Polyimidazopyrrolone Model Compounds

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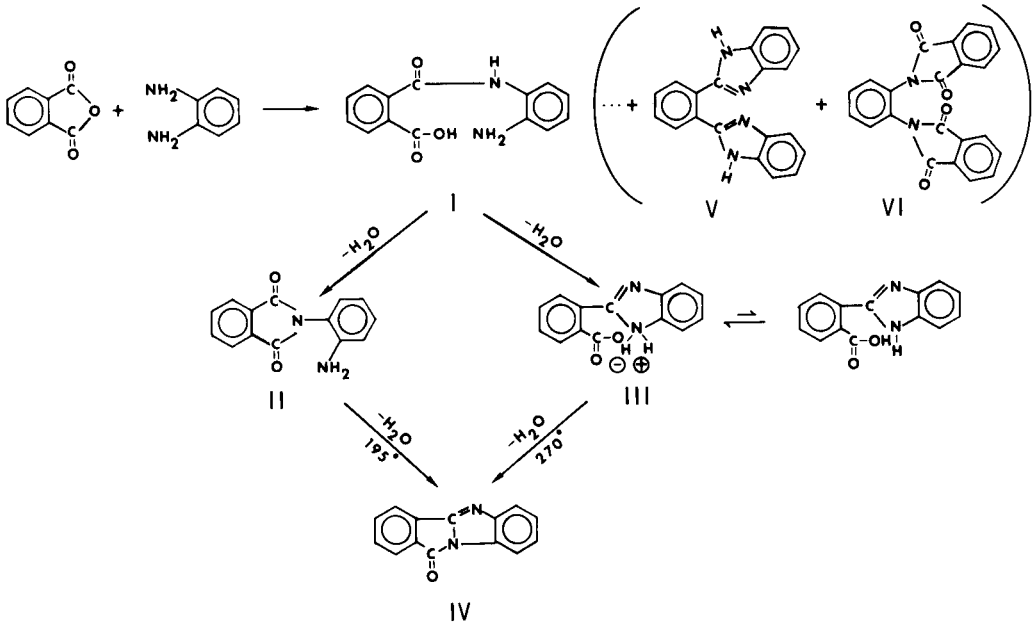
The model reactions between phthalic anhydride and *o*-phenylenediamine were studied under conditions analogous to the polymerization and post cyclization of dianhydrides with bis(*o*-diamines) to form polyimidazopyrrolones (Pyrrones). The route from the initial amide-acid-amine to the tetracyclic Pyrrone model when the reactions are conducted in aprotic solvents is highly competitive between isolatable benzimidazole-acid and imide-amine intermediates. Solid-state thermal conversion of the amide-acid-amine affords a unique dimeric species containing amide, imide, and benzimidazole functions. It was confirmed that melt techniques lead to disproportionation products. The application of these findings to related polymer synthesis is discussed.

Introduction.

Recent interest in the reactions of aromatic dianhydrides with aromatic tetraamines has led to the thermally stable polyimidazopyrrolones (1-3). These stepladder and ladder polymers, which are commonly referred to as Pyrrones, have been the subject of a great deal of research (4-6). An understanding of the mode of ring closure of the precursor polymer to the fully cyclized product is of fundamental importance to the chemistry of these polymers. Early publications indicated that ring closure proceeds through an imide-amine intermediate (2,3,7). However, as experience with this new class of polymers increased, it became apparent that a more detailed study of the reaction mode was warranted.

Due to the intractable nature of these polyhetero-

Scheme 1



aromatics, it was decided to conduct a detailed model compound study to provide information on the chemistry of the analogous polymer systems. The simplest model system, that of phthalic anhydride and *o*-phenylenediamine, has been intensively studied, but under conditions which were totally unrelated to ultimate polymer synthesis (8,9). An excellent melt reaction study has been made (3) but it should not be used to explain the solution polymerization. One study was made of the model reaction in polar aprotic solvents (2), but there were certain inconsistencies between the results of that study and our preliminary experimental data. Thus a detailed investigation was made into the entire series of reactions of phthalic anhydride and *o*-phenylenediamine and the intermediates leading to the tetracyclic Pyrrone model.

Results and Discussion.

The following reaction scheme, which parallels that for the polymer, was studied *via* model compounds:

See Scheme I

Characterization of Model Compounds.

