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# Benzimidazole Polymers from Aldehydes and Tetraamines

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## Synopsis

A new method for the preparation of benzimidazole polymers is described. The solution polymerization of aromatic tetraamines with isophthalaldehyde bis bisulfite adduct in *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (MP), and dimethyl sulfoxide (DMSO) produced polybenzimidazoles with viscosities ($\eta_{\mathrm{inh}}$) in the range of 0.3–0.5 measured in formic acid solution. Also a model compound study with benzaldehyde, benzaldehyde diethyl acetal, and benzaldehyde bisulfite adduct with *o*-phenylenediamine was carried out. The results showed that the reaction of benzaldehyde bisulfite adduct with *o*-phenylenediamine in DMAc as the solvent gave quantitative yields of 2-phenylbenzimidazole. Excellent yields of 2-phenylbenzthiazole, 2-phenylbenzoxazole, and 2-pyridylbenzimidazole were also obtained with the benzaldehyde bisulfite adduct and picoline-2-carboxaldehyde bisulfite adduct with *o*-aminothiophenol, *o*-aminophenol, and *o*-phenylenediamine. The reaction conditions for the preparation of the polymers and the model compounds are very mild and the reaction times range from 15 min to 1 hr for the model compounds and 3–5 hr for the polymers. Longer reaction times did not increase the viscosities of the polymers to any extent.

## MODEL COMPOUND STUDY

In 1961 Vogel and Marvel[1] were successful in preparing high molecular-weight polybenzimidazoles by the melt condensation of phenyl esters with aromatic tetraamines. More recently, Gray and co-workers[2] were successful in preparing poly-2,2′-(1,4-phenylene)-5,5′-bibenzimidazole from 3, 3′,-4,4′-tetraaminodiphenyl and 1,4-diacetylbenzene using a reaction initially described by Elderfield and Meyer[3] for preparaing simple benzimidazoles. A model compound study of this reaction using acetophenone and *o*-phenylenediamine showed that methane was evolved in the final stage of the reaction.

Another method which appeared to be promising for the preparation of polybenzimidazoles is the condensation of aldehydes with amines. The reaction of benzaldehyde with *o*-phenylenediamine has been reported several times in the literature,[4,5] but side reactions, such as the formation of disubstituted benzimidazoles (aldehydines), have prevented this reaction from being useful as a means of producing polymers.

In order to determine if aromatic aldehydes and their derivatives would be useful in the formation of heterocyclic polymers, a systematic study of the condensation of benzaldehyde (I), benzaldehyde diethyl acetal (II), benzaldehyde bisulfite adduct (III), and picoline-2-carboxaldehyde bisulfite adduct (IV) was carried out in DMF and DMAc with *o*-phenylenediamine (V), *o*-aminothiophenol (VI), and *o*-aminophenol (VII). The products obtained in this study were 2-phenylbenzimidazole (VIII), 2-phenylbenzthiazole (IX), 2-phenylbenzoxazole (IX), and 2-pyridylbenzimidazole (XI). The results of this study are outlined in Table I.

TABLE I
Model Compounds

| Reactants | Solvent | Time heated in nitrogen, hr | Time heated in air, hr | Product obtained | Yield, % |
|---|---|---|---|---|---|
| I, V | DMF | 2 | 20 | VIII | 25–31 |
| I, V | 10% HOAc–DMF | 2 | 18 | VIII | 26 |
| II, V | DMF | 2 | 18 | VIII | 26 |
| II, V | DMF[a] | 2 | 18 | VIII | 27 |
| III, V | DMF | 2 | 18 | VIII | 92–95 |
| III, V | DMAc | 20 | 0 | VIII | 98–99 |
| III, V | DMAc | 15 min | 0 | VIII | 98–99 |
| III, VI | DMAc | 30 min | 0 | IX | 93 |
| III, VII | DMAc | 30 min | 8[b] | X | 84 |
| IV, V | DMAc | 40 min | 0 | XI | 91 |

[a] Trichloroacetic acid (0.1 g.) added as catalyst.

