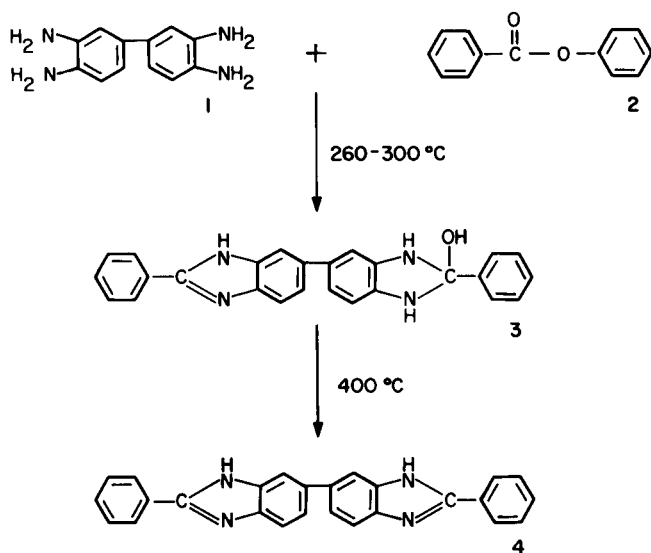


Hydrates of 2,2'-Diphenyl-5,5'-bibenzimidazole

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In an earlier paper (1) evidence was presented that indicated that the condensation of diphenyl isophthalate and 2,2',3,3'-tetraaminobiphenyl to poly-2,2'-(*m*-phenylene)-5,5'-bibenzimidazole is not complete below 400°. It was shown that the prepolymer formed at 260 to 500° contains both the benzimidazole and hydroxybenzimidazoline structures. A model compound study involving the thermal condensation of 2,2',3,3'-tetraaminobiphenyl (1) and phenyl benzoate (2) did not yield the expected 2,2'-diphenyl-5,5'-bibenzimidazole (4) but what was thought to be the previously unknown 2,2'-diphenyl-2-hydroxy-3-hydro-5,5'-bibenzimidazole (3).



Dehydration can be accomplished by heating to 400° or by the action of cold, concentrated sulfuric acid or hot glacial acetic acid. No significant difference between the infrared spectra of 3 and 4 could be seen since the -N-H and -O-H vibrations are hydrogen-bonded and not readily separated as discrete entities. Since the elemental analysis for 3 would be the identical to that of 4 monohydrate the assignment of structure 3 was largely based on the high temperatures required for the conversion (3 → 4). We now have direct evidence for two types of dehydration that can occur with this system and that the loss of water at high temperatures cannot be ascribed to

the complete aromatization of 3.

Figure 1 is a Differential Thermal Analysis (DTA) of a sample dried for six hours (vacuum) at 300°. No changes in the thermogram are noted until 410° where a sharp endotherm is observed. After cooling, a reheat indicates a melting point (endotherm) of 340-342° (reported for 4: 332-333° (3) and 350-352° (2)). Another sample was placed in a 75% relative humidity environment for four days and then dried for two days at 60°. A DTA thermogram of this material (Figure 2) shows a sharp endotherm at 100-105° not seen in the sample dried at the higher temperature. Except for this low temperature endotherm the two thermograms are essentially identical. Mass spectrometric thermal analysis confirmed that water was being evolved in two stages at temperatures consistent with the DTA data. The exotherm on the cooling curves indicates that supercooling occurs before solidification of the melt. It was found that a sample taken to 410°, cooled to 25° in a dry argon atmosphere, and kept at this temperature for several days will then show a DTA endotherm at 410-411° without the simultaneous evolution of water.

These data prove that the compound prepared *via* the condensation of 2,2'-3,3'-tetraaminobiphenyl and phenyl benzoate is not 3 but a very stable 4 hydrate.

EXPERIMENTAL

2,2'-Diphenyl-5,5'-bibenzimidazole Hydrate (4-Hydrate).

A mixture of 5.35 g. (0.025 mole) of 2,2'-3,3'-tetraaminobiphenyl and 10.0 g. (0.050 mole) of phenyl benzoate was heated for 1 hour at 275-300°. The crude material was recrystallized from warm glacial acetic acid to which ether was added to precipitate the product. The precipitate was filtered and dried, 300°, 0.1 Torr, for six hours.

Anal. Calcd. for C₂₆H₂₀N₄O: C, 77.21; H, 4.98; N, 13.85. Found: C, 77.90; H, 4.81; N, 13.39.

2,2'-Diphenyl-5,5'-bibenzimidazole Dihydrate (4-Dihydrate).

A 0.5 g. sample of 2,2'-diphenyl-5,5'-bibenzimidazole hydrate in an open culture plate was placed in a desiccator for four days at room temperature. The relative humidity in the desiccator was maintained at 75% by means of a saturated sodium chloride solution at room temperature. The sample was removed after four days and then dried at 60° in a flowing air oven for two days.

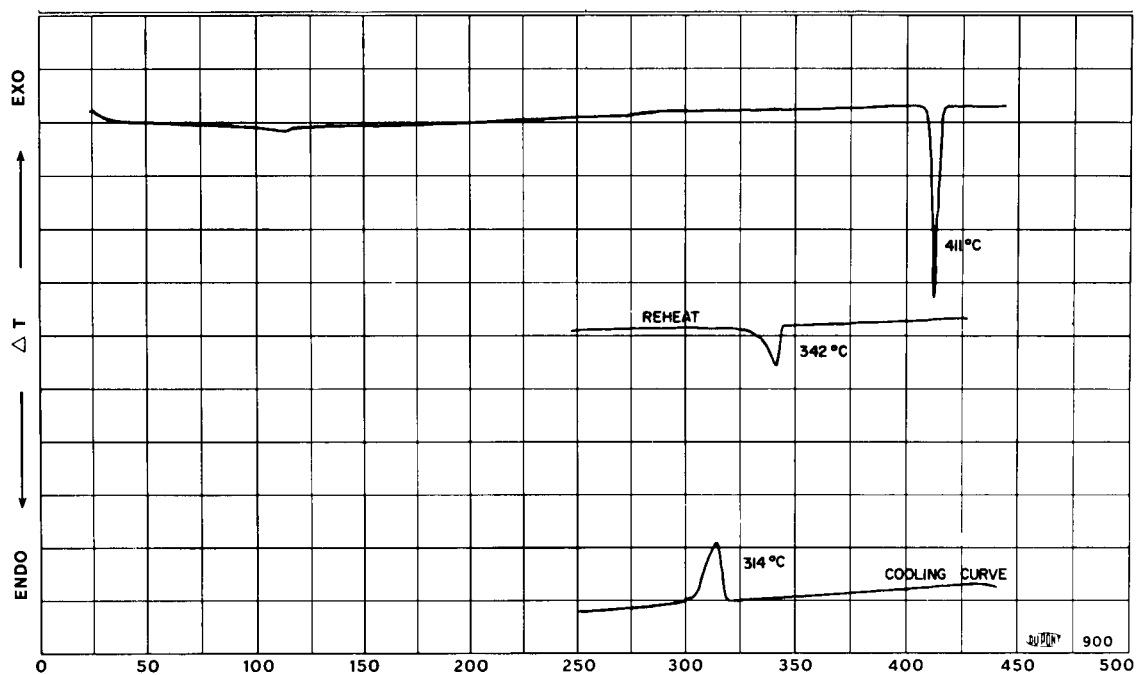


FIGURE 1. DIFFERENTIAL THERMAL ANALYSIS OF
2,2'-DIPHENYL-2-HYDROXY-3-HYDRO-5,5'-BIBENZIMIDAZOLE

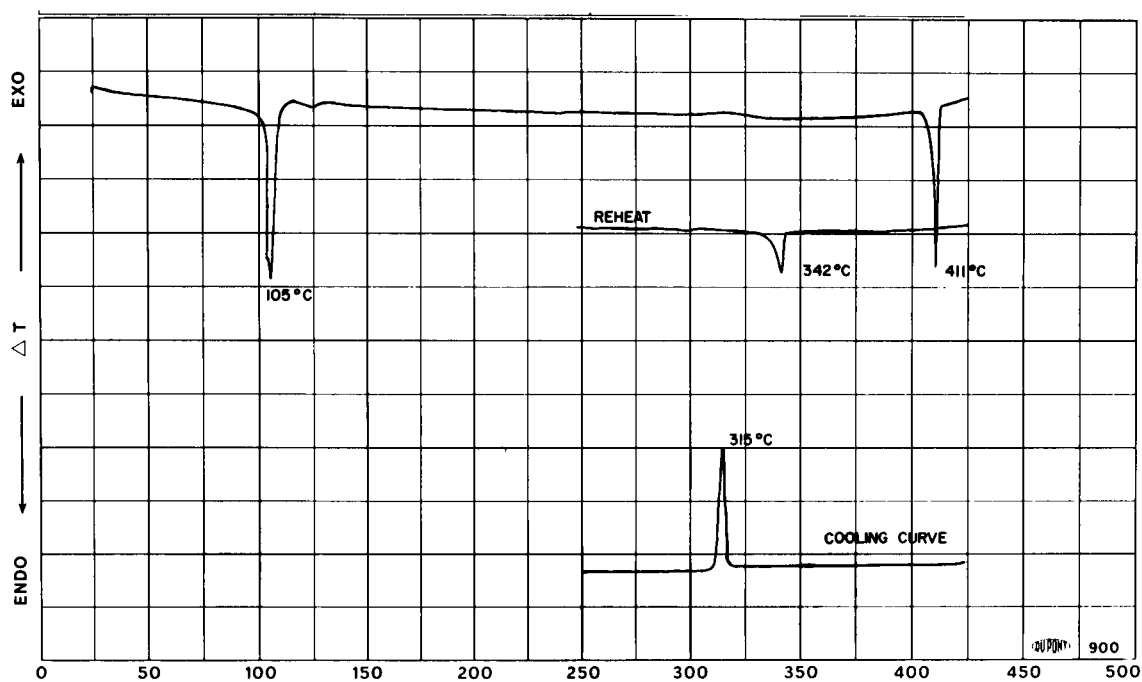


FIGURE 2. DIFFERENTIAL THERMAL ANALYSIS OF
2,2'-DIPHENYL-2-HYDROXY-3-HYDRO-5,5'-BIBENZIMIDAZOLE HYDRATE

Differential Thermal Analysis.

DTA thermograms were obtained with a DuPont 900 DTA apparatus at a heating rate of $10^{\circ}/\text{min.}$ in static air. Cooling curves were not programmed but averaged about $20^{\circ}/\text{min.}$

Mass Spectrometric Thermal Analysis.

A Varian M-66 Mass Spectrometer with a solid sample wand accessory was used for the mass spectrometric thermal analysis. The analyzer temperature was set at 100° and this temperature was used as the starting point for the run. The probe containing the sample was pushed into this temperature region and the mass range $5 \rightarrow 100$ was scanned at five minute intervals. With 4-dihydrate as the sample a large initial water peak was noted, however this peak decayed rapidly. The temperature of the probe was then raised to 400° in 50° increments. Water evolution peaked at

$350\text{-}400^{\circ}$ for both 4-hydrate and 4-dihydrate.

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