Each model compound shown in Scheme I was prepared and characterized by infrared spectroscopy and elemental analysis before a study of the mode of ring closure was

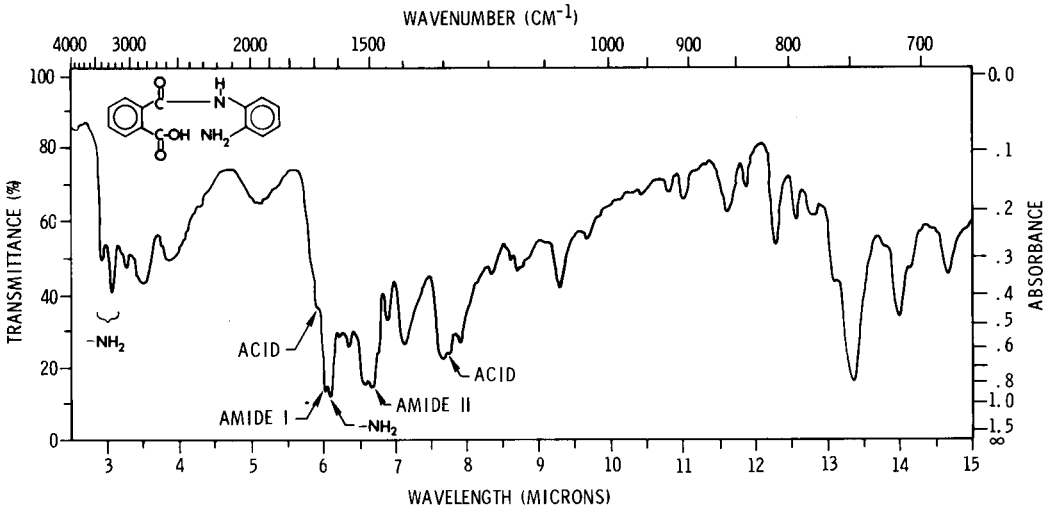


Figure 1. Infrared Spectrum of Amide-Amine (I).

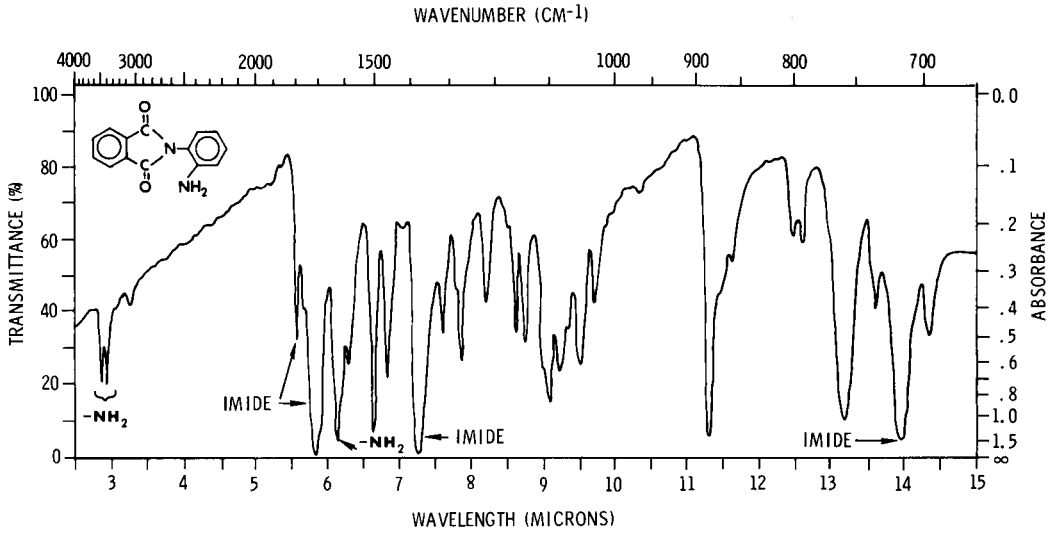


Figure 2. Infrared Spectrum of Imide-Amine (II).

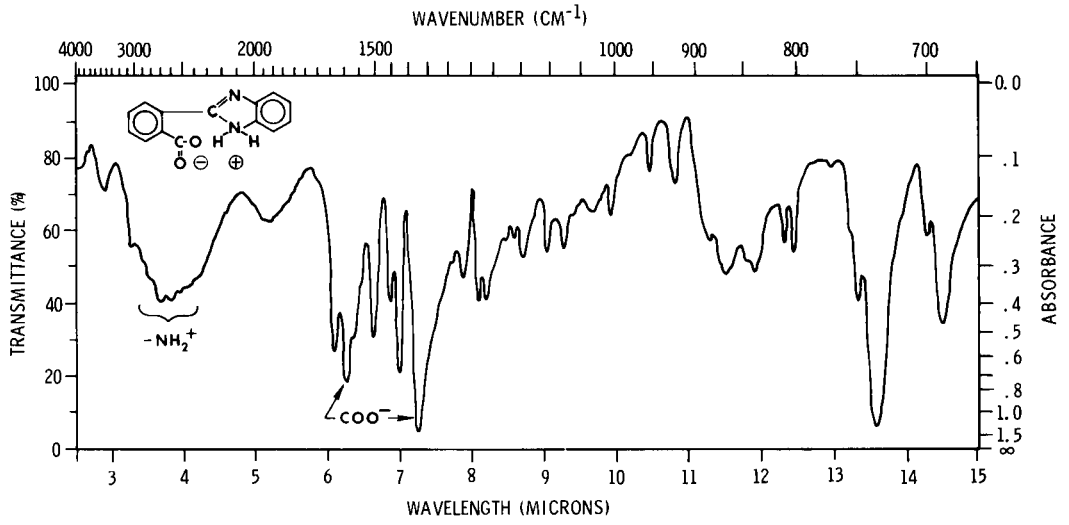


Figure 3. Infrared Spectrum of Benzimidazole-Acid Zwitterion (III).