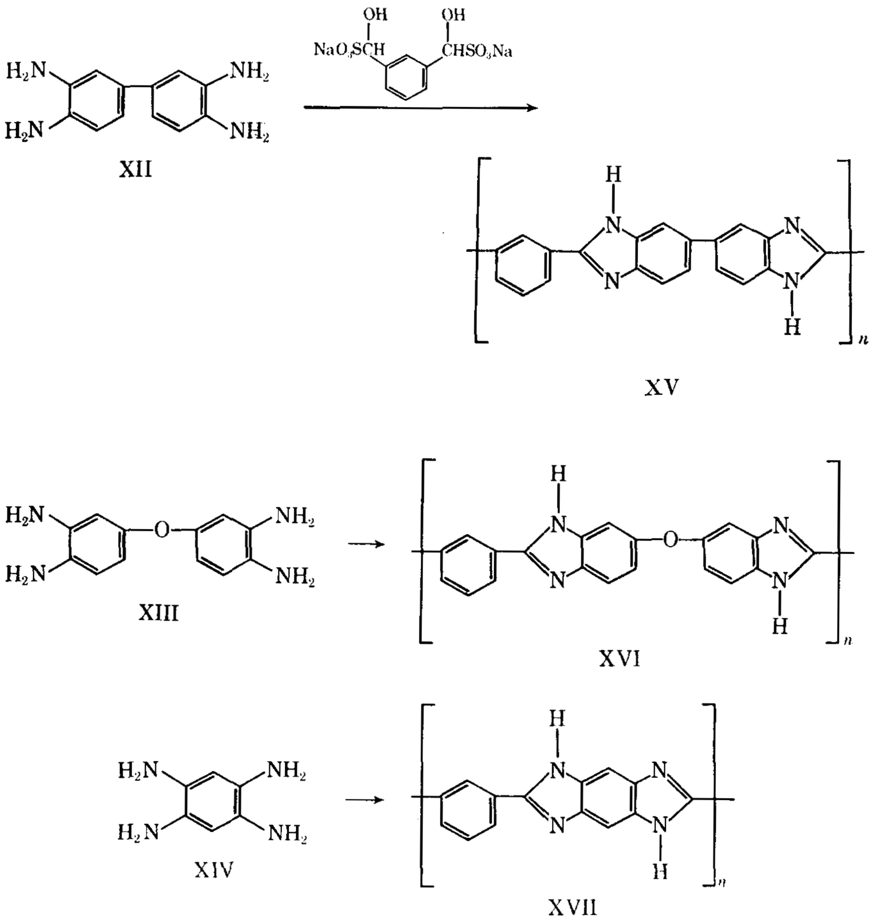
[b] Refluxed with an equivalent amount of sulfur.

The results in Table I show that the benzaldehyde bisulfite adduct condensed with *o*-phenylenediamine is the best method for preparing heterocyclics under these reaction conditions. The yield of 2-phenylbenzimidazole is essentially quantitative. By washing the product only once with water, it melted over a 3°C temperature range (294–297°C). Similar product isolation techniques with benzaldehyde and benzaldehyde diethyl acetal gave a thick oil, and diethyl ether was used as the washing solvent. The aliphatic aldehydes when reacted as the bisulfite adducts would not eliminate hydrogen under these reaction conditions. Also sulfur was required to extract hydrogen in the case of 2-phenylbenzoxazole under these reaction conditions.

It is not exactly clear why the bisulfite adducts proceed to such good yields while the aldehydes and acetal give such poor yields. It is known,[4,5] however, that when aldehydes are reacted with diamines the major byproducts (in many cases the major product) are the aldehydines. These disubstituted benzimidazoles were predicted to arise from the diimines formed in the initial stages of the reaction. The diimines undergo rearrangement under the reaction conditions to produce the aldehydines. From this knowledge it may be that the bisulfite adducts are less reactive thus giving more time for ring closure and preventing the formation of the diimines. The reaction of benzaldehyde bisulfite adduct with *o*-phenylenediamine appears to begin around 60–70°C. This can be predicted by a sharp color change to bright yellow and the precipitation of sodium bisulfite.

## POLYMERIZATIONS

Three polymerizations were chosen for these studies. They consisted of the condensation of isophthalaldehyde bis(bisulfite adduct) with 3,3′,4,4′-tetraaminodiphenyl (XII),[1] 3,3′,4,4′-tetraaminodiphenyl ether (XIII),[5] and 1,2,4,5-tetraaminobenzene (XIV).[1] The results of these studies are outlined in Table II. The yields were essentially quantitative.



The polymerizations were carried out by refluxing the reactions in the selected solvents for a short time in a nitrogen atmosphere and then continuing the reactions open to the air for the remaining reaction time or by refluxing in a nitrogen atmosphere for the entire reaction time.

