Synthesis and Characterization of Isomeric
cis- and trans-Pyrrone Model Compounds

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Isomeric *cis*- and *trans*-imidazopyrrolones, obtained from the reaction of pyromellitic dianhydride and o-phenylenediamine, were prepared as models for pyrrone polymers. The characterization of these model compounds, which represent the repeat unit of the completely cyclized polymer, provided information which could not be obtained by studying the polymer itself. Isomerism was proven by the nuclear magnetic resonance spectra of soluble ester-benzimidazole derivatives. This study indicated that a single band around 1755 cm^{-1} should appear in the infrared spectrum of the completely cyclized polymer. The high melting points of the model imidazopyrrolones indicate the extreme thermal stability to be anticipated from perfectly formed pyrrone polymers.

Introduction.

Reactions between aromatic five-membered dianhydrides and bis(o-diamines) have produced a class of thermally stable polymers referred to as polyimidazopyrrolones, or pyrrones (1-6). Theoretically, both *cis*- and *trans*-imidazopyrrolone isomers can exist in the repeat units of the fully cyclized polymer (4). In fact, the broadness of the infrared absorption in the carbonyl region of certain pyrrones has been attributed to the presence of a mixture of these *cis* and *trans* isomers (3,5). Since the intractable nature of the cyclized polymer makes the separation and/or identification of these isomers virtually impossible, the contribution of *cis-trans* isomerism to the total pyrrone chemistry cannot be fully appreciated. The study of model compounds was, therefore, considered necessary to provide basic information on the polymer and to aid in the interpretation of its infrared spectra.

The model compounds for this study were prepared by reacting pyromellitic dianhydride and o-phenylenediamine. The reactions involved in their syntheses and proof of structure are given in Scheme I. Similar studies, particularly those pertaining to dye chemistry (7,8), resulted either in a mixture of the *cis* and *trans* isomers V and VI or a compound proposed to have the *trans* structure VI. However, no structural proof was offered and the isolation of the *cis* isomer was not reported. In this work, the isolation and characterization of these isomeric pyrrone model compounds is reported, and the results provide new information on the chemistry of analogous polymer systems.

Results and Discussion.

The isolation of the pure imidazopyrrolone isomers V and VI was complicated by the formation of a *meta*- and *para*-(amide-acid-amine) mixture I which resulted from the initial ring opening reaction between pyromellitic dianhydride and o-phenylenediamine. The cyclization of mixture I led to a sequence of reactions terminating in an inseparable mixture of V and VI. Thus, the approach for obtaining each of the key *cis*- and *trans*-pyrrone models had to be dependent on the isolation and subsequent cyclization of each of their respective benzimidazole-acid intermediates III and IV and had to bypass the imide intermediate II which would have cyclized to a mixture of V and VI. The isolation of the isomerically pure *cis*-and *trans*-imidazopyrrolone structures could be assured only when the benzimidazole route was followed.

The isomeric mixture of amide-acid-amines I was heated in solution to yield a mixture of compounds III and IV. A separation of these two intermediates was achieved due to their difference in solubility in the reaction solution. However, the isomerism of their respective structures could not be determined due to poor solubility in nmr solvents. The reaction of each of these two isomers with acetic anhydride yielded the two isomerically pure pyrrone models. Again, insolubility prevented the determination of nmr spectra. However, the soluble ester derivatives VII and VIII were obtained by reacting each of the pyrrone isomers with sodium methoxide. Their nmr spectra are given in Figure 1. Chemical shifts near 500 ppm for the two aromatic protons on the