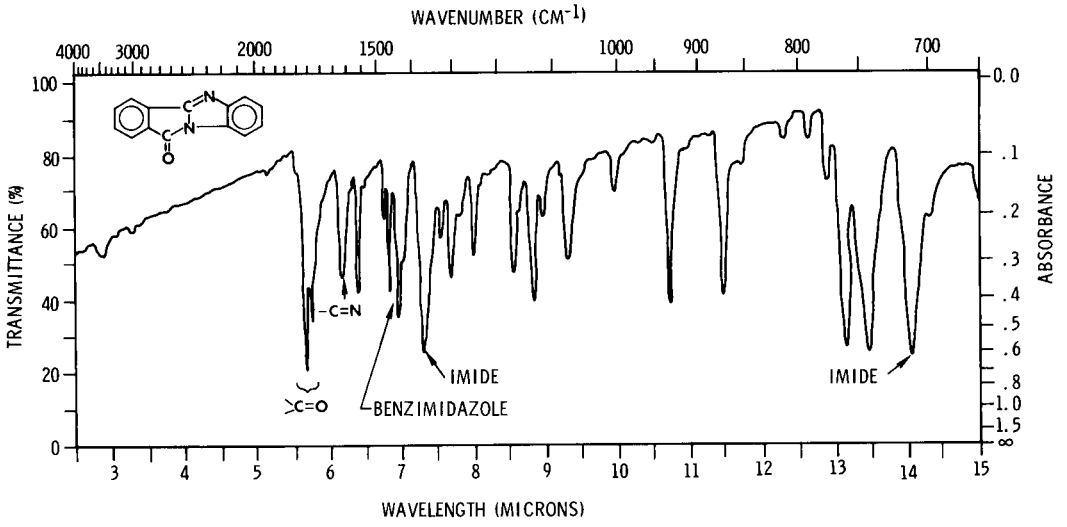


Figure 4. Infrared Spectrum of Pyrrone Model (IV).

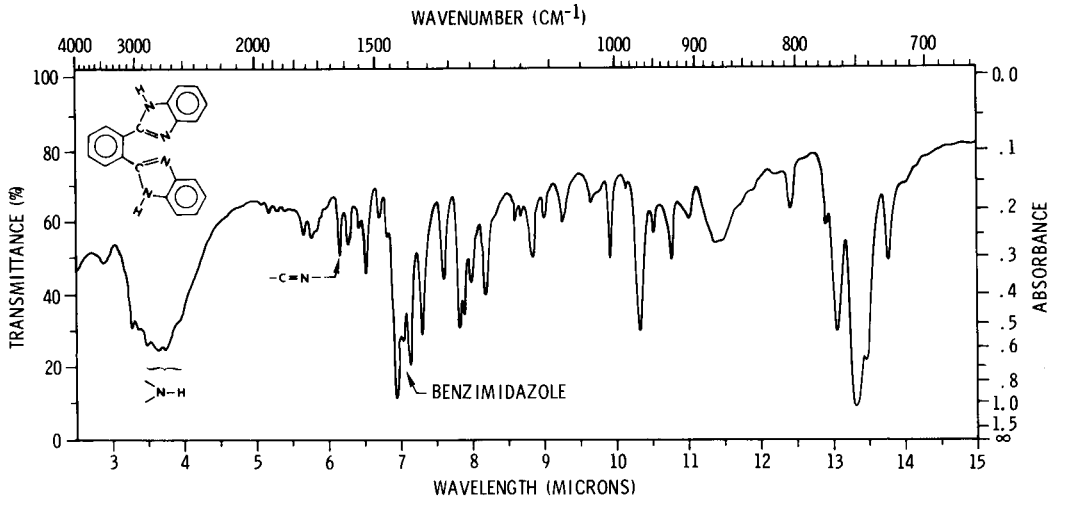


Figure 5. Infrared Spectrum of Dibenzimidazole (V).

