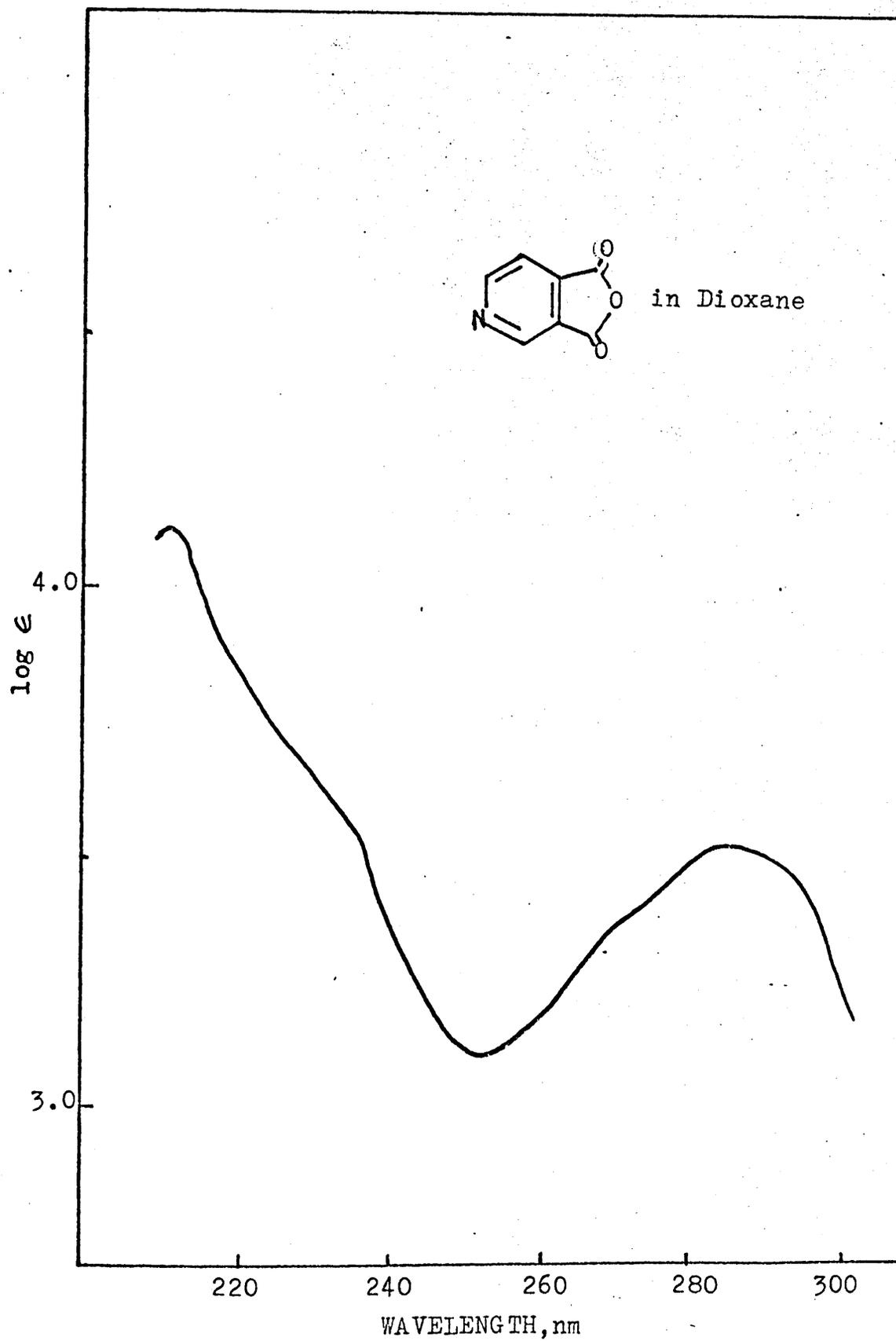


Fig. 15 UV Spectrum of 4-Azaphthalic Anhydride

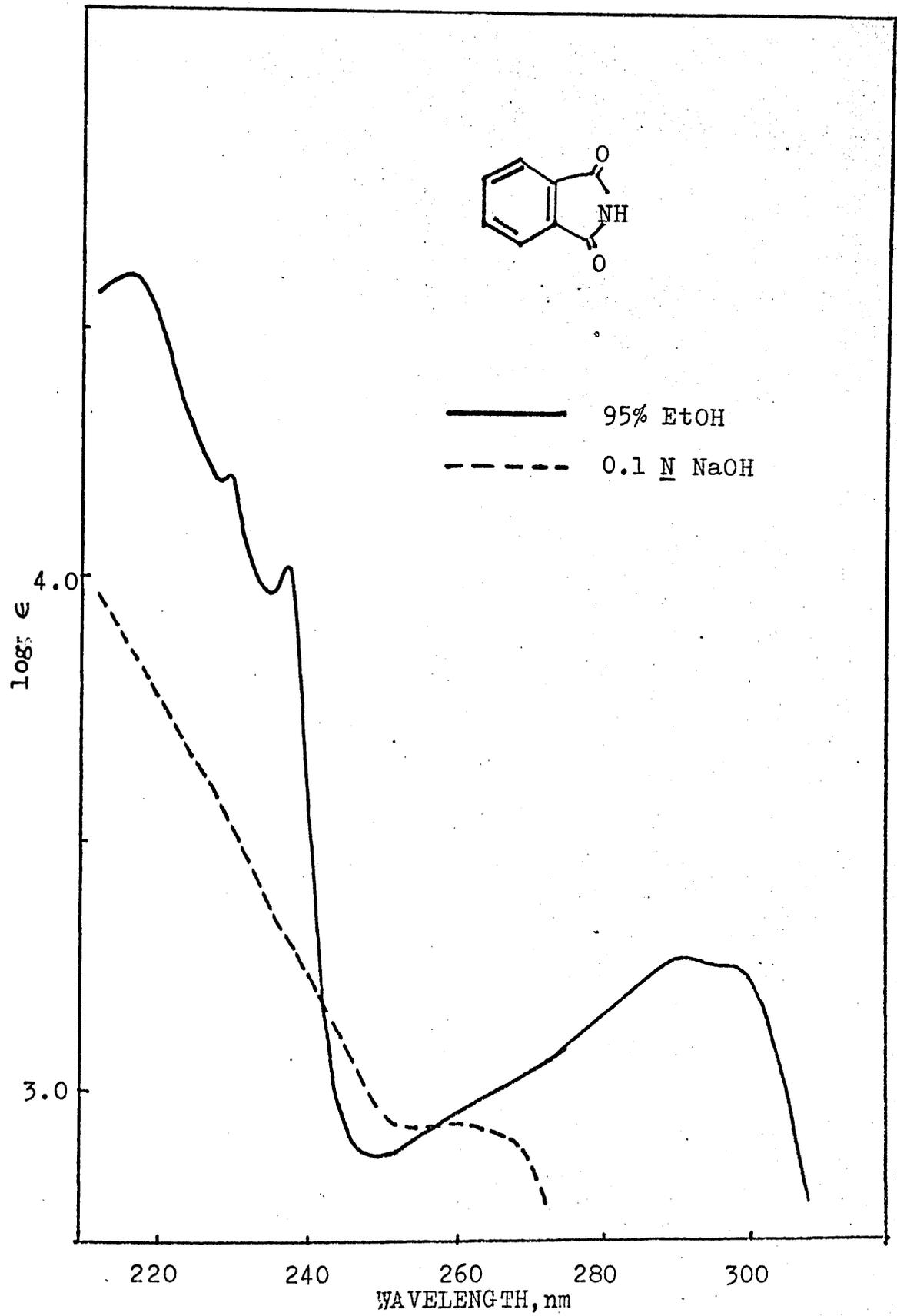


Fig. 16 UV Spectra of Phthalimide

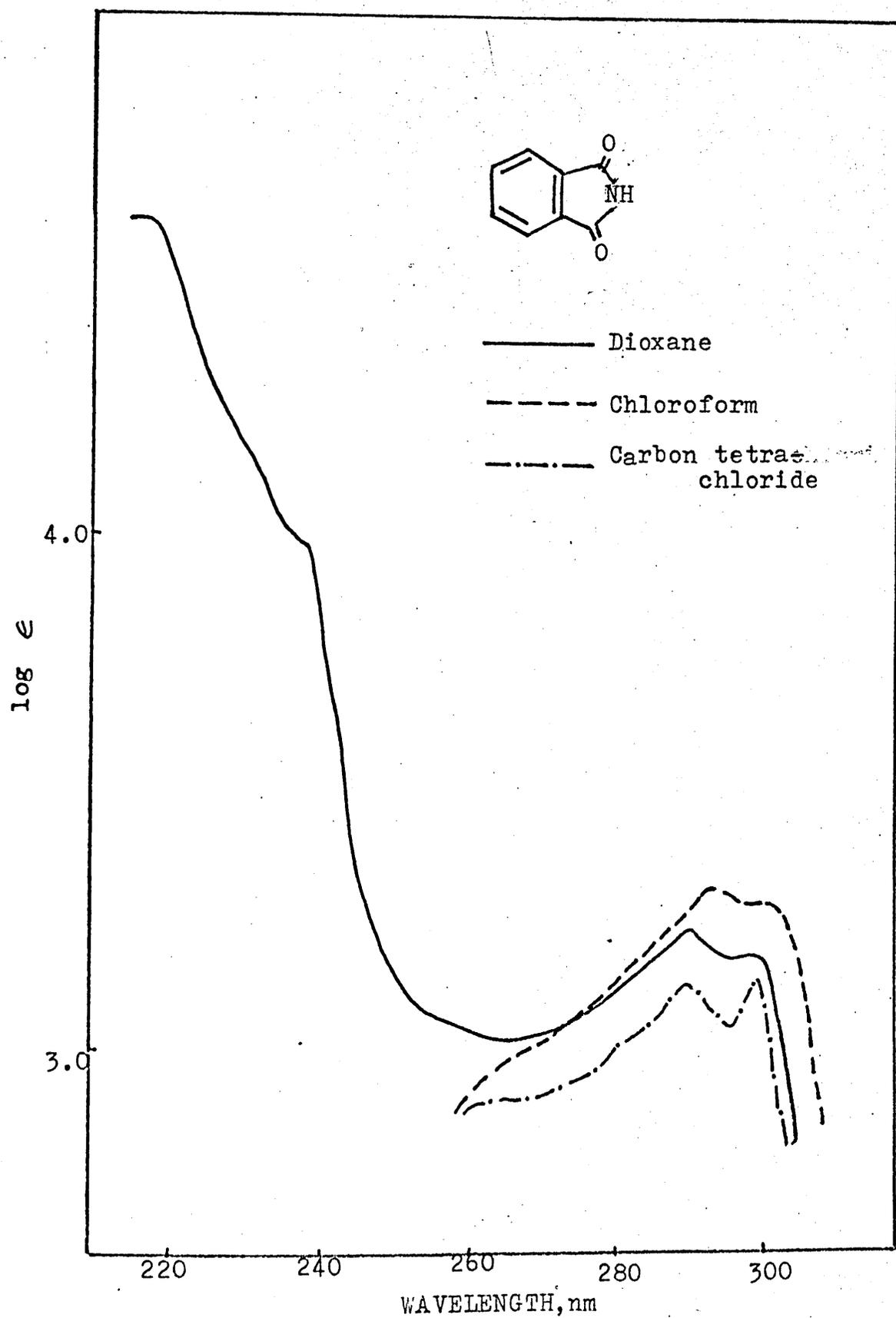


Fig. 17 UV Spectra of Phthalimide

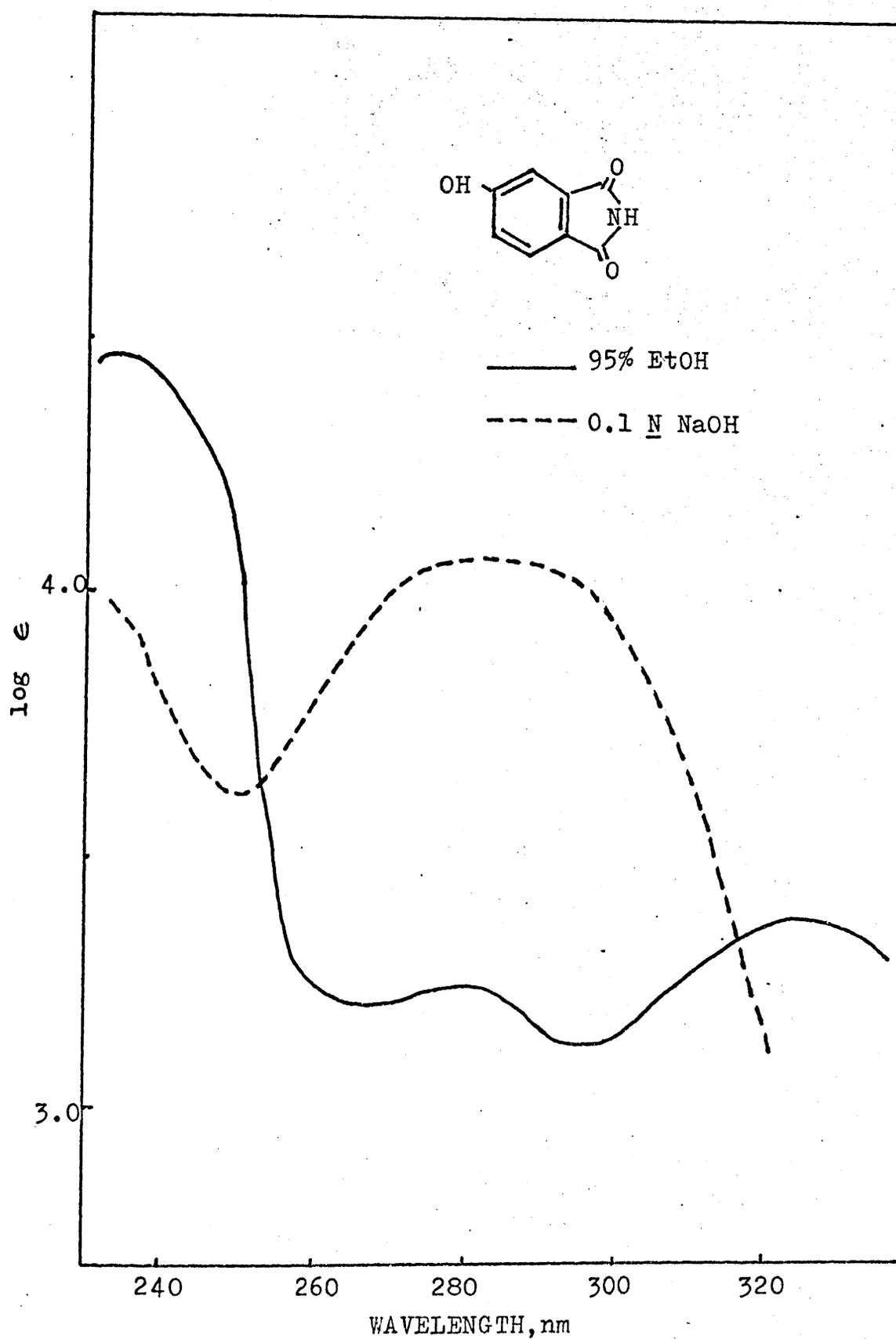


Fig. 18 UV Spectra of 4-Hydroxyphthalimide

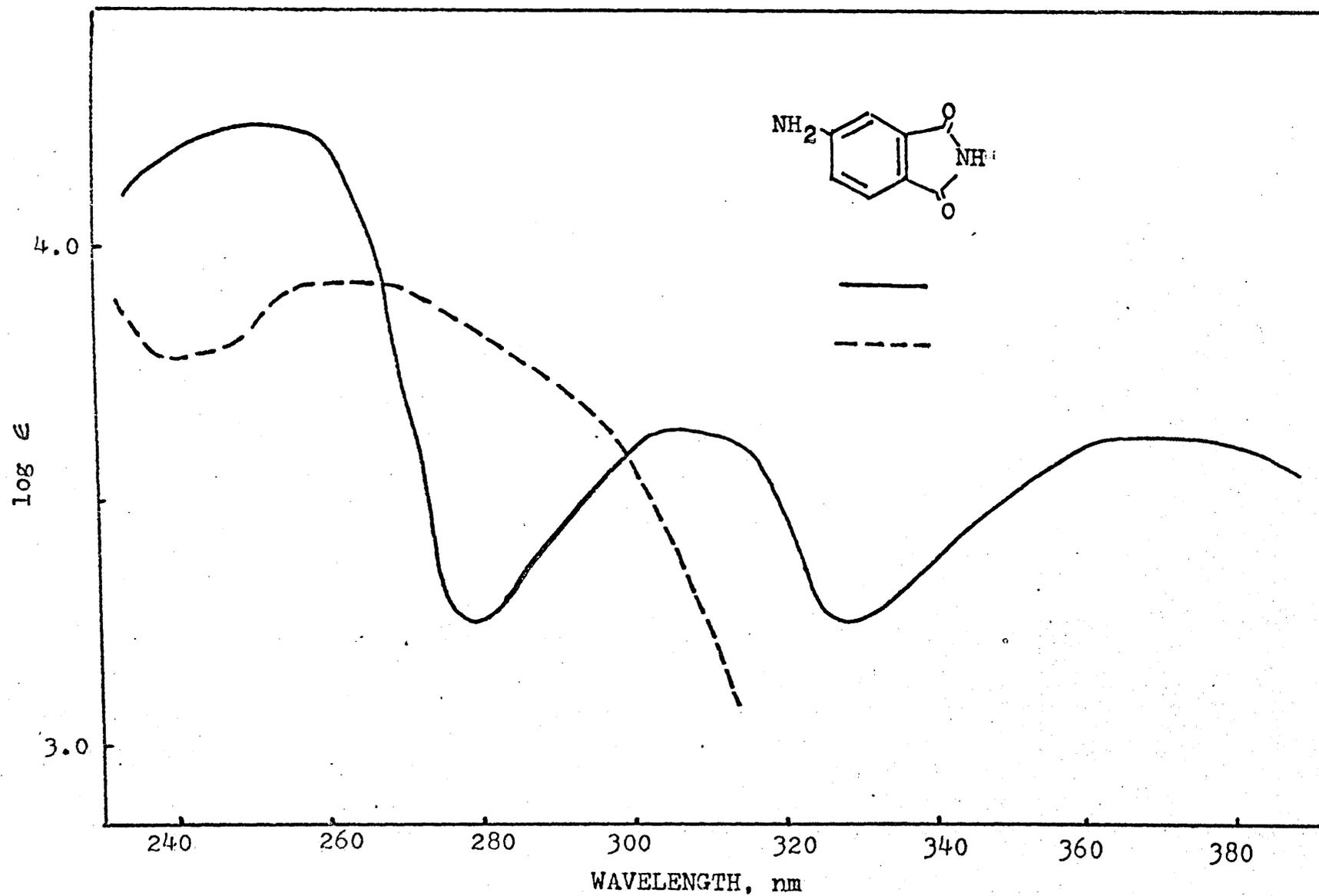


Fig. 19 UV Spectra of 4-Aminophthalimide

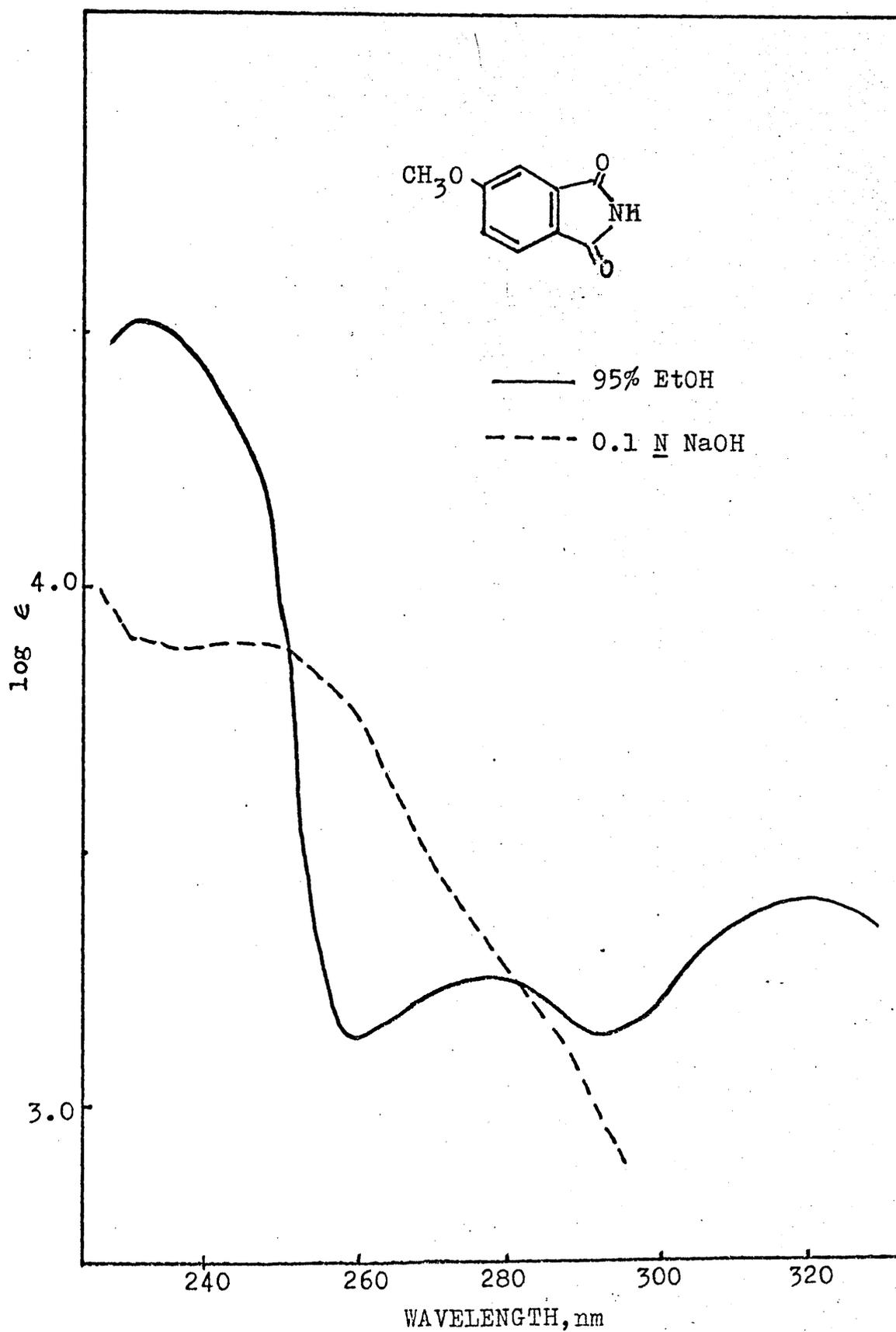


Fig. 20 UV Spectra of 4-Methoxyphthalimide

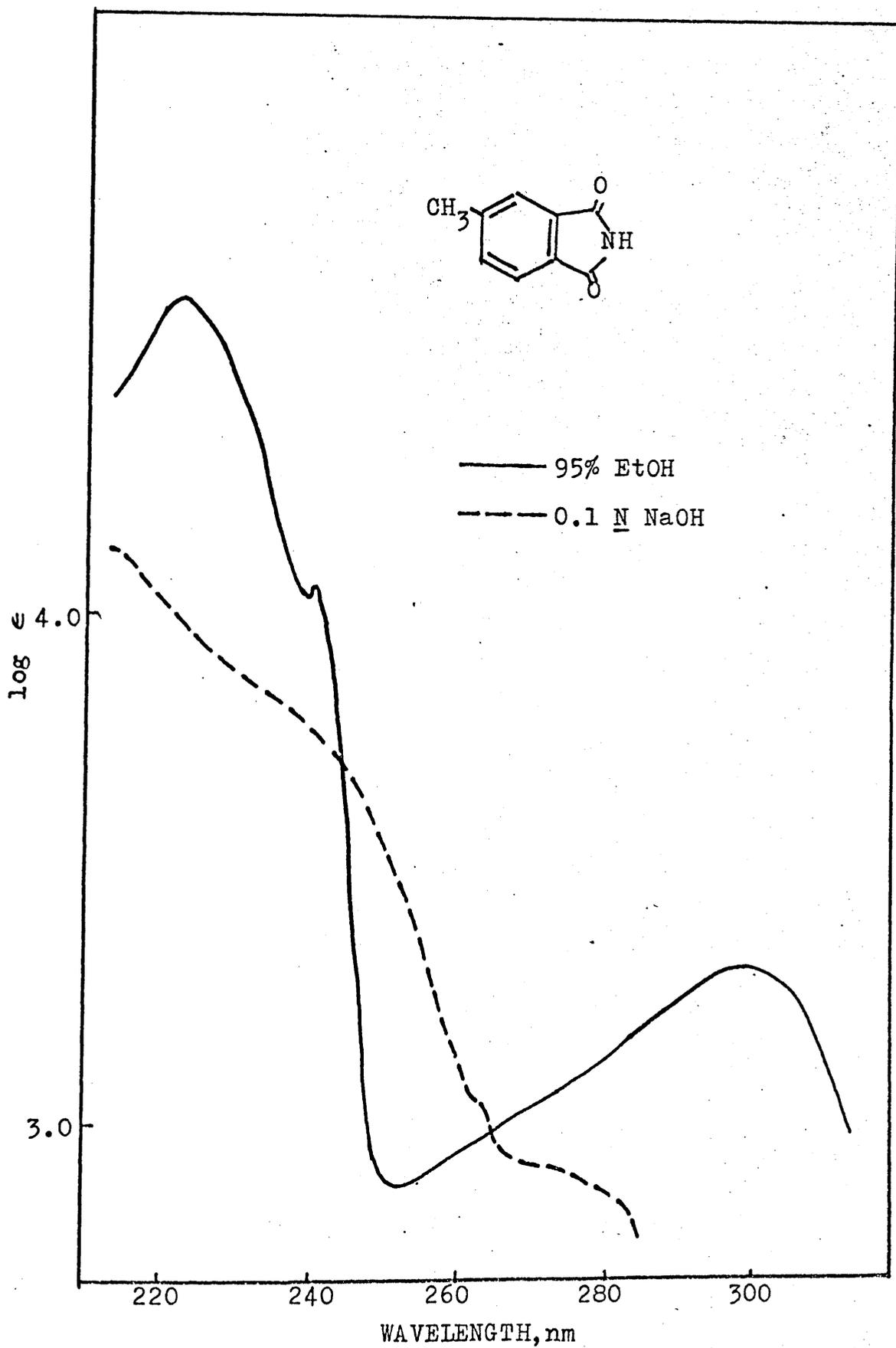


Fig. 21 UV Spectra of 4-Methylphthalimide

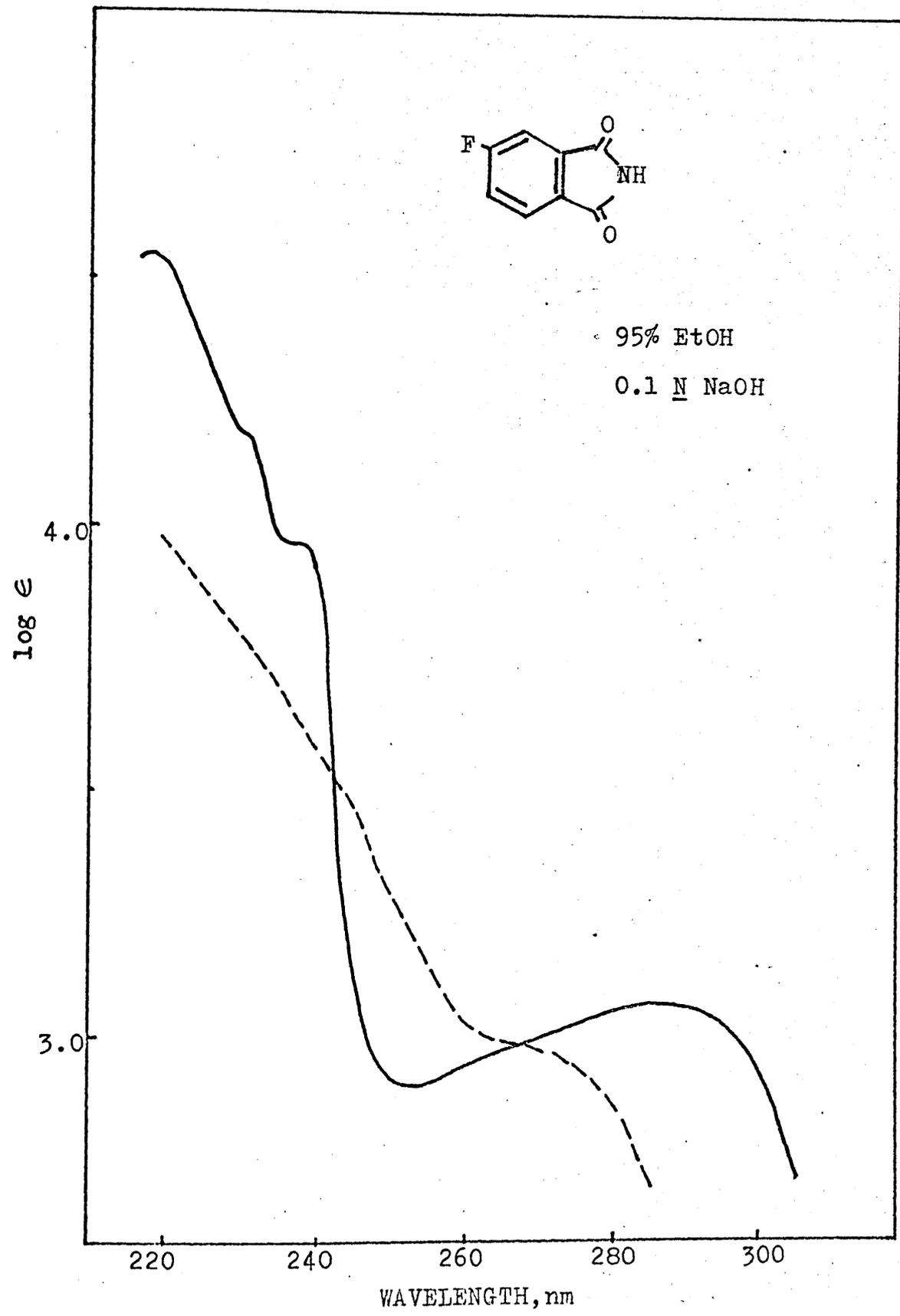