All polymers were soluble in formic acid, however, as the viscosity values approached 0.5 the polymers were only slightly soluble in DMF, DMAc, and DMSO.

The bis(bisulfite adduct) was easily prepared from isophthalaldehyde in a 15% water solution of methanol.

TABLE II
Polymerizations

| Reaction number | Tetraamine[a] | Solvent | Time heated in nitrogen, hr | Time heated in air, hr | Viscosity $\eta_{inh}$[b] | $\lambda_{max}$, mμ ($H_2SO_4$) |
|---|---|---|---|---|---|---|
| 1 | XII | DMF | 2 | 18 | 0.34 | 337<br>253 |
| 2 | XII | MP[c] | 3 | 18 | 0.29 | 338<br>253 |
| 3 | XII | MP[c] | 5 | 16 | 0.33 | 337<br>253 |
| 4 | XII | DMAc | 3 | 18 | 0.45 | 335<br>252 |
| 5 | XIII | DMAc | 2 | 16 | 0.38 | 326<br>245 |
| 6 | XIII | DMSO | 5 | 14 | 0.55 | 323<br>245 |
| 7 | XII | DMSO | 5 | 14 | 0.51<br>0.24[d] | 335<br>252 |
| 8 | XII | DMAc | 20 | 0 | 0.42 | 338<br>253 |
| 9 | XIII | DMAc | 20 | 0 | 0.38 | 327<br>245 |
| 10 | XIV | DMAc | 40 | 0 | 0.45 | 346<br>241 |
| 11 | XII | DMAc | 40 | 0 | 0.52 | 338<br>252 |
| 12 | XII | DMAc | 3 | 0 | 0.31 | 337<br>253 |
| 13 | XII[e] | DMAc | 5 | 0 | 0.47 | 336<br>252 |
| 14 | XII[f] | DMAc | 5 | 0 | 0.38 | 337<br>252 |

[a] Equal molar quantities of monomers were used except where indicated.

[b] Measured in formic acid except where indicated (0.025–0.500 g/100 ml).

[c] *N*-Methyl-2-pyrrolidone.

[d] Measured in DMSO.

[e] A 3% weight excess of isophthalaldehyde bis(bisulfite adduct) was used.

[f] A 3% weight excess of 3,3′,4,4′-tetraaminodiphenyl was used.

## EXPERIMENTAL

### Model Compounds

#### *2-Phenylbenzimidazole from Benzaldehyde and o-Phenylenediamine*

**Nonacid-Catalyzed Reaction.** Benzaldehyde (10.60 g, 0.10 mole) and *o*-phenylenediamine (10.80 g, 0.10 mole) were added to 100 ml of DMF and refluxed in a nitrogen atmosphere for 2 hr. The reaction vessel was then opened to the air and the solution refluxed for 20 hr. After the refluxing period all but about 15–20 ml of the DMF was distilled at 50–60 mm pressure. Diethyl ether (50 ml) was added and the mixture stirred for 30 min. The 2-phenylbenzimidazole was filtered and dried at 100°C *in vacuo* overnight to give 6 g (31%) of cream-colored product melting at 280–292°C. Concentration of the ether solution yielded 1–3 g of additional product.

**Acid-Catalyzed Reaction.** The same procedure as above was carried out in a 10% acetic acid–DMF solution. A 5–6 g yield of 2-phenylbenzimidazole was obtained (26–31%). The crude product melted at 279–290°C. Recrystallization ($C_2H_5OH$–$H_2O$) gave a pure product which melted at 295–297°C; lit.[1] mp, 300°C.

#### *2-Phenylbenzimidazole from Benzaldehyde Diethyl Acetal and o-Phenyl-enediamine*

**Non-Acid-Catalyzed Reaction.** Benzaldehyde diethyl acetal (18.00 g, 0.10 mole) and *o*-phenylenediamine (10.80 g, 0-10 mole) were added to 100 ml DMF and refluxed in a nitrogen atmosphere for 2 hr. The reaction vessel was then opened to the air and refluxed for an additional 18 hr. All but about 15–20 ml of the DMF was removed by distillation at 50–60 mm pressure. Ethyl ether (50 ml) was added and the mixture stirred for 30 min. After filtering and drying, 5 g (26%) of 2-phenylbenzimidazole was obtained. The product melted at 296–298°C.