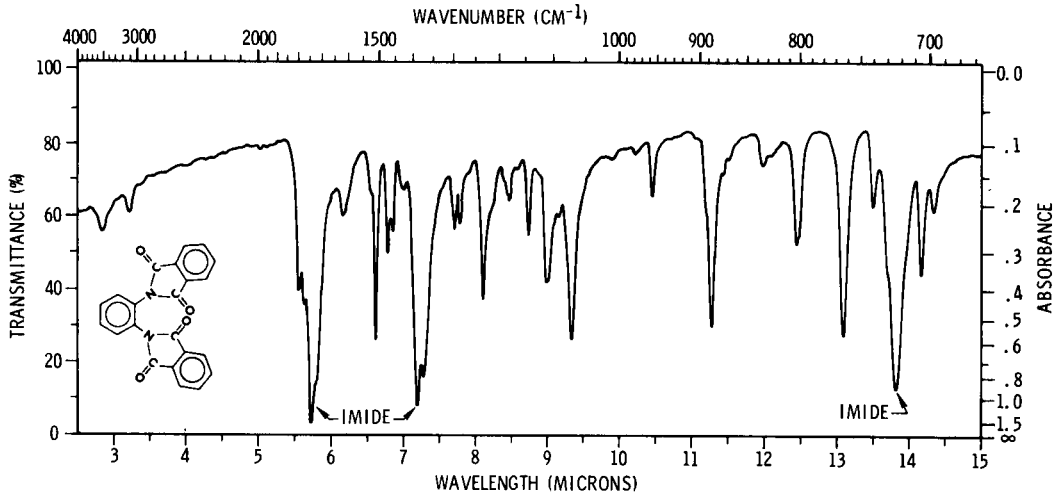


Figure 6. Infrared Spectrum of Diimide (VI).

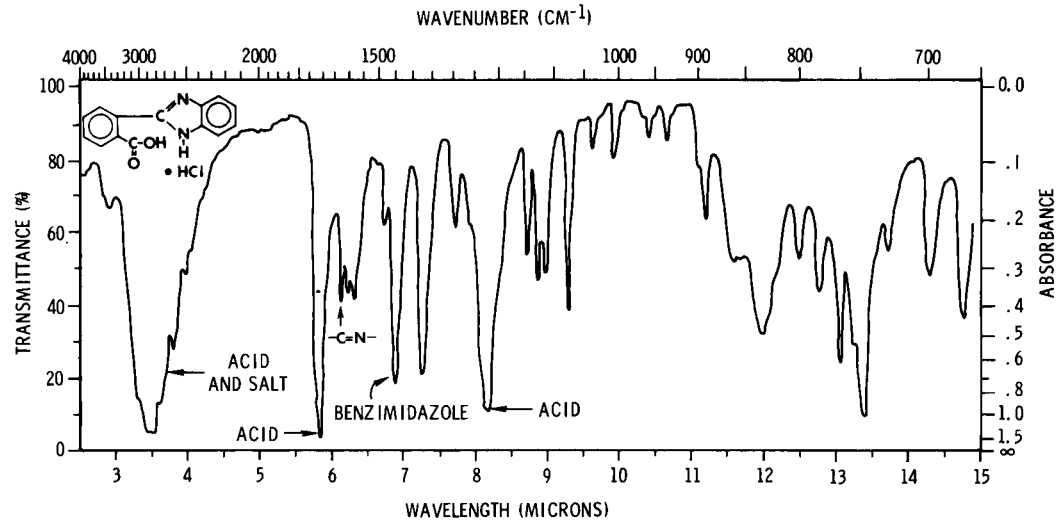


Figure 7. Infrared Spectrum of Benzimidazole-Acid Hydrochloride.

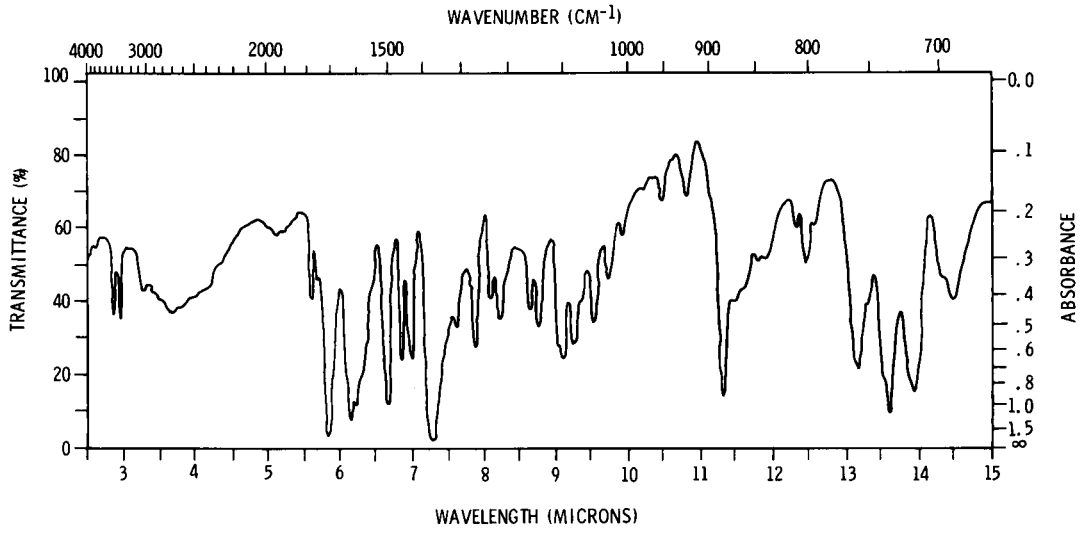


Figure 8. Infrared Spectrum of Equimolar Mixture of Imide-Amine (II) and Benzimidazole-Acid (III).