Fig. 22 UV Spectra of 4-Fluorophthalimide

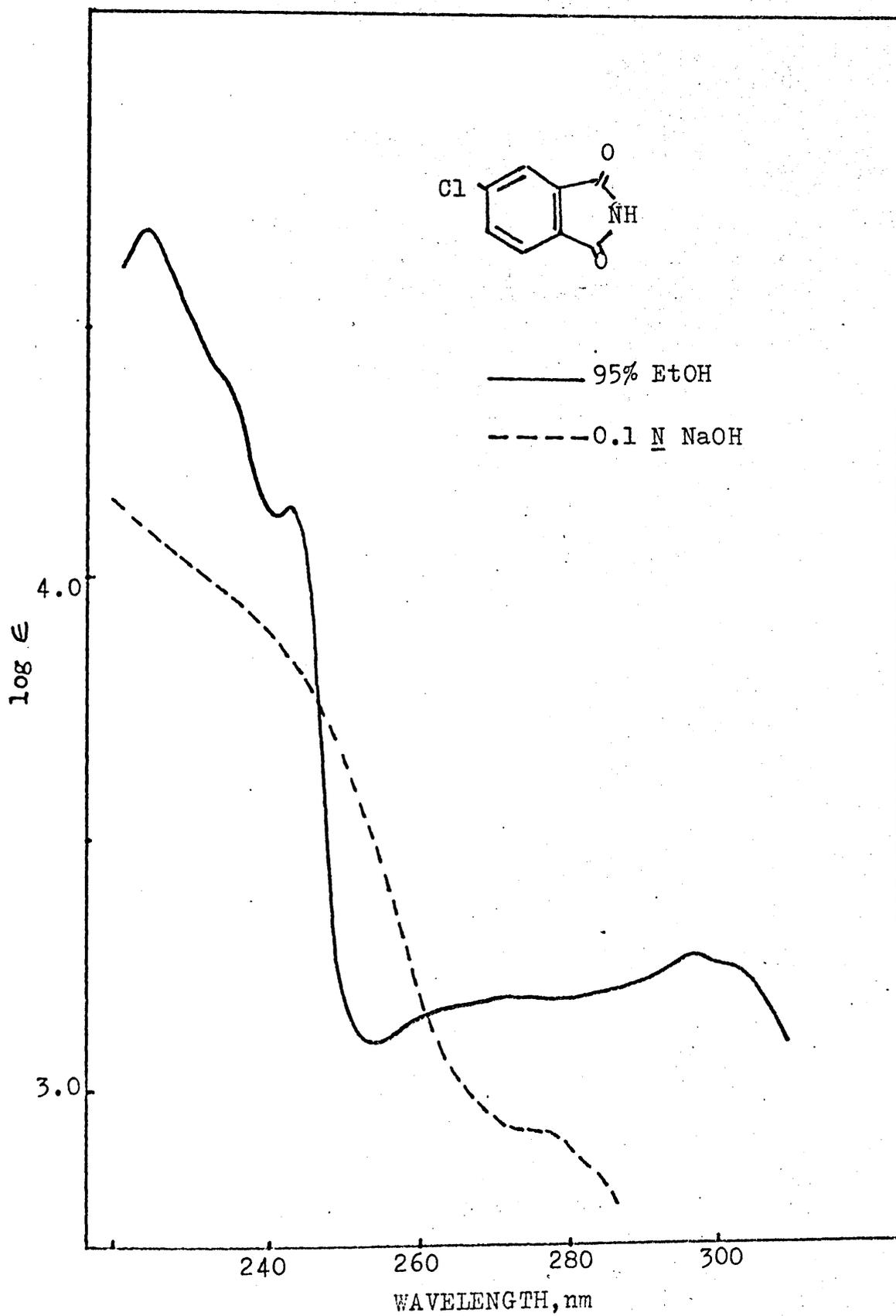


Fig. 23 UV Spectra of 4-Chlorophthalimide

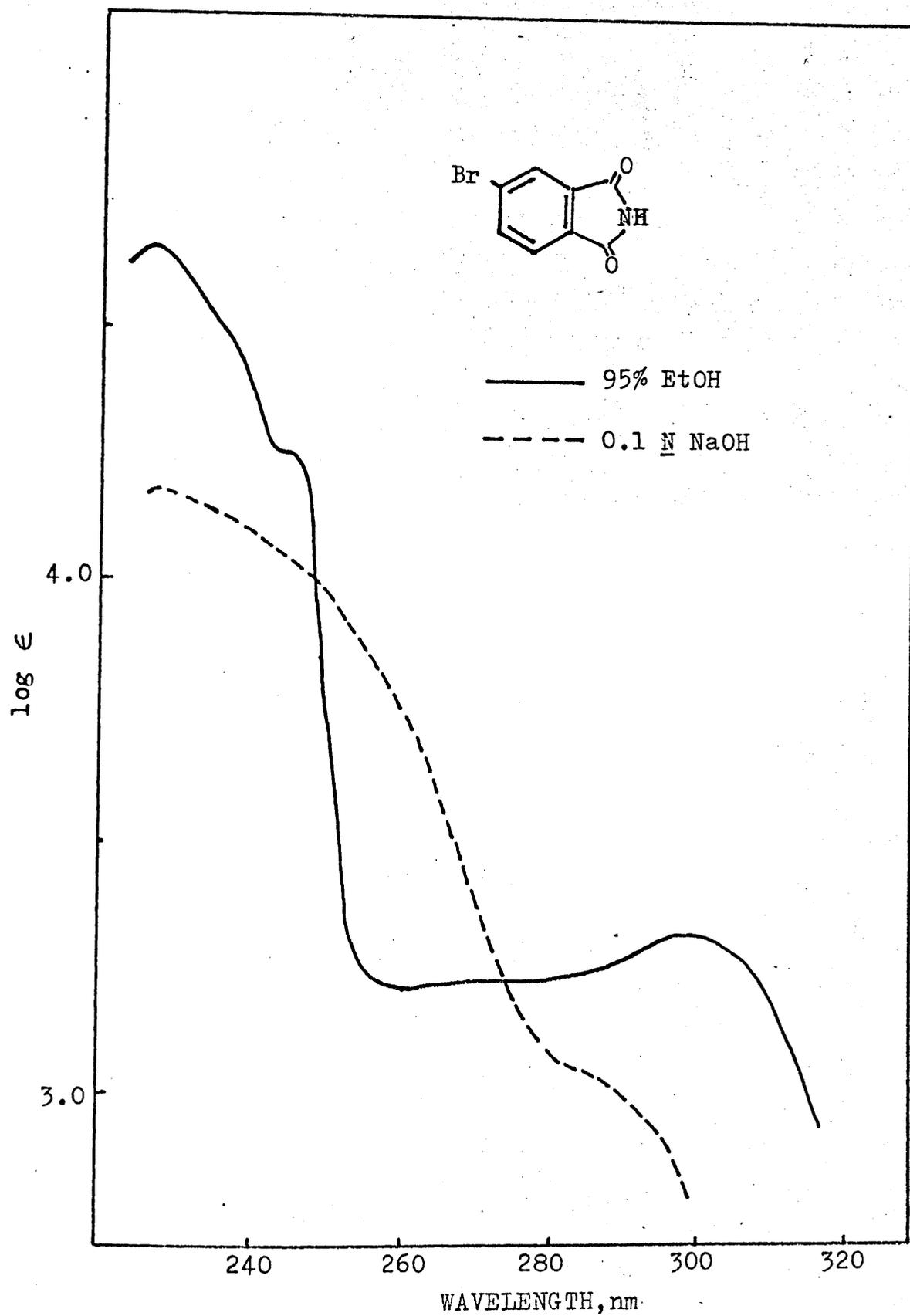


Fig. 24 UV Spectra of 4-Bromophthalimide

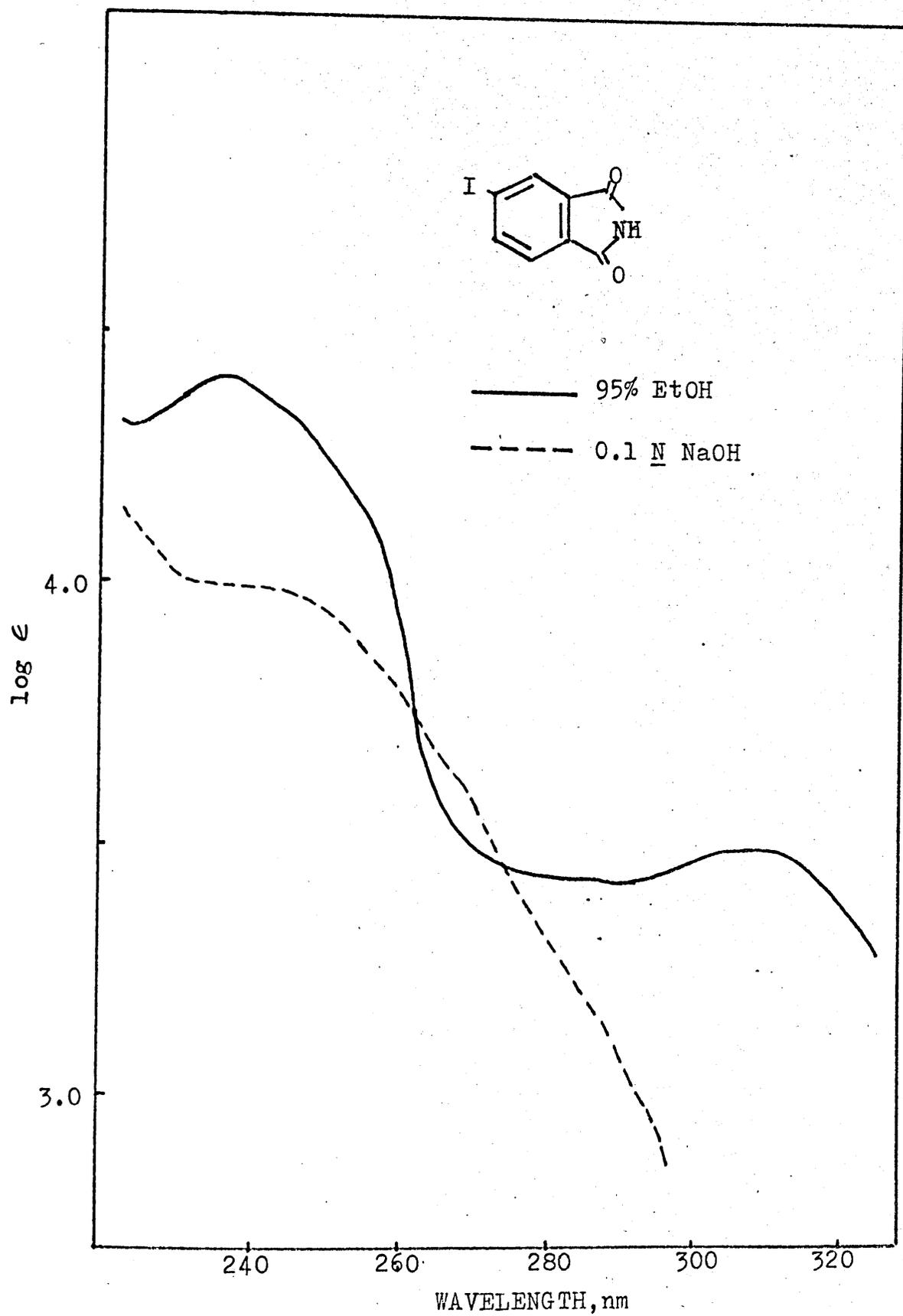


Fig. 25 UV Spectra of 4-Iodophthalimide

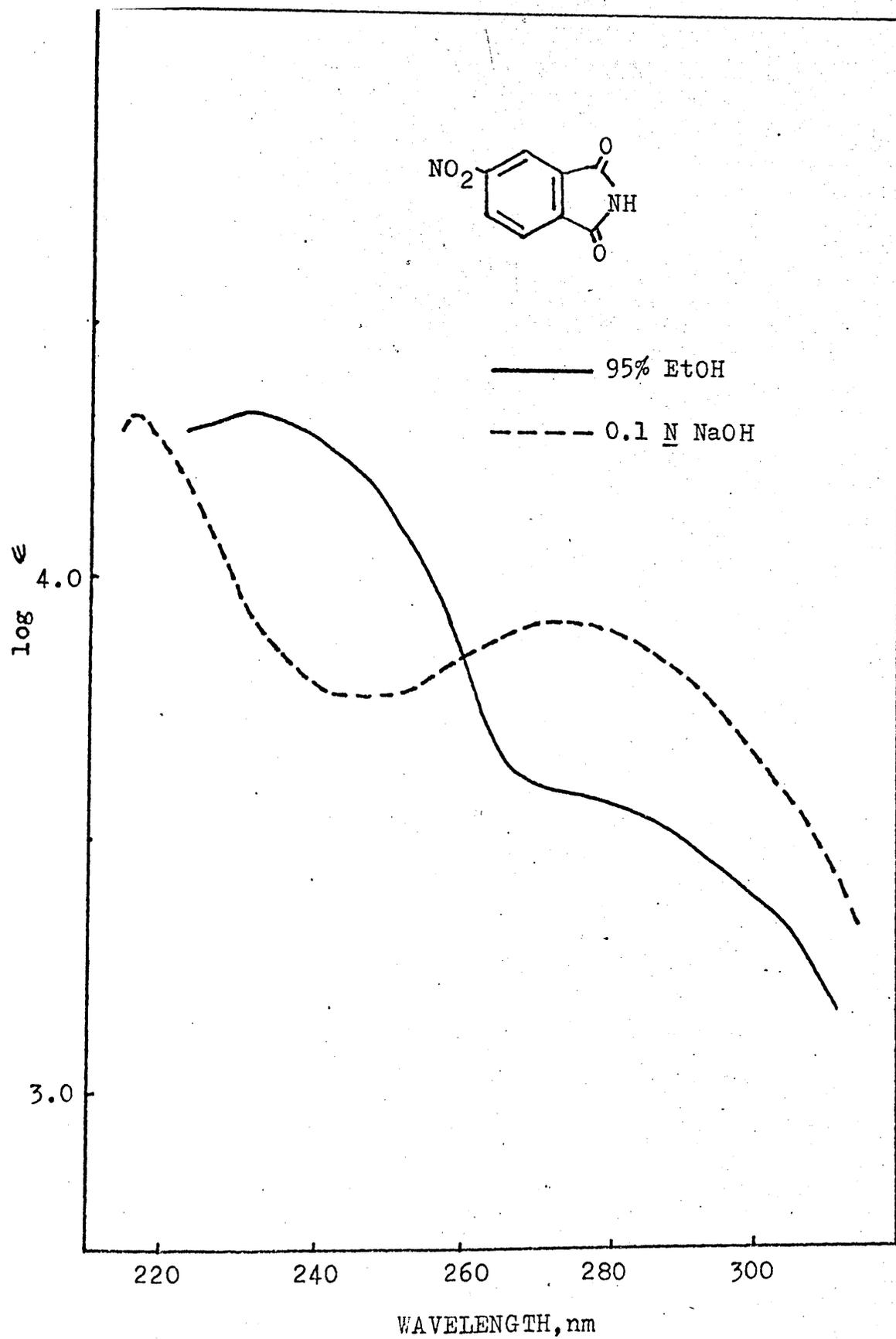


Fig. 25 UV Spectra of 4-Nitrophthalimide

APPENDIX II

Dipole Moment Measurements and Calculations

A. Calibration of DFL 1 type sample holding cell

The dielectric constants of the four calibration liquids were measured with a WTW type DM 01 Dipolemeter at 20°C. The average of three to five