SCHEME I
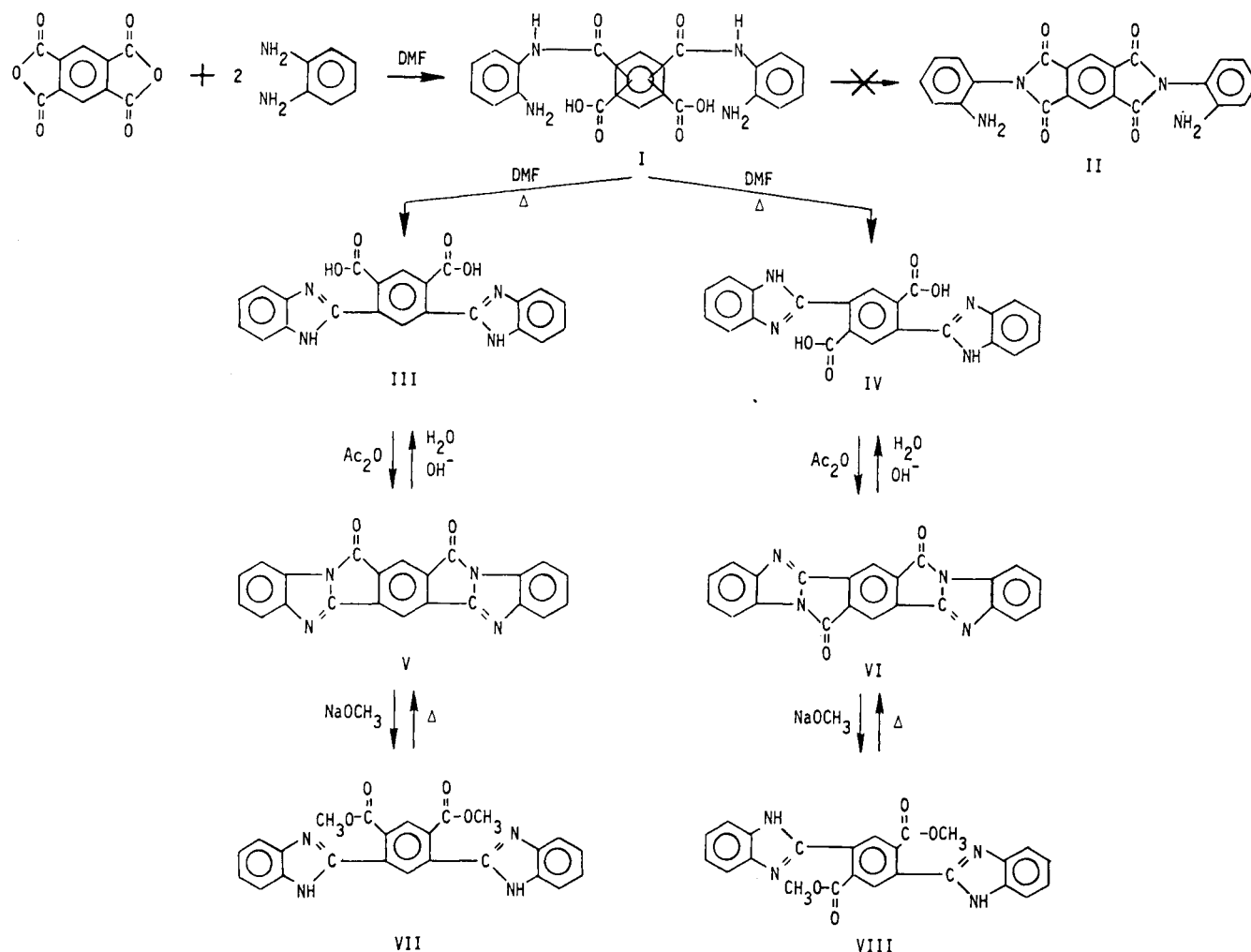
middle (anhydride) ring characterize these isomers. Since the protons are equivalent for the *para* isomer VIII and nonequivalent for the *meta* isomer VII, the chemical shifts appear as one (494 ppm) and two peaks (489 and 512 ppm), respectively. This correlation proves the orientation of the *cis-* and *trans*-pyrrone models V and VI and their respective benzimidazole intermediates III and IV, since all configurations are retained for the reactions shown in Scheme I. This was proven by thermal conversion of VII and VIII to the respective *cis-* and *trans*-pyrrone models V and VI which, in turn, were hydrolyzed to the original benzimidazole intermediates III and IV.

The ir spectra of the compounds shown in Scheme I are given in Figures 2-9. Prominent characterizing bands are noted. The spectra for the amide-acid-amine I, Figure 2, and the imide-amine II, Figure 3, are similar to those for the corresponding model compounds obtained from phthalic anhydride and o-phenylenediamine (9). In addi-

tion, the absence of carbonyl absorption in the spectrum of the *para*-benzimidazole-acid, Figure 5, indicates that the compound is a zwitterion, as was the corresponding compound from phthalic anhydride. However, the spectrum of the *meta*-benzimidazole-acid III, Figure 4, is not completely understood. The presence of some absorption around 1700 cm^{-1} suggests that this isomer may be only partly ionized. The spectra of the *meta-* and *para*-benzimidazole-ester models VII and VIII, Figures 8 and 9, are almost identical and could not be used to distinguish between the isomers.

The infrared spectra of the *cis-* and *trans*-pyrrone models, V and VI, are given in Figures 6 and 7 and are characterized only by subtle differences. One difference is the reversal in relative intensities of the 1620 cm^{-1} -C=N- and the 1375 cm^{-1} imide-related bands. Also, the carbonyl absorption for the *cis* isomer V occurs as a single band at 1755 cm^{-1}, while the *trans* isomer VI exhibits

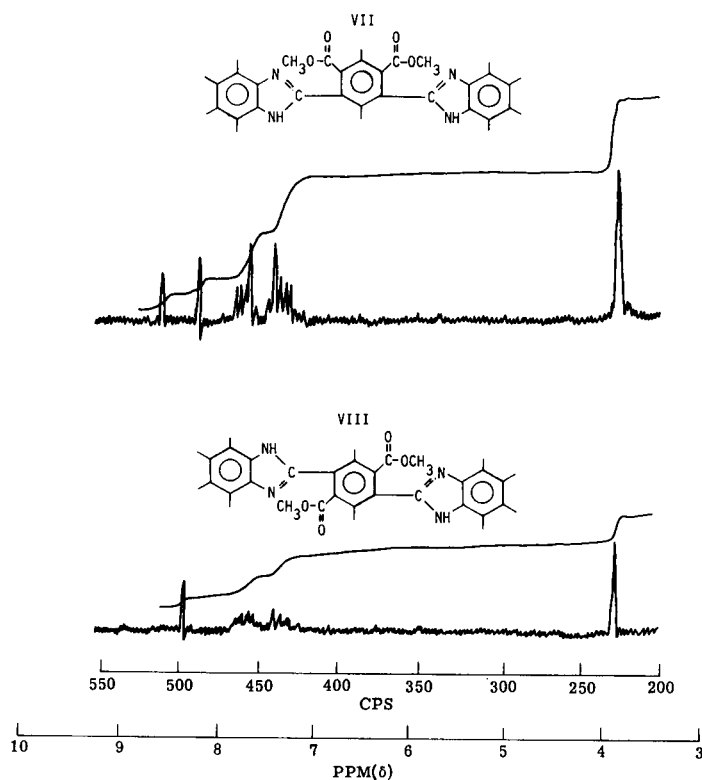Figure 1.- Nmr spectra of meta-(VII) and para-(VIII) benzimidazole-ester derivatives.

maximum absorption at 1762 cm⁻¹ with a small shoulder at 1751 cm⁻¹. The carbonyl absorption appears as a single band at 1755 cm⁻¹ in the spectrum of an equimolar mixture of the two isomers. Therefore, the doublet which appears in the carbonyl region of certain cured pyrrone polymers (10) and which is split by as much as 30 cm⁻¹ is probably not due solely to *cis* and *trans* isomerism in the imidazopyrrolone moieties.

An important point to note is that the corresponding pyrrone model IX obtained from phthalic anhydride and o-phenylenediamine has only one carbonyl group and yet
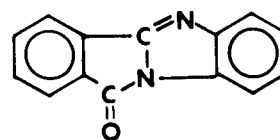
IX

exhibited a doublet at 1760 and 1738 cm⁻¹ (9). This was attributed to Fermi resonance arising through interaction of the first overtone of an 872 cm⁻¹ band with the fundamental carbonyl absorption. This absorption occurred at 847 cm⁻¹ and 854 cm⁻¹ for V and VI, respectively, and consequently was too low in wavenumber to couple with the fundamental carbonyl band.

The uv spectra of the two pyrrone isomers are given in Figure 10. The slightly more complicated spectrum of the *trans* isomer was consistent with the more highly conjugated nature of its structure. The *trans* isomer was bright orange while the *cis* isomer was a golden color. The orange substance reported by Arient was probably the *trans* isomer, as proposed (7).

Finally, the extremely high melting points of these two isomers provided an indication of the thermal stability that could be expected from true pyrrone polymers, *i.e.*, those containing only fully-cyclized imidazopyrrolone units. The *cis* isomer V melted at 405-410° and the *trans* isomer VI melted at 447-455°.

EXPERIMENTAL

Melting points were determined on a Dupont 900 Differential Thermal Analyzer using a 10°/minute temperature program. Nmr spectra were run in deuterated dimethyl sulfoxide on a

TABLE I

Elemental Analysis of Model Compounds

| Compound	Formula	Calculated				Found			
		C	H	N	O	C	H	N	O
I	$C_{22}H_{18}N_4O_6$	60.83	4.17	12.90	22.10	60.45	4.41	12.54	22.18
II	$C_{22}H_{14}N_4O_4$	66.33	3.54	14.06	16.07	66.05	3.79	13.37	16.14
III	$C_{22}H_{14}N_4O_4$	66.33	3.54	14.06	16.07	65.95	3.69	14.33	16.06
IV	$C_{22}H_{14}N_4O_4$	66.33	3.54	14.06	16.07	65.62	3.84	13.67	16.62
V	$C_{22}H_{10}N_4O_2$	72.93	2.78	15.46	8.83	73.13	3.01	15.61	9.24
VI	$C_{22}H_{10}N_4O_2$	72.93	2.78	15.46	8.83	73.10	3.11	15.62	9.21
VII	$C_{24}H_{18}N_4O_4$	67.60	4.25	13.14	15.01	67.34	4.41	13.04	15.30
VIII	$C_{24}H_{18}N_4O_4$	67.60	4.25	13.14	15.01	67.32	4.14	12.68	15.39
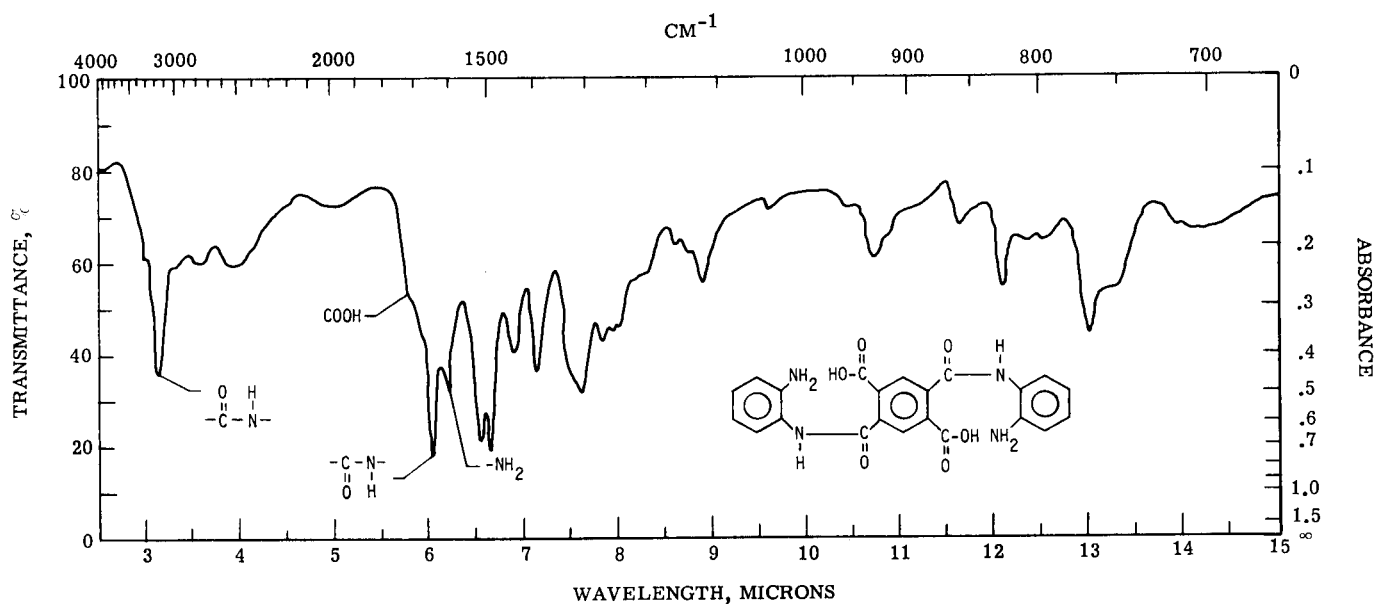
Figure 2.- Infrared spectrum of amide-acid-amine I.
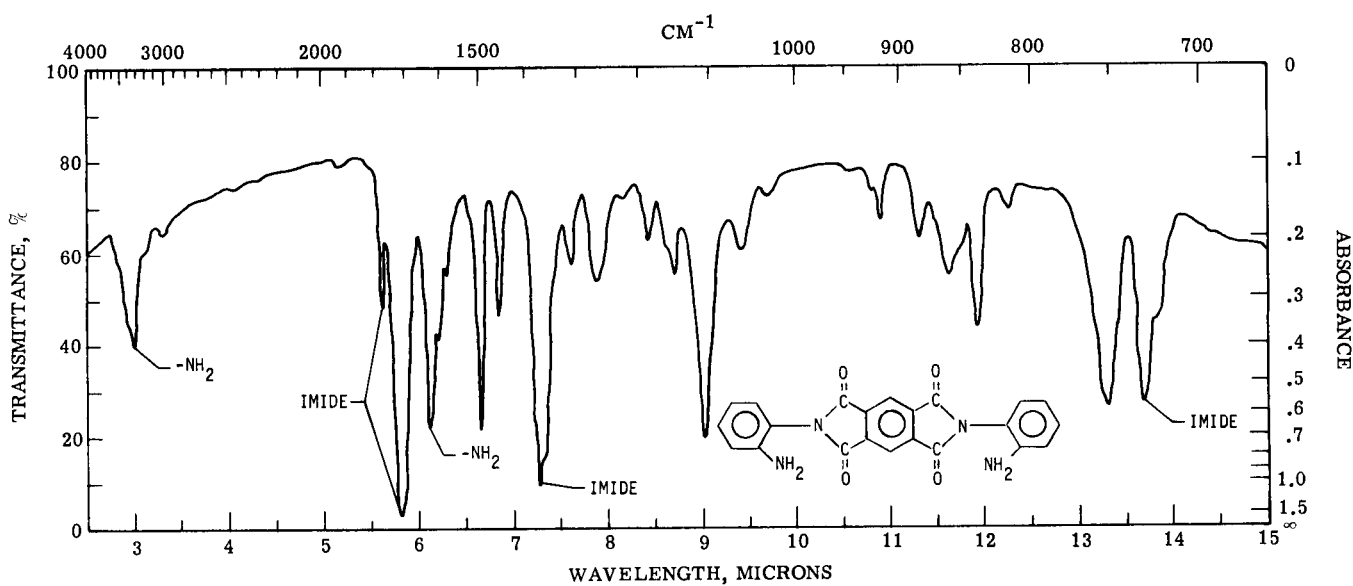

Figure 3.- Infrared spectrum of imide-amine II.

Varian A-60A spectrometer. Ir measurements were made on potassium bromide pellets using Perkin-Elmer Models 137B and 421 spectrometers. The uv spectra were determined in dimethyl sulfoxide with a Beckman Model DK-1 spectrophotometer.

Huffman Laboratories, Inc., Wheatridge, Colorado, performed the elemental analyses. The results are summarized in Table I.

All starting materials were obtained from commerical sources and were sublimed or recrystallized several times before use. Solvents were used as received from the supplier.

Amide-acid-amine (I) as Isomer Mixture.

A solution of 6.54 g. (0.03 mole) of pyromellitic dianhydride (PMDA) in 65 ml. of dimethylacetamide (DMAc) was added to a stirred solution of 6.48 g. (0.06 mole) of o-phenylenediamine in 65 ml. of DMAc. The solution was stirred for 30 minutes and diluted with 700 ml. of benzene. Filtrations after 24 hours and 192 hours yielded 4.69 g. (36%) and 3.80 g. (29%), respectively, of crystalline amide-acid-amine I. Soxhlet extraction of the first crop for 10 hours with benzene removed complexed DMAc and
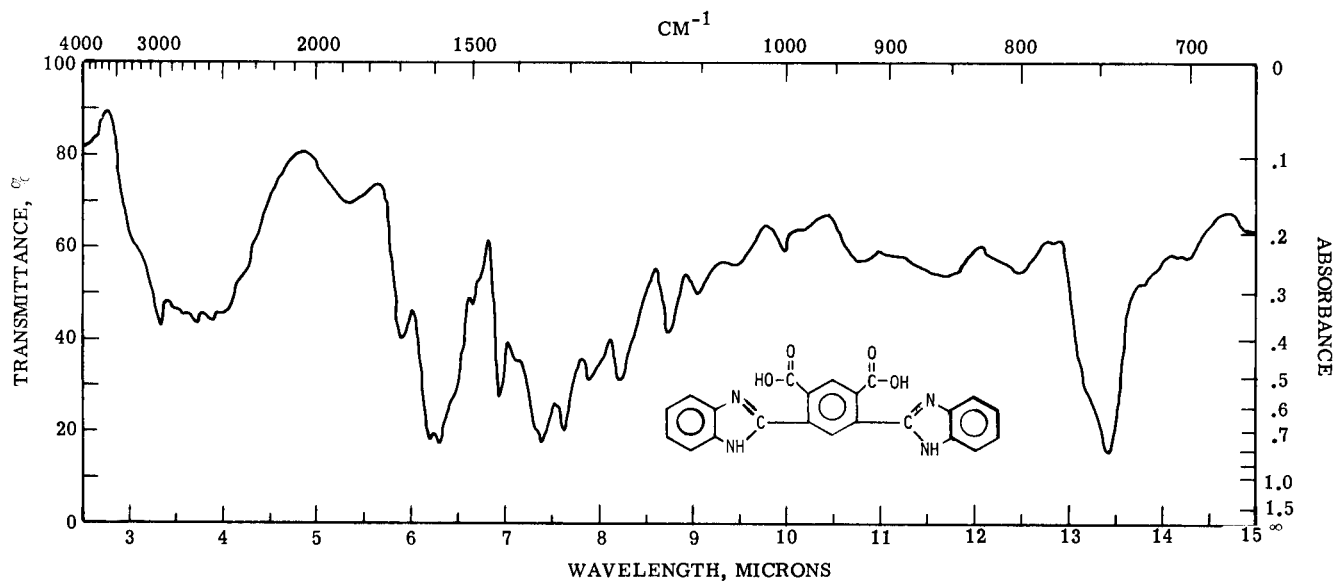
Figure 4.- Infrared spectrum of <u>meta</u>-benzimidazole-acid III.
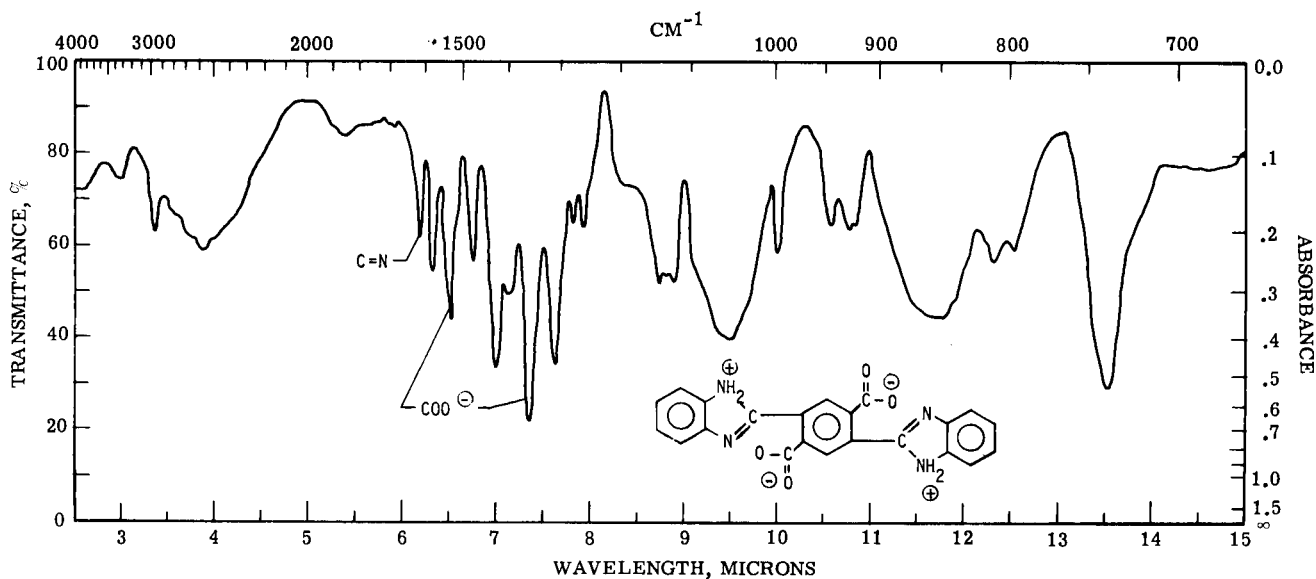
Figure 5.- Infrared spectrum of <u>para</u>-benzimidazole-acid IV.

afforded a colorless, crystalline analytical sample which exhibited an endotherm between 225-260° but did not melt. All attempts to separate the *meta* and *para* isomers were unsuccessful.

N,N'-Bis(o-aminophenyl)pyromellitimide (II).

A slurry of 50 ml. of ethanol, 5 ml. of concentrated hydrochloric acid, and 2.0 g. of amide-acid-amine I was boiled for 1 hour and filtered hot. The insoluble imide-amine hydrochloride residue when washed with water afforded 0.4 g. (22%) of imide-

amine II. The brownish-red compound, which was purified by crystallization from acetone, exhibited an endotherm between 249-265° but did not melt.

4,6-Bis(2-benzimidazolyl)-1,3-benzenedicarboxylic Acid (III) and 3,6-Bis(2-benzimidazolyl)-1,4-benzenedicarboxylic Acid (IV).

A solution of 21.8 g. (0.1 mole) of PMDA in 220 ml. of dimethylformamide (DMF) was added to a stirred solution of 21.6 g. (0.2 mole) of o-phenylenediamine in 216 ml. of DMF.
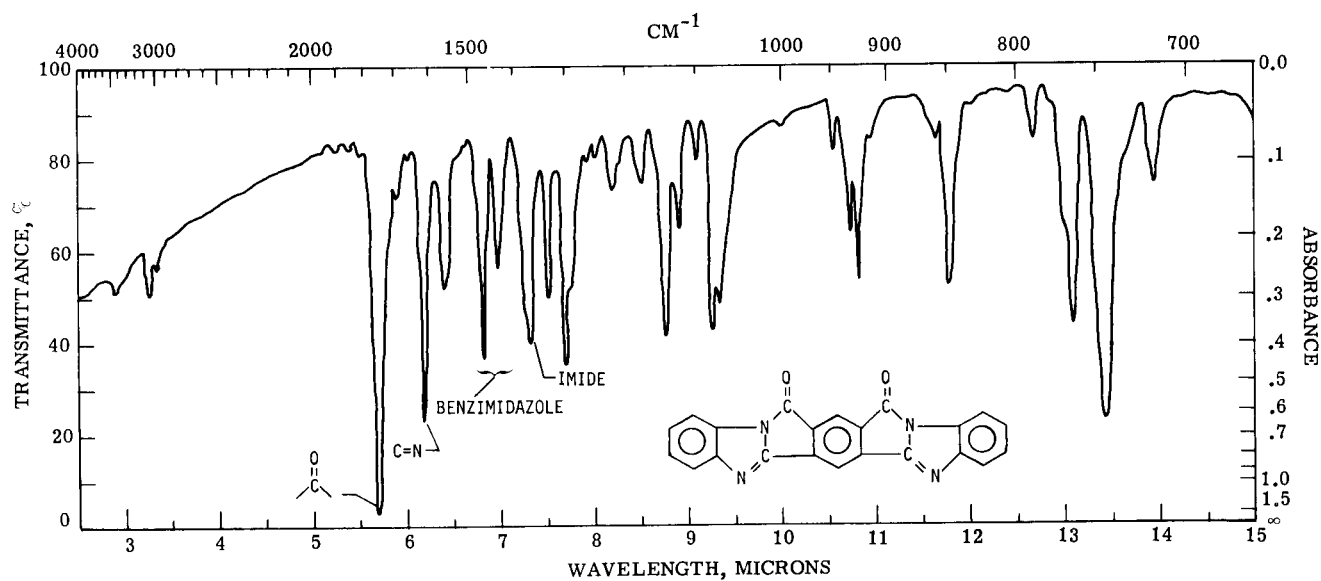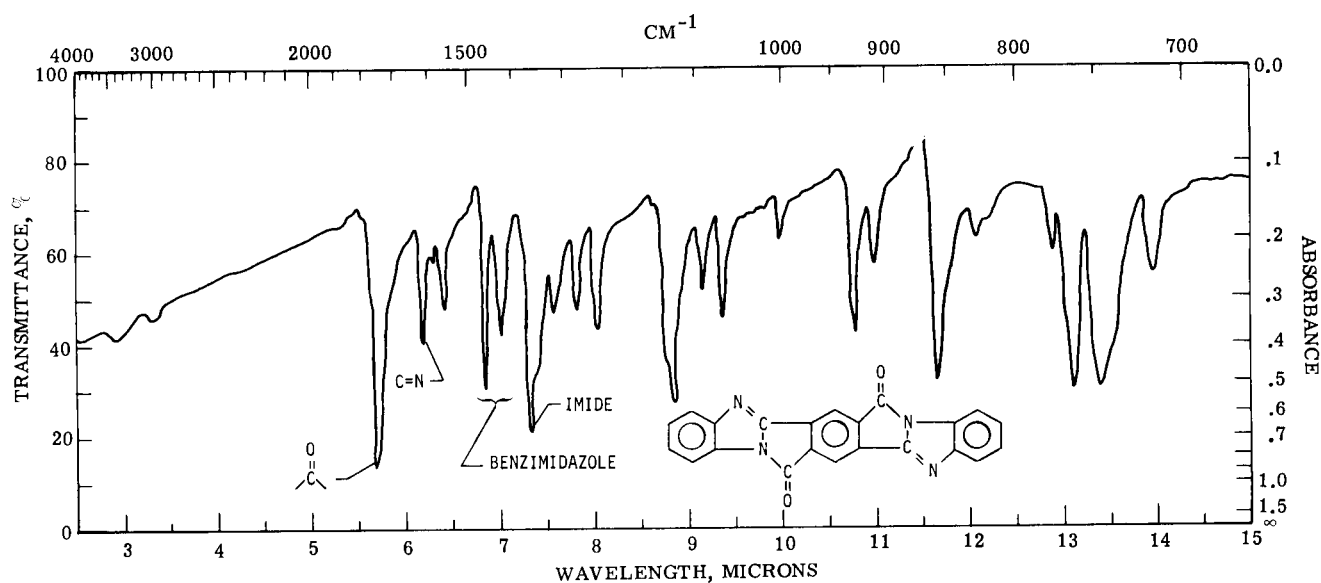
Figure 6.- Infrared spectrum of cis-imidazopyrrolone V.

Figure 7.- Infrared spectrum of trans-imidazopyrrolone VI.

Stirring was continued for 1 hour at room temperature. The resultant solution of amide-acid-amine I was then refluxed for 1 hour, during which time a precipitate formed. The solid was recovered and washed several times with benzene to yield 10.85 g. of analytically pure para-benzimidazole-acid IV. The yellow powder did not melt but displayed an endotherm between 315-355°.

The original DMF filtrate was concentrated on a flash evaporator and precipitated by pouring into benzene in a blendor. The precipitate, 25.7 g., was partly dissolved in an aqueous solution containing 6.9 g. of sodium carbonate. The mixture was filtered and the filtrate acidified ($pH \sim 4$) with hydrochloric acid to yield 12.0 g. of crude meta-benzimidazole-acid III. A white, crystalline analytical sample of III was obtained by crystallizing
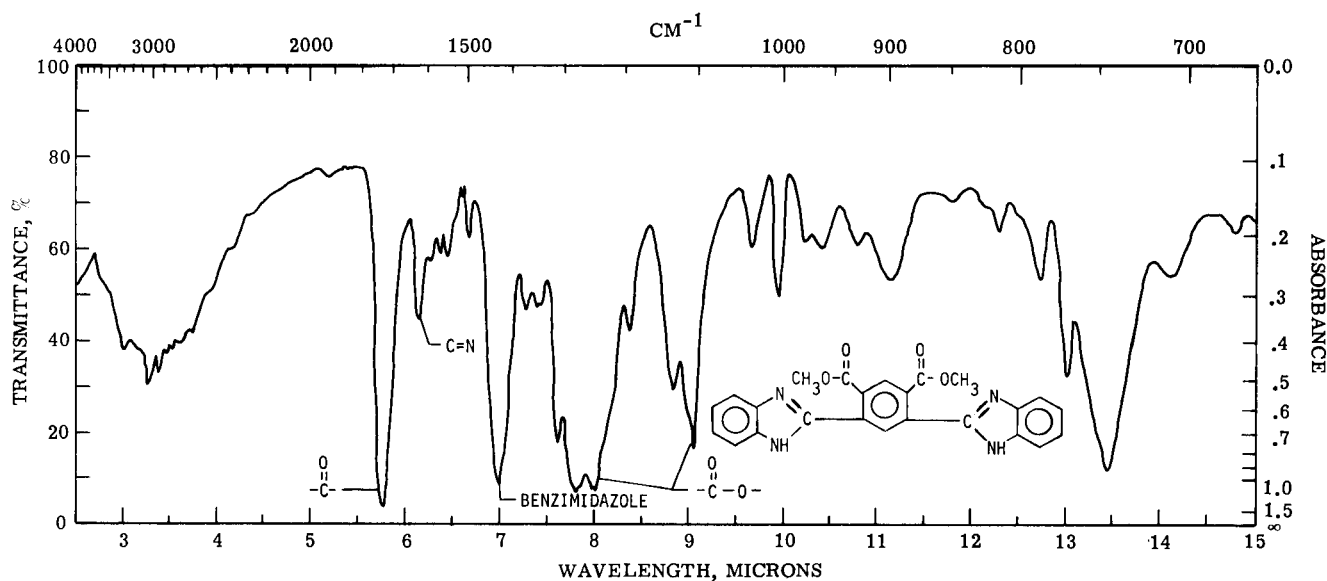
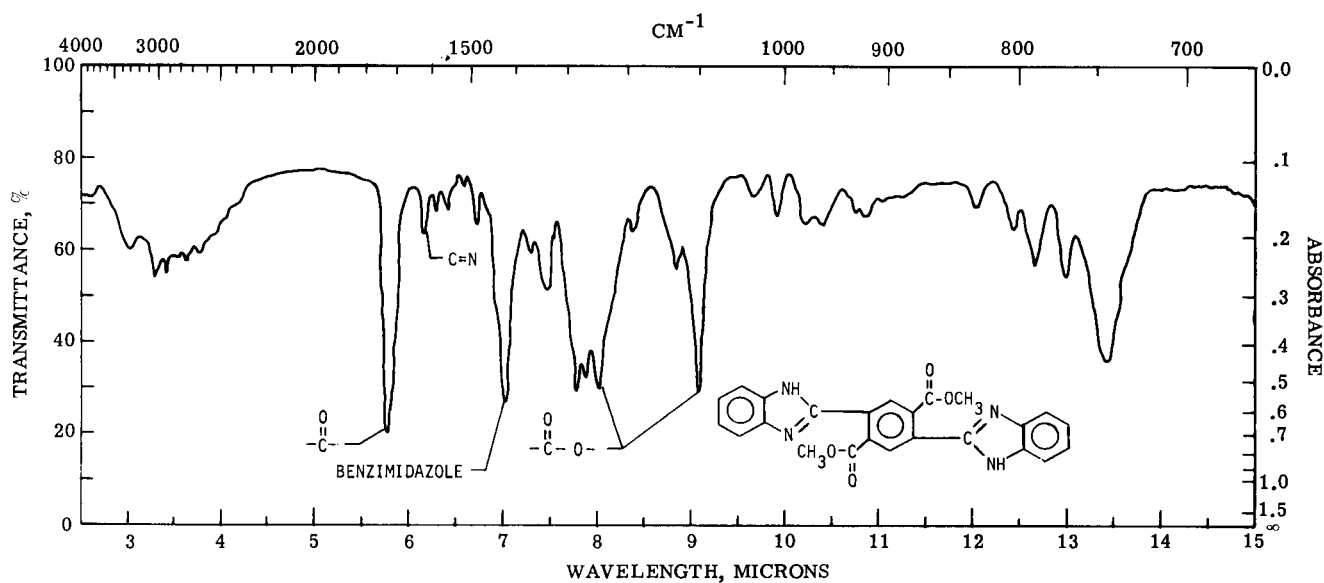Figure 8.- Infrared spectrum of meta-benzimidazole-ester VII.

Figure 9.- Infrared spectrum of para-benzimidazole-ester VIII.

the crude product twice from pyridine and vacuum drying at 100° for 2 hours. The compound exhibited an endotherm between 225-265° but did not melt. The base insoluble residue could not be identified but was not amide-acid-amine I or imide-amine II.

13H,15H-Bisbenzimidazo[1,2-a:1′,2′-a′]benzo[1,2-c:4,5-c′]dipyrrole-13,15-dione (V).

A 3.00 g. (0.0075 mole) slurry of meta-benzimidazole-acid III in 30 ml. of acetic anhydride was refluxed for 1 hour and filtered

hot. The residue was washed with benzene yielding 2.01 g. (74%) of a golden powder. Vacuum sublimation at 260° yielded the purified *cis* isomer V, m.p. 405-410°.

7H,15H-Bisbenzimidazo[1,2-a:1′,2′-a′]benzo[1,2-c:4,5-c′]dipyrrole-7,15-dione (VI).

The acetic anhydride cyclodehydration was repeated on 3.00 g. (0.0075 mole) of para-benzimidazole-acid IV and 2.50 g. (92%) of an orange powder was obtained. Vacuum sublimation at 260°
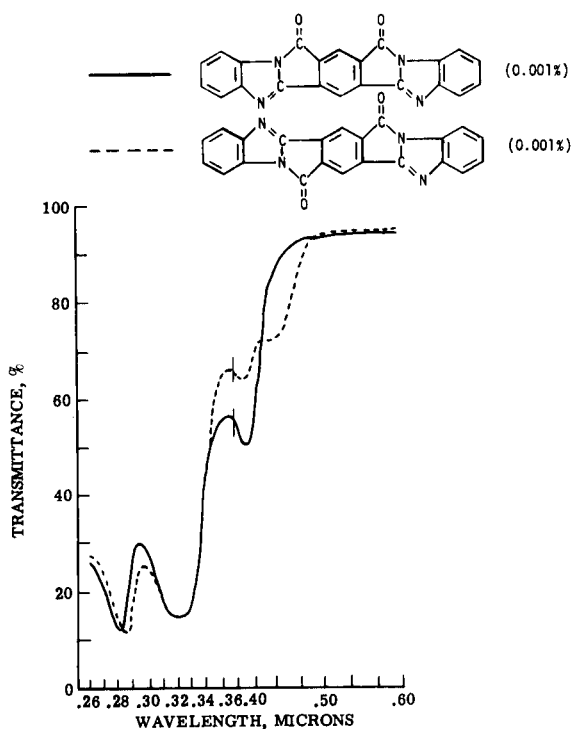
Figure 10.- UV spectra of cis and trans Pyrrone models.

yielded the purified *trans* isomer VI, m.p. 447-453°.

Dimethyl 4,6-Bis(2-benzimidazolyl)-1,3-benzenedicarboxylate (VII).

Sodium methoxide, 0.61 g. (0.110 mole), was added to 2.00 g. (0.0055 mole) of *cis* isomer V slurried in 35 ml. of ethanol. The

mixture was refluxed for 1 hour, poured into 100 ml. of water, and 1.85 g. (79%) of the *meta* ester VII was obtained. The compound was purified by crystallization from methanol followed by heating 4 hours at 110° in vacuum to remove complexed solvent. The colorless crystals exhibited an endotherm at 205-230° but did not melt.

Dimethyl 3,6-Bis(2-benzimidazolyl)-1,4-benzenedicarboxylate (VIII).

The reaction with sodium methoxide was repeated on 2.00 g. (0.0055 mole) of *trans* isomer VI and yielded 2.13 g. (91%) of the *para* ester VIII. Crystallization from chloroform yielded pale yellow, nonmelting crystals which exhibited an endotherm at 215-235°.

Acknowledgements.

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