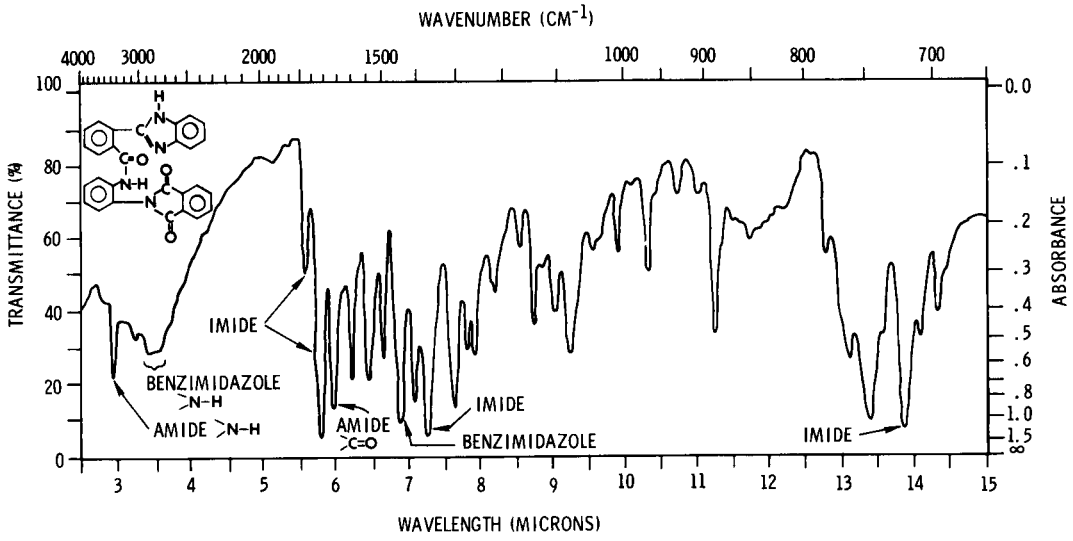


Figure 9. Infrared Spectrum of Benzimidazole-Amide-Imide (VIII).

made. Nuclear magnetic resonance spectra lacked the desired characterizing features and are not included. For convenience, the compounds in Scheme I will be referred to as amide-acid-amine (I), imide-amine (II), benzimidazole-acid (III), Pyrrone model (IV), dibenzimidazole (V), and diimide (VI). The infrared spectra of these compounds are given in Figures 1-6, along with the distinguishing features of each. For the most part, these spectra are straightforward. However, two of them merit additional consideration.

The infrared spectrum of the benzimidazole-acid (III), Figure 3, shows no acid carbonyl absorption. Apparently this compound exists as a zwitterion, with bands at 1595 and 1380 cm^{-1} assigned to carboxylate ion (COO^-) and the absorption from 3000-2200 cm^{-1} attributed to NH_2^+. It is interesting to note that the spectrum of the hydrochloride of this compound, Figure 7, prepared by a commonly referenced literature preparation (8), is what would be expected for the benzimidazole-acid had it not formed an internal salt. Acid absorption for this compound occurs at 1700 and 1220 cm^{-1}. Apparently the formation of a benzimidazole hydrochloride suppresses the formation of a carboxy-benzimidazole zwitterion.

Except for the carbonyl region, the spectrum of the Pyrrone model (IV), Figure 4, indicates that the compound is, indeed, part imide (1375 and 715 cm^{-1} bands) and part benzimidazole (1620 and 1450 cm^{-1} bands). The doublet at 1760 and 1738 cm^{-1} initially caused a great deal of concern since only one band had been anticipated. However, despite numerous recrystallizations and sublimations of IV, the highly characteristic doublet remained, both in solid state and solution spectra. The spectrum was also the same whether model IV was prepared by sublimation from the imide-amine at 200° or from the benzimidazole-acid at 275°. Apparently the splitting of this band is due to Fermi resonance which arises through interaction of the fundamental carbonyl band and the imide-like band at 872 cm^{-1}.

Reaction Study.

Much has been written about the reactions between phthalic anhydride and *o*-phenylenediamine (2,3,8,9). However, few reactions have been run under conditions analogous to polymerization and subsequent cyclization. This aspect was explored and the previously developed infrared spectra were used to identify the products.

At room temperature and 10 percent solids in dimethylformamide (DMF), the major product of the condensation reaction was the amide-acid-amine (I) which was isolated by the addition of water to the DMF solution. When I was stored in an aqueous DMF solution for several days at room temperature, it condensed to approximately a 2:1 mixture of imide-amine (II) and benzimidazole-acid (III), thus showing that cyclodehydration is favored even in the presence of water. The sum of the yield of I, II, and III for this reaction, which parallels the solution polymerization, was almost 100 percent. Only 1 percent of the dibenzimidazole (V) precursor was found. Although some diimide (VI) precursor might also have been expected, it was not observed.