readings for each liquid was corrected with correction diagram to obtain the corrected dipolemeter reading, S. These data and the dielectric constants of these four liquids are listed in Table 24 below:

TABLE 24
Calibration of the Dipolemeter

Calibration Liquid	Dielectric Constant,	Measured Value	Correction From Diag.	Corrected Value, S
Cyclohexane	2.0228	842.3	-0.15	842.15
Carbon tetra- chloride	2.2363	1342.5	-0.04	1342.46
Benzene	2.2825	1452.8	-0.3	1452.5
n-Butyl ether	3.0830	3351.5	+0.5	3352.0

Note: The dielectric constants were from F. Oehme and H. Wirth⁸⁷

The equation for the calibration curve is calculated both by the method of averages and by graphic method:

1. The method of averages:

Two sets of data are taken as a pair, the ratio of

the value $\Delta\epsilon/\Delta S$ for each pair is calculated. The slope of the line of corrected dipolemeter readings, S , versus dielectric constants, ϵ , are obtained by taking the average of these five possible ratios.

Pair	ϵ^{20}	20	$\Delta\epsilon$	ΔS	$\frac{\Delta\epsilon}{\Delta S} \times 10^4$
Cyclohexane CCl ₄	2.0228 2.2363	842.15 1342.46	0.2135	500.31	4.267
Cyclohexane Benzene	2.0228 2.2825	842.15 1452.5	0.2597	610.35	4.254
CCl ₄ Benzene	2.2363 2.2825	1342.46 1452.5	0.0462	110.0	4.200
