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A series of new 2,5-dibenzoxazolylphenols and related compounds was prepared by condensation of hydroxy- and methanesulfonamidoterephthalic acids with 2-aminophenols. These displayed excited state intramolecular proton-transfer fluorescence at room temperature and above with quantum yields as high as 0.48 and emission peaks of 492-517 nm. The methanesulfonamido group was found about as effective a proton donor as the phenolic hydroxyl group. Incorporation of substituents onto the benzoxazole moieties increased solubility of the fluors in hydrocarbon solvents in some cases, but reduced quantum yields. These fluors are of interest as wavelength shifters in a scintillating detecting medium for ionizing radiation.

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Introduction.

Detection of ionizing radiation caused by particle collisions in the Super-Conducting Supercollider (SSC) and in other sub-atomic particle accelerators may be accomplished by surrounding the collision area with plates or fibers of scintillating polymer in which is dissolved a scintillation fluor of large Stokes shift, or a primary fluor plus a shifter [1]. When plates are used the scintillation light pulses may be transported to the photodetectors by means of fiber light guides in which a shifter is dissolved. The properties required of fluors to be used as primary scintillators or shifters incorporated into polystyrene fibers have been listed many times [2]. Primary fluors from members of the oligophenylene family exist which have excellent radiation hardness and are generally very satisfactory [3].

In contrast, no previously known shifter is really satisfactory, especially in fibers of several meters length. The only useful shifters are those that do not absorb at their own emission wavelengths. Conventional fluors such as 1-phenyl-3-mesityl-2-pyrazoline (PMP) with large Stokes' shifts are not adequate because of spectral overlap [4]. Chemists discovered a molecular feature that provides