When the 10 percent amide-acid-amine/DMF solution was heated at 152-154° for one hour, both imide-amine (II) and benzimidazole-acid (III) were again isolated in substantial yields. This is in contrast to a reported 94 percent yield of imide-amine (II) obtained under similar conditions (2). Inspection of the spectra of these two compounds, Figures 2 and 3, shows that in the carbonyl region the benzimidazole-acid (III) exhibits no absorption

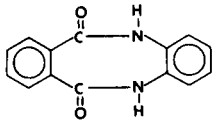
TABLE I

Elemental Analyses of Model Compounds

Model Compound	Formula	Calculated					Found			
		C	H	N	O	Cl	C	H	N	O	Cl
Amide-Acid-Amine (I)	$C_{14}H_{12}N_2O_3$	65.62	4.72	10.93	18.73	----	65.94	4.60	11.01	18.45	----
Imide-Amine (II)	$C_{14}H_{10}N_2O_2$	70.58	4.23	11.76	13.43	----	70.17	4.09	12.04	13.63	----
Benzimidazole-Acid (III)	$C_{14}H_{10}N_2O_2$	70.58	4.23	11.76	13.43	----	70.27	4.08	12.49	13.52	----
Pyrrone Model (IV)	$C_{14}H_8N_2O$	76.35	3.66	12.72	7.27	----	76.54	3.93	12.77	7.23	----
Dibenzimidazole (V)	$C_{20}H_{14}N_4$	77.40	4.55	18.05	----	----	76.76	4.87	18.12	----	----
Diimide (VI)	$C_{22}H_{12}N_2O_4$	71.74	3.28	7.61	17.37	----	71.88	3.43	7.86	17.46	----
Benzimidazole-Acid Hydrochloride	$C_{14}H_{11}N_2O_2Cl$	61.21	4.04	10.20	11.65	12.91	61.35	4.01	10.52	12.27	12.55
Benzimidazole-Amide-Imide (VIII)	$C_{28}H_{18}N_4O_3$	73.35	3.96	12.22	10.47	----	72.79	4.10	12.34	10.48	----

while the imide-amine (II) has several strong bands. Both have strong 1380 cm^{-1} bands and absorption in the 1660 cm^{-1} region. Furthermore, the intensity of the infrared absorption bands of the benzimidazole-acid are weak relative to those of the imide-amine and the latter masks the former in spectra of mixtures of II and III. For example, Figure 8 shows the spectrum of an equimolar mixture of the two compounds; the presence of the benzimidazole-acid zwitterion is not readily apparent. These observations along with the fact that both compounds have the same empirical formula probably explain why the contribution of the benzimidazole route in the reactions outlined in Scheme I has been difficult to recognize.

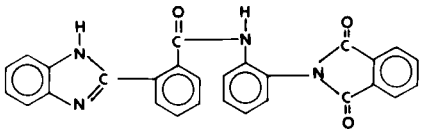
The eight-membered diamide (VII) shown below has been suggested as a possible intermediary to the Pyrrone structure (3,9). However, when its preparation (10) was



repeated, a very low yield of product was recovered which was separated into pure benzimidazole-acid (III) and diimide (VI). Since the diamide intermediate (VII) was not detected, it is considered unlikely that it is involved in the reactions leading to the Pyrrone model (IV). Paudler and Zeiler also were unable to obtain VII by the referenced preparation but were able to obtain the compound by another route (11).

The melt reaction between *o*-phenylenediamine and phthalic anhydride (3) was also run and afforded significant yields of 1:2 and 2:1 disproportionation products. Approximately 16 percent of dibenzimidazole (V) and 22 percent of diimide (VI) were obtained under melt conditions. Thus, it is apparent that the initial anhydride opening reaction under melt conditions does not yield the same 1:1 product that is obtained when the reaction is conducted in solution at room temperature.

A final experiment was conducted which more closely parallels the thermal cyclization of the precursor amide-acid-amine polymer. The amide-acid-amine model (I) was heated in the solid phase at 155° for 30 minutes and a mixture of products was obtained. Compound IV and benzimidazole-acid (III) accounted for 19 percent and 36 percent, respectively, of the recovered yield. Absence of imide-amine (II) indicates that the cyclic product (IV) apparently formed *via* the imide route. The remainder of the product was a compound which has been tentatively assigned as resulting from an intermolecular reaction between two amide-acid-amine molecules followed by the elimination of two moles of water. The proposed structure is given below. The infrared spectrum and characterizing bands for this benzimidazole-amide-imide are given



VIII

in Figure 9. The mass spectrum revealed a parent peak at m/e 458 and fragments typical of the amide-like structure. The compound converts to a 3:2 mixture of the Pyrrone model (IV) and dibenzimidazole (V) between 280-300°.