CCl ₄ Butyl ether	2.2363 3.0830	1342.46 3352.0	0.8467	2009.5	4.213
Benzene Butyl ether	2.2825 <u>3.0830</u>	1452.5 <u>3352.0</u>	0.8005	1899.5	4.214
Average:	2.4062	1747.2		Slope	4.230×10^{-4}

The intercept of the line is calculated from:

$$\begin{aligned} \bar{\epsilon} &= m\bar{S} + b, \text{ that is } b = \bar{\epsilon} - \bar{S}(m) \\ &= 2.4062 - 1747.2 (4.230 \times 10^{-4}) \\ &= 1.667 \end{aligned}$$

The equation for the calibration curve is then in the form of $\epsilon = (4.230 \times 10^{-4})S + 1.667$

The dielectric constant of the solvent used for the compounds are thus obtained by substituting its S value into the equation. For dioxane, the corrected dipolemeter reading on that day was 1303.8, its dielectric constant, ϵ_1 , was calculated as

$$\begin{aligned} \epsilon_1^{20} &= 4.230 \times 10^{-4} (1303.8) + 1.667 \\ &= 2.2185 \end{aligned}$$

2. The graphic method

In the graphic method, the dielectric constants, ϵ , is plotted versus the corrected dipolemeter readings, S , and the best fitted line is drawn. The slope and the intercept is obtained from the graph. This graph for the data in the table was plotted in the figure following. The slope and intercept obtained from the graph agree well with that from the method of averages.