**Acid-Catalyzed Reaction.** The same reaction as above was carried out in DMF containing 0.10 g of trichloroacetic acid. About 6 g (31%) of 2-phenylbenzimidazole was obtained. The product melted at 294–297°C.

#### *2-Phenylbenzimidazole from Benzaldehyde Bisulfite Adduct and o-Phenylenediamine*

Benzaldehyde bisulfite adduct (22.42 g, 0.107 mole) and *o*-phenylenediamine (11.56 g, 0.107 mole) were added to 100 ml of DMF and the reaction mixture was heated at reflux for 15–20 min in a nitrogen atmosphere. The DMF was removed by distilling at reduced pressure, and 50 ml of water was added and the mixture stirred for 30 min. The 2-phenylbenzimidazole was filtered, washed twice with 20-ml portions of water, and dried to give an almost white product (19 g, 98%) melting at 294–297°C.

### *2-Phenylbenzthiazole from Benzaldehyde Bisulfite Adduct and o-Aminothiophenol*

Benzaldehyde bisulfite adduct (4.48 g, 0.021 mole) and *o*-aminothiophenol (2.62 g, 0.021 mole) were added to 50 ml DMAc and the reaction mixture refluxed for 30–45 min in a nitrogen atmosphere. The DMAc was removed by distilling at reduced pressure, and 30 ml of water was added. The reaction mixture was stirred for 30 min, filtered, and washed with two 20-ml portions of water, and dried to give about 4 g (91–94%) of 2-phenylbenzthiazole melting at 111–113°C; lit.[7] mp, 111°C.

### *2-Phenylbenzoxazole from Benzaldehyde Bisulfite Adduct and o-Aminophenol*

Benzaldehyde bisulfite adduct (4.48 g, 0.021 mole) and *o*-aminophenol (2.29 g, 0.021 mole) were added to 50 ml DMAc and refluxed for 30 min in a nitrogen atmosphere. The reaction flask was then opened to the air 0.9 g of sulfur was added. The reaction was refluxed for 8 hr and the DMAc was then removed by distilling at reduced pressure. About 30 ml of water was added and the reaction mixture stirred until the product crystallized. The crude 2-phenylbenzoxazole was dissolved in 100 ml of ether; the ether solution was filtered and the ether removed at water aspirator pressure to yield about 3 g (80–84%) crude product. The crude product was sublimed to give a white crystalline product melting at 104–105°C; lit.[8] mp, 103°C.

### *2-Pyridylbenzimidazole from Picoline-2-carboxaldehyde and o-Phenylenediamine*

Picoline-2-carboxaldehyde bisulfite adduct (4.62 g, 0.021 mole) and *o*-phenylenediamine (2.27 g, 0.021 mole) were added to 50 ml DMAc and the reaction mixture refluxed for 40–50 min in a nitrogen atmosphere. The DMAc was removed by distilling at reduced pressure, and 30 ml of water was added to the reaction mixture and stirred for 30 min. The product was

[redacted]

## Polymerizations

The following procedure is typical of all the polymerization reactions. The ultraviolet and infrared spectra of the polymers were identical to those reported previously.[1]

### *Preparation of Poly-2,2′-(1,3-phenylene)-5,5′-bibenzimidazole*

3,3′,4,4′-Tetraaminodiphenyl (0.6310 g, 0.00294 mole) and isophthalaldehyde bis(bisulfite adduct) (1.0388 g, 0.00304 mole 3% excess) were added to 100 ml DMAc and refluxed for 5 hr in a nitrogen atmosphere After a short time some polymer began to precipitate. After the reaction time about two-thirds of the DMAc was removed by distilling at 40–50 mm pressure and the remaining solution poured into 100 ml of distilled water. The cream-colored polymer precipitated and was removed by suction filtration. The polymer cake was washed thoroughly twice with 25-ml portions of water and dried *in vacuo* at 160°C for 10 hr. A quantitative yield of poly-2,2′-(1,3-phenylene)-5,5′-bibenzimidazole was obtained. The inherent viscosity, measured in formic acid, was 0.47.

Also equimolar quantities of isophthalaldehyde *bis*(bisulfite adduct) with 3,3′,4,4′-tetraaminodiphenyl ether (XIII) and 1,2,4,5-tetraaminobenzene (XIV) gave quantitative yields of polymers with viscosities similar to those reported for 3,3′,4,4′-tetraaminodiphenyl (XII) (see Table II).

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