Implications for Polymer Synthesis.

A number of points can be made for consideration in work related to polymer synthesis. Foremost, these studies have indicated that competition between the intermediate imide-amine and benzimidazole-acid during cyclization of the precursor polymer is to be expected. However, as previously discussed, the presence of benzimidazole-acid may not be readily apparent in the infrared spectra of polymer due to zwitterion formation. The tendency for model species to disproportionate under melt conditions is of importance since the analogous reaction in the synthesis of the polymer could lead to a cross-linked structure. Since very little disproportionation product was obtained from the solution reaction, it is probable that the solution polymerization initially leads to a predominantly linear polymer. However, isolation of the dimeric species VIII indicates that intermolecular reactions may occur during thermal conversion of the precursor polymer if there is sufficient mobility in the polymer chains at that stage.

EXPERIMENTAL

Infrared measurements were made on potassium bromide pellets and recorded on the Perkin-Elmer Models 134 and 421 spectrophotometers. Melting points were obtained on the DuPont 900 Differential Thermal Analyzer using a 10°/minute temperature program. Nuclear magnetic resonance spectra were recorded on the Varian A-60A spectrometer and were run in deuterated dimethyl sulfoxide. Elemental analyses were performed by Huffman Laboratories, Inc., Wheatridge, Colorado, and are summarized in Table I.

All starting materials, unless noted, were obtained from commercial sources and were recrystallized several times before use. Solvents were used as received from the supplier.

A. Preparation of Model Compounds.

N-(*o*-Aminophenyl)phthalamic Acid (I).

A solution of 29.6 g. (0.20 mole) of phthalic anhydride in 148 ml. of DMF was added to a stirred solution of 21.6 g. (0.20 mole) of *o*-phenylenediamine in 108 ml. of DMF. The solution was stirred for 30 minutes and 750 ml. of water was added. White crystals, 40.8 g. (80%), were recovered, m.p. 147-150° (lit. (2) m.p. 151-152°).

N-(*o*-Aminophenyl)phthalimide (II).

A solution of 3.70 g. (0.025 mole) of phthalic anhydride in 37 ml. of DMF was added to a stirred solution of 2.70 g. (0.025 mole) of *o*-phenylenediamine in 27 ml. of DMF. The solution was stirred for 1 hour and 100 ml. of water was added. After 48 hours a small amount of crystalline amide-acid-amine (I) was recovered by filtration. Two hundred and fifty ml. of water was added to the filtrate and 1.71 g. (29%) of crude imide-amine (II) precipitated within 8 hours. Pure imide-amine was obtained by washing this precipitate with sodium carbonate and recrystallizing the insoluble portion from chloroform. Yellow needle-like crystals were obtained, m.p. 194-195° (lit. (2) m.p. 194-195°).

2-(*o*-Carboxyphenyl)benzimidazole (III).

A solution of 3.00 g. (0.02 mole) of *o*-carboxybenzaldehyde in 15 ml. of boiling ethanol was added to a solution of 2.16 g. (0.02 mole) of *o*-phenylenediamine in 11 ml. of boiling ethanol. The solution was boiled for 3 hours. The white precipitate which began forming after 1 hour was recovered by filtration from the cooled solution to yield 0.70 g. (15%) of crude benzimidazole-acid (III). The pure compound was obtained by recrystallization from ethanol/water, m.p. 245°.

This compound was also obtained by recrystallizing its hydrochloride (8) from 1:1 ethanol/water, or by boiling a 1 percent aqueous slurry of compound IV for 2 hours (until solution was accomplished). Upon cooling, benzimidazole-acid (III) crystallized from solution.

11*H*-Isoindolo[2,1-*a*]benzimidazol-11-one (IV).

This compound was prepared by sublimation from the imide-amine (II) at 200° and from the benzimidazole-acid (III) at 275°. Besides sublimation as a means of purification, the compound can be crystallized from diglyme to yield yellow needle-like crystals, m.p. 214-215° (lit. (2) m.p. 214-215°).

o-Phenylenebibenzimidazole (V), and *N,N'*-Diphthaloyl-*o*-Phenylenediamine (VI).

These two compounds were obtained as by-products of the melt reaction between phthalic anhydride and *o*-phenylenediamine (3). Phthalic anhydride, 7.40 g. (0.05 mole), and 5.40 g. (0.05 mole) of *o*-phenylenediamine were thoroughly ground and transferred to a round-bottom flask. The flask was purged with nitrogen and heated to 140° at approximately 3°/minute in a silicone oil bath. Vacuum was applied and the melt was maintained at 140° for 1 hour and cooled. The cake was pulverized and dissolved in 70 ml. of boiling acetic anhydride. The yellow needle-like crystals and clear diamond-shaped crystals which precipitated together from the cooled solution were manually separated. The yellow crystals were identified as the Pyrrone model (IV) (44%). The large clear crystals (22%) were recrystallized from benzene and identified as *N,N'*-diphthaloyl-*o*-phenylenediamine (VI), m.p. 302-305° (lit. (11) m.p. 298°).