B. Procedure of measuring and the calculation of the dipolemoment of 4-nitrophthalic anhydride

The dipole moment of 4-nitrophthalic anhydride was measured on the same day the calibration in section A was done.

Four solutions of 4-nitrophthalic anhydride were made by dissolving a weighted amount of solid substance in a weighted amount of dioxane. The weight percent (W_2) was calculated from the formula:

$$W_2 = \frac{m_2}{m_1 + m_2}$$

where m_1 and m_2 are the weight of solvent and solute, respectively.

The refractive index of each solution (n_{12}) was measured just before the solution is ready to be introduced into dipolemeter cell.

The dielectric constant, ϵ_{12} , was calculated by substituting its corrected dipolemeter reading, S , into the equation for the calibration curve.

These data were listed in the table below.

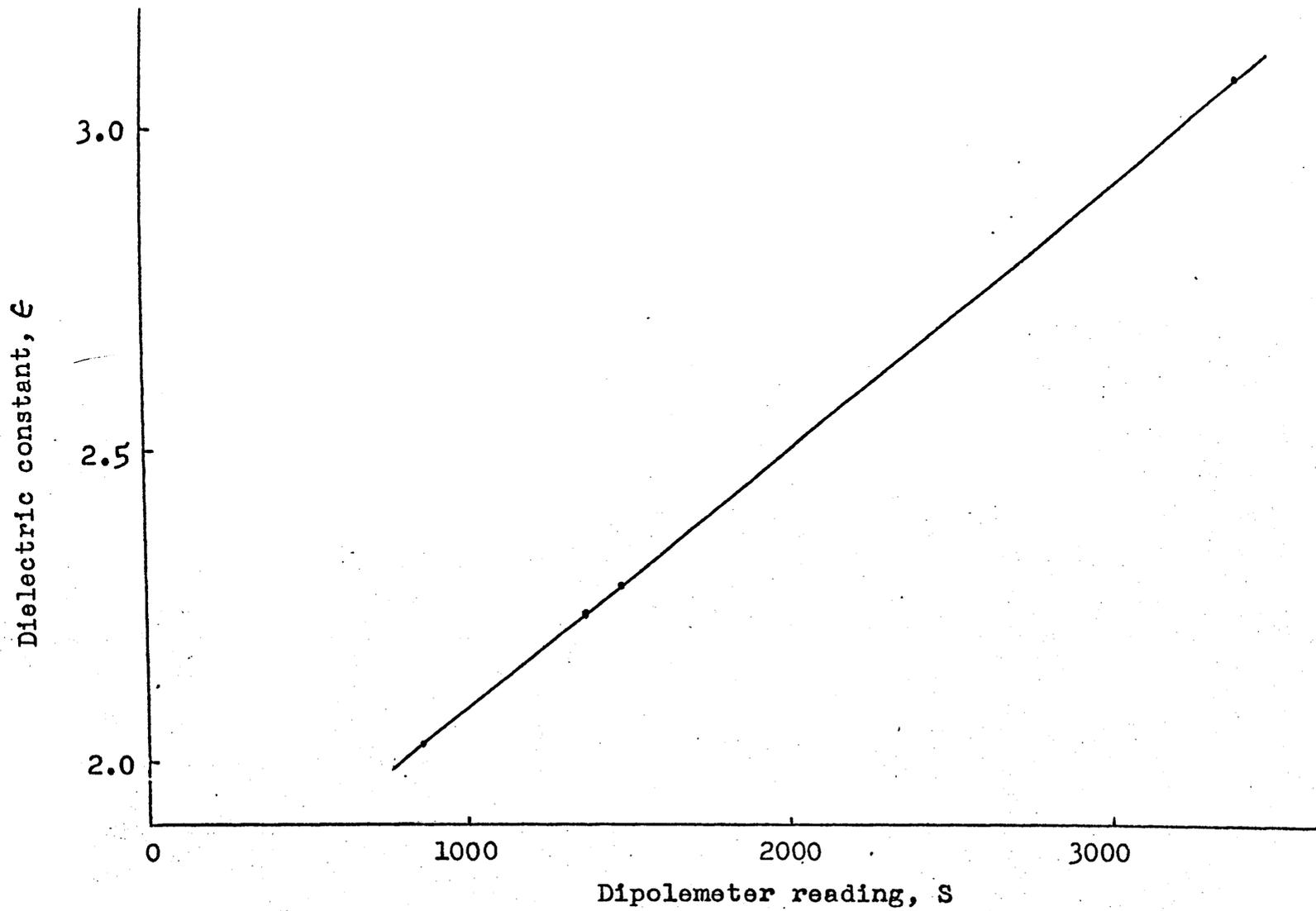


FIGURE 27. Calibration Curve for Dielectric Constants

TABLE 25

Experimental Data for the Calculation of Dipole
Moment of Thiophthalic Anhydride

Sample No.	Wt. Frac- tion, $W_2 \times 10^3$	Cor- rected Dipole Meter Read- ing, S	Dielec- tric Con- stant, ϵ_{12} (note)	$\epsilon_{12} \cdot W_2$ $\times 10^3$	$\epsilon_1 W_2$ $\times 10^3$	$W_2^2 \times 10^6$
1	3.29	1417.9	2.2668	7.458	7.299	10.8241
2	6.15	1502.47	2.3026	14.161	13.644	37.8225
3	11.30	1657.07	2.3679	26.757	25.069	127.6900
4	20.04	1920.2	2.4792	49.683	44.459	401.6016
5	30.39	2235.0	2.6124	<u>79.391</u>	<u>67.420</u>	<u>923.5521</u>
				177.450	157.891	1501.4903

Note: ϵ_{12} calculated from $\epsilon_{12} = (4.230 \times 10^{-4})S + 1.667$

The slope of the line ($\epsilon_{12} - \epsilon_1$) versus W_2 is
calculated by the following relationship:⁸⁷

$$A = \frac{\epsilon_{12} \times W_2 - \epsilon_1 \times W_2}{W_2}$$

$$= \frac{(177.45 - 157.89) \times 10^{-3}}{1501.49 \times 10^{-6}} = 13.03$$

TABLE 26

Experimental Data for the Calculation of Dipole
Moment of Thiophthalic Anhydride

Sample No.	Wt. Fraction $W_2 \times 10^3$	Refractive Index, n_{12}	$(n_{12}^2 - n_1^2) \times 10^4$ (note)	$(n_{12}^2 - n_1^2) \times W_2 \times 10^7$
1	3.29	1.4226	17.07	56.16
2	6.15	1.4230	28.45	174.97
3	11.30	1.4236	45.53	514.49
4	20.04	1.4246	74.01	1483.16
5	30.39	1.4266	131.04	<u>3982.31</u>
				6211.09

n_1 = Refractive index of dioxane = 1.4220

The slope of the line $(n_{12}^2 - n_1^2)$ versus W_2 is calculated by the relationship:⁸⁷

$$A_n = \frac{n_{12}^2 W_2 - n_1^2 W_2}{W_2^2} = \frac{(n_{12}^2 - n_1^2) W_2}{W_2^2}$$

$$= \frac{6211.09 \times 10^{-7}}{1501.49 \times 10^{-6}} = 0.414$$

The slopes A and A_n are also obtained from the graphic method by plotting $(\epsilon_{12} - \epsilon_1)$ versus W_2 and $(n_{12}^2 - n_1^2)$ versus W_2 .

