# Polymorphism in 2,2'-Diphenyl-5,5'-bibenzimidazole

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The characterization of 2,2'-diphenyl-5,5'-bibenzimidazole (I) presented an unanticipated problem because of its enigmatic melting behavior. In the course of optimizing the preparative procedure by thermal condensation of 3,3'-diaminobenzidine and phenyl benzoate, a high yield of product melting at 411° was obtained. Previous workers reported melting points of 332-333° (1), 350-352° (2), and 358° (3). Moreover it was previously reported (3) that the high melting (over 360°) product is actually 2,2'-diphenyl-2-hydroxy-2,3-dihydro-5,5'-bibenzimidazole (II) which after heat treatment at 360° dehydrates to form I, m.p. 358°. These findings are not confirmed by the present authors. It has in fact been demonstrated that the two melting points 340° and 417° (melting endotherms by differential thermal analysis) or 350° and 411° (uncorrected melting points in a heated chamber) represent two different solid modifications of I.

Gray and Shulman (3) reported the synthesis of II by thermal condensation (275-300°) of 3,3'-diaminobenzidine with phenyl benzoate. After recrystallization from glacial acetic acid-ethyl ether, II did not melt below 360°. Further heating of II in vacuo at 360° or the action of either concentrated sulfuric acid or warm glacial acetic acid on II converted it to I, m.p. 358° (Eq. I). By differential thermal analysis (DTA) they demonstrated that I exhibits a sharp endotherm at 400°.

II.

I.
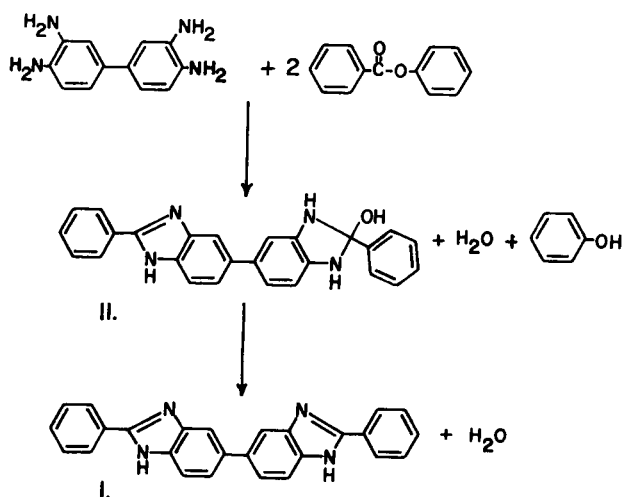
EQUATION I.

On reheating it exhibited an endotherm at 350°. From the DTA data it was concluded that the inflection at 400° was a dehydration endotherm which converted II to I. Compound I then exhibits a melting endotherm at 350° on reheating. Further supporting evidence for the structure assigned to II included accurate elemental analysis, mass spectrometric thermal analysis which indicated that water was indeed evolved at 400° and X-ray powder diffraction patterns which revealed that I and II had different and unique patterns. No significant differences were reported in the infrared spectra of I and II. This observation was attributed to the fact that the -OH and -NH vibrations are hydrogen bonded and not readily separated. Ultraviolet data revealed that the spectra of I and II were identical in sulfuric and glacial acetic acid in spite of the fact that II is recrystallized from glacial acetic acid while sulfuric acid converts II to I.

The thermal condensation was repeated in this laboratory following the procedure previously reported (2,3). After completion of reaction, the product was heated under vacuum at 350-400° for two hours to effect removal of residual water and phenol and conversion of II to I. The product obtained melted at 411°. A portion of this product was heated (in melt) at 430° in a further attempt to effect dehydration to convert the higher melting II to lower melting I. After fusion the material melted at 406-410°. This solid was then purified by sublimation (360°, vacuum) to give a buff colored microcrystalline solid which analyzed correctly for $C_{26}H_{18}N_4$ (I) and melted at 412.0-413.5°. DTA curves for this product are essentially identical before and after melting at 430° and compare to those reported (3) for II. The thermograms (Figure 1a,b) reveal the "dehydration" endotherm at 417° on first heating and the melting endotherm at 350° on the second heating cycle. Thus elemental analysis indicates the reaction product is I while melting point and DTA data indicate it is II..

A more careful examination of the DTA curves of this product reveals several interesting features. Increased instrument sensitivity reveals a sharp exotherm at 195° and a broad one at 280-320°. Typically a sample is cooled to about 150° before the reheating cycle which then reveals a single endotherm at 340° (Figure 1c). However, if the sample and instrument are cooled to room temperature before the reheat cycle, a mixed endo-exotherm

appears at 330° and is followed by the so-called dehydration endotherm at 417°. These observations suggest several phase transitions and that the observed melting point of the solid is a function of its thermal history.

A simple melting point experiment confirms the latter suggestion. A sample of reaction product which previously had been melted at 430° and quickly fused was placed in the melting point apparatus at room temperature and slowly heated. Between 325° and 350° the solid became microcrystalline in appearance. When the temperature reached 350° a second sample was introduced. The second sample liquified immediately while the original or "annealed" sample did not melt until 406-410°. An identical experiment on product which had been recrystallized from glacial acetic acid-ether gave the same results.

Consideration of these results make it reasonable to conclude that the products melting at 340° and 417° (DTA endotherms) are chemically identical and differ only in physical state. The lower melting polymorph (IA) can be prepared either by rapid cooling of a melt or recrystallization from glacial acetic acid-ether. The higher melting polymorph (IB) is then obtained by heat treatment of IA.

Infrared spectra of IA and IB reveal distinct differences which apparently result from the phase changes. Moreover, the spectral changes are gradual as shown by the spectra of samples as they are heated from room temperature to 430° (melt). Examination of typical spectra (Figures 2a,b) reveals that as IA changes to IB the bands at 890 cm⁻¹ and 1515-1560 cm⁻¹ decrease in intensity. Splittings, band sharpening and intensity changes are seen developing at 1420-1460, 1350-1390, 1265-1305, 755-805 and 640-690 cm⁻¹. After melting at 430°, the spectrum is identical to the room temperature spectrum. Finally after reannealing at 375°, the spectrum is again typical of IB.

Qualitative comparison of the spectral changes with DTA data support the suggestion of irreversible phase changes (Table I).
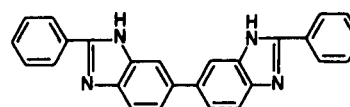
Structural features which might account for the observed phase changes are possibly related to the fact that I can exist in the three tautomeric forms.
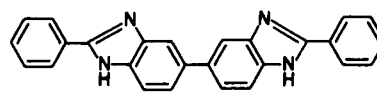
2,2'-DIPHENYL-5,5'-BIBENZIMIDAZOLE
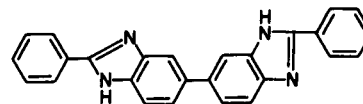
2,2'-DIPHENYL-5,6'-BIBENZIMIDAZOLE

2,2'-DIPHENYL-6,6'-BIBENZIMIDAZOLE

Indirect support for this suggestion is found in the fact that DTA thermograms for 2-phenylbenzimidazole (III) and 4,4'-di(benzimidazolyl)biphenyl (IV) do not reveal any exothermic inflections. This indicates that III and IV (neither of which are capable of tautomeric isomerism) do not undergo any polymorphic transformations. However the relationship between the polymorphism exhibited by
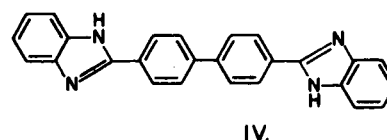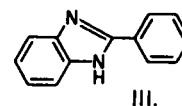

III.

IV.

Table I

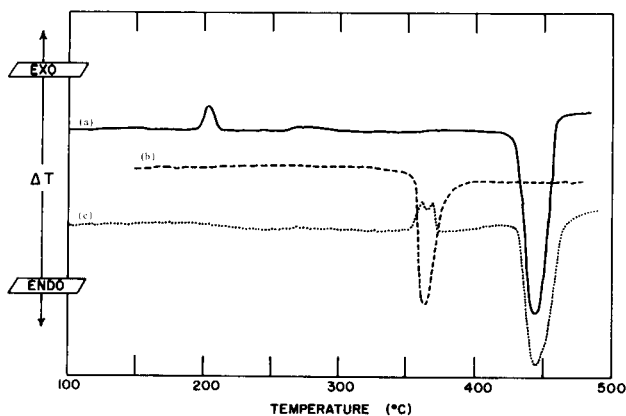| IR Observations		DTA Inflections	
Temp. Range °C	Observation	Temp. Range °C	Observation
25-120°	No significant change	25-120°	No inflection
120-200°	Minor changes	195°	Exotherm
280-300°	Minor changes	280-320°	Exotherm
300-400°	No changes	330-400°	No inflection
430°	Same as 25°	430° (liquid)	No inflection

FIGURE I. DTA THERMOGRAPHS OF 2,2'-DIPHENYL-5,5'-BIBENZIMIDAZOLE
(a) ———— FIRST HEATING CYCLE
(b) ----- SECOND HEATING CYCLE (from 150°)
(c) ········ THIRD HEATING CYCLE (from 25°)
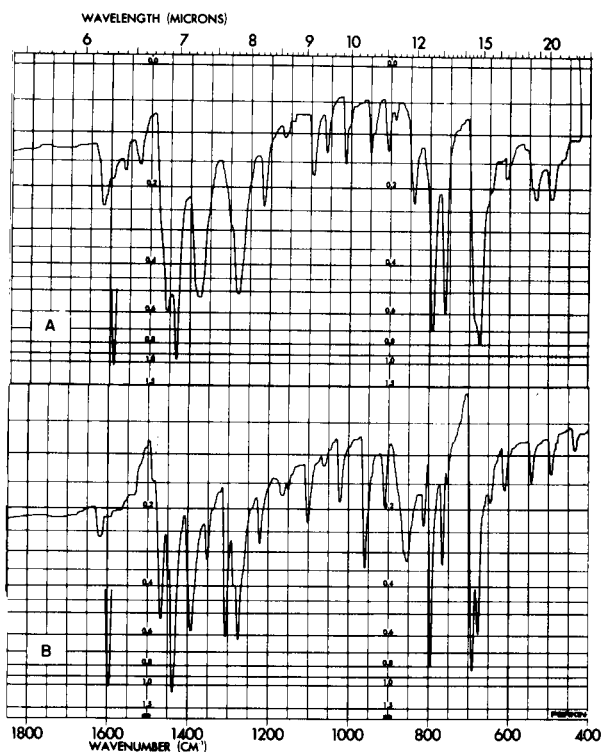

FIGURE 2.   INFRARED SPECTRA OF 2,2'-DIPHENYL-5,5'-BIBENZIMIDAZOLE
(A) TYPICAL SPECTRA OF LOW MELTING PHASE
(B) TYPICAL SPECTRA OF HIGH MELTING PHASE

compound I and tautomeric isomerism remains to be more convincingly demonstrated particularly since the isolation of tautomeric isomers of benzimidazoles is traditionally considered unlikely (4,5,6,7).

The results of Gray and Shulman (3) remain to be explained. Their most convincing points involved elemental analysis and mass spectrometric thermal analysis.

Both of these observations might be explained by the presence of an equivalent of water of hydration in compound I. If their higher melting product is indeed compound II, then its isolation was not repeated in the present investigation.

EXPERIMENTAL

Melting Points.

All melting points were determined with a Mel-Temp melting point apparatus and are recorded in °C.

Differential Thermal Analysis.

All DTA determinations were performed on a DuPont '900' Differential Thermal Analyzer. All determinations in this investigation were carried out at a heating rate of 20° per minute in a nitrogen atmosphere.

Infrared Spectra.

All infrared determinations were performed on a Perkin-Elmer 621 Spectrophotometer in potassium bromide pellets. Spectra were run and pellets prepared at room temperature on samples which previously had been heated under helium.

2,2'-Diphenyl-5,5'-Bibenzimidazole.

A mixture of 10.0 g. (0.050 mole) phenyl benzoate and 5.35 g. (0.025 mole) 3,3'-diaminobenzidine was heated under nitrogen for 1½ hours at 275-300°. After evolution of water and phenol was complete, the crude product was cooled, pulverized and heated under vacuum at 375-400° for two hours. The product was obtained in near quantitative yield and purified by vacuum sublimation at 360°.

Anal. Calcd. for $C_{26}H_{18}N_4$: C, 80.81; H, 4.69; N, 14.50. Found: C, 80.60; H, 4.78; N, 14.39.

Preparation of 4,4'-Di)2-benzimidazolyl)biphenyl.

A 150 g. portion of polyphosphoric acid (115%) was heated to 125° under a stream of helium for ½ hour. After cooling the acid to 70°, a premixed sample containing 5.0 g. of 4,4'-biphenyl-dicarboxylic acid and 4.60 g. of o-phenylenediamine was added while stirring vigorously. The temperature was raised to 185° over a half hour period and was maintained at that point for 5 hours. The progress of the reaction was monitored by infrared analysis of aliquots removed intermittently. After completion of the reaction, the mixture was cooled at 80° and poured over ice. The dark yellow precipitate was filtered, agitated in a blender with 200 ml. of acetone, refiltered, washed with 200 ml. of ether, and dried in a vacuum oven. The yellow solid was collected and weighed (69 g., yield, 75%). Infrared analyses indicated a very close similarity between this compound and other model compounds of the imidazole series.

The solid was sublimed at 365° and 5 microns pressure; the melting point of the light yellow sublimate was over 500° as checked by both a hot stage melting point block and a DTA unit.

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