A precipitate was produced when the filtrate was diluted with water. This was washed with diglyme and the insoluble portion was identified as *o*-phenylenebibenzimidazole (V) (16%). The white compound was purified by precipitation from acetic acid with water, m.p. 429-433°.

2-(*o*-Carboxyphenyl)benzimidazole Hydrochloride.

Separate attempts to repeat Arient's preparation (8) of 2-(*o*-carboxyphenyl)benzimidazole afforded only the hydrochloride salt of III as colorless needles which began to melt at 245°.

This compound was also formed by using dilute hydrochloric

acid in recrystallization of the benzimidazole-acid (III). As with the free base, the hydrochloride salt also converted to compound IV when heated at 275°.

N,N'-o-Phenylenephthalic Acid Diamide (VII).

Preparation of this compound was attempted according to the procedure given by Stetter (10). Separate solutions of 0.51 g. (0.0025 mole) of phthaloyl chloride (12) in 250 ml. of benzene and 0.54 g. (0.005 mole) of *o*-phenylenediamine in 250 ml. of benzene were prepared in two constant rate addition funnels which were attached to a 2 l. 3-neck round-bottom flask containing 750 ml. of benzene. Nitrogen was bubbled through the stirred reaction medium, the temperature taken to 75°, and the two reactants simultaneously added dropwise at identical rates in 5 hours. The solution was cooled and amine hydrochloride filtered. Solvent was then removed on a rotary evaporator and the residue (15% yield) was fractionally recrystallized from ethanol/water. The major crop was identified as diimide (VI) and the other as benzimidazole-acid (III). No diamide (VII) was isolated.

B. Reaction Study.

The reactivity of several of these compounds precluded the use of certain techniques for obtaining total product recovery. A quantitative chromatographic separation would have provided more meaningful information than did the unsophisticated separation methods used here. However, numerous thin layer and column chromatography attempts proved unsuccessful. Since the presence of the various components was more important than the actual ratio of products, elementary separation techniques were employed which afforded a good estimate of product recovery but did not allow the products to react further.

Room Temperature Solution Study.

A solution of 3.70 g. (0.025 mole) of phthalic anhydride in 35 ml. of DMF was added to a stirred solution of 2.70 g. (0.025 mole) of *o*-phenylenediamine in 27 ml. of DMF. The solution was stirred for 30 minutes at 25° and diluted with 150 ml. of water. After 24 hours, 0.40 g. of highly crystalline amide-acid-amine (I) was recovered. The filtrate was diluted at three 24-hour intervals with 100, 250, and 125 ml. of water and the solutions filtered after each addition. The combined yellow precipitates were washed with sodium carbonate and the insoluble fraction recrystallized from chloroform to yield imide-amine (II). When the base solution was acidified, benzimidazole-acid (III) as a white precipitate was obtained and recrystallized from ethanol/water. The original DMF/water mother liquor was taken to dryness *in vacuo*. During removal of the solvent, a minor fraction which converted thermally to dibenzimidazole (V) was recovered. A similar amount of diimide (VI) precursor might, therefore, have been expected but was not found. Additional imide-amine and benzimidazole-acid were obtained by base extraction of the dried residue. The following weight percents of products was calculated from a total recovery of 4.57 g.: amide-acid-amine (I), 9%; imide-amine (II), 59%; benzimidazole-acid (III), 31%; dibenzimidazole (V) precursor, 1%.

Heated Solution Study.

A solution of 1.00 g. of amide-acid-amine (I) in 10 ml. of DMF was refluxed for 1 hour. The solvent was removed on a rotary evaporator and a yellow residue was obtained which was extracted with chloroform. Imide-amine (II), 0.28 g., was isolated from the chloroform extracts and 0.35 g. of crude benzimidazole-acid (III) remained as an insoluble residue.

Amide-Acid-Amine Melt Study.

A 1.00 g. sample of amide-acid-amine (I) was heated at 155° for 30 minutes. The compound melted, turned yellow, and solidified. The solid was ground and washed with sodium carbonate. The washings when acidified with hydrochloric acid afforded 0.26 g. of benzimidazole-acid (III). The residue insoluble to base extraction was further extracted with chloroform and 0.12 g. of soluble Pyrrone model (IV) and 0.32 g. of insoluble benzimidazole-amide-imide (VIII) were recovered. Essentially the same results were obtained by extracting the powder with chloroform before the base wash. Compound VIII was recrystallized from DMF/water, m.p. 282°. It converts to a 3:2 mixture of compound IV and compound V at its melting point. The mass spectrum of VIII exhibited major peaks at m/e 458, 237, 221, and 193. The elemental analysis is given in Table I.

Acknowledgments.

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