The dipole moment of thiophthalic anhydride is then calculated from the equation

$$\begin{aligned}\mu^2 &= \frac{27KT}{4\pi N} \cdot \frac{M_2}{d_1(\epsilon_1 + 2)^2} \cdot (A_\epsilon - A_n) \\ &= 1.433 \times 10^{-37} \frac{164.14}{1.03364(2.2185 + 2)^2} (13.03 - 0.414) \\ &= 16.1494 \times 10^{-36} \text{ (esu-cm)}^2 \\ &= 4.02 \text{ Debyes}\end{aligned}$$

To obtain the average deviations of A and A_n , use the following equations

$$\pm \frac{1}{n} \epsilon / A_\epsilon - \frac{\epsilon_{12} - \epsilon_1}{W_2} \quad \text{and} \quad \pm \frac{1}{n} \epsilon / A_n - \frac{n_{12}^2 - n_1^2}{W_2}$$

give

$$A_\epsilon = 13.03 \pm 0.514 \quad (\text{that is } 13.544 \text{ to } 12.516)$$

$$A_n = 0.414 \pm 0.146 \quad (\text{that is } 0.560 \text{ to } 0.268)$$

The average deviation of the dipole moment is then calculated as following:

For the upper limit, used the largest $(A_\epsilon - A_n)$, that is $A_\epsilon = 13.544$ and $A_n = 0.268$

$$\begin{aligned}\mu^2 &= 1.433 \times 10^{-37} \frac{164.14}{1.03364 (4.2185)^2} (13.276) \\ &= 16.9892 \times 10^{-36} \text{ (esu-cm)}^2 \\ \mu &= 4.12 \text{ Debyes}\end{aligned}$$

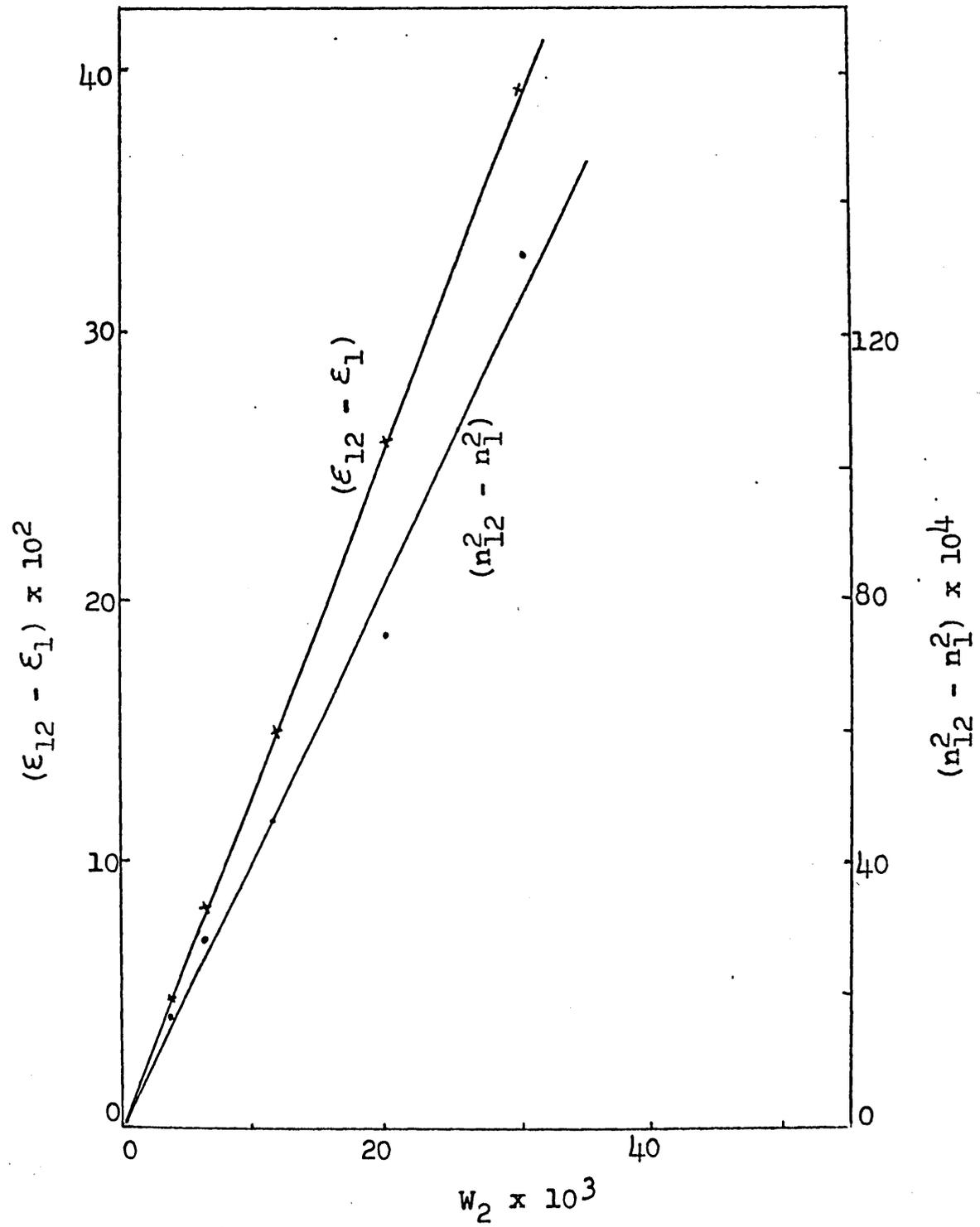


FIGURE 28. Evaluation Diagram for Determination of the Values A_ϵ and A_n

For the lower limit, use the smallest ($A_E - A_N$), that is $A_E = 12.516$ and $A_N = 0.560$.

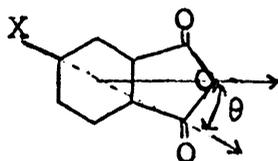
$$\begin{aligned}\mu^2 &= 1.433 \times 10^{-37} \frac{164.14}{1.03364(4.2185)^2} (11.955) \\ &= 15.2987 \times 10^{-36} \text{ (esu-cm)}^2 \\ \mu &= 3.91 \text{ Debyes}\end{aligned}$$

Therefore, the dipole moment of thiophthalic anhydride is 4.02 ± 0.10 Debyes.

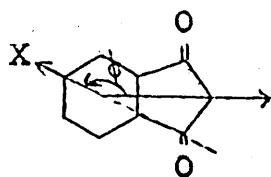
C. Calculation of the dipole moment of 4-substituted phthalic systems from the dipole moments of chlorobenzene and phthalic anhydride (or phthalimide).

The moment of the phthalic systems, μ_0 , is assumed in the plane of the molecule and directing toward the ether oxygen and bisecting the molecule.

The 4-substituted phthalic systems should then have an additional moment, μ_x , due to the substituent, forms an angle of -30° or 150° from the moment μ_0 . The angle depends upon whether the group is electron donating or withdrawing in nature, thus, for electron donating groups, $\theta = -30^\circ$



for electron withdrawing groups, the angle $\theta = 150^\circ$



The moments of the 4-substituted phthalic system, μ , is the vector sum of μ_x and μ_o . Thus

$$\begin{aligned}\mu^2 &= \mu_o^2 + \mu_x^2 + 2\mu_o\mu_x\cos\phi \\ &= \mu_o^2 + \mu_x^2 + 2\mu_o\mu_x(0.866)\end{aligned}$$

4-Methylphthalimide as an example, dipole moment of phthalimide in dioxane is 2.14 ± 0.02 that is 2.16 to 2.12; dipole moment of toluene is 0.43.

Lower range:

$$\begin{aligned}\mu^2 &= (2.12)^2 + (0.43)^2 + (1.732)(2.12)(0.43) \\ &= 6.258 \\ \mu &= 2.50 \text{ Debyes}\end{aligned}$$

Upper range:

$$\begin{aligned}\mu^2 &= (2.16)^2 + (0.43)^2 + (1.732)(2.16)(0.43) \\ &= 6.459 \\ \mu &= 2.54 \text{ Debyes}\end{aligned}$$

The calculated dipole moment for 4-methylphthalimide is therefore 2.52 ± 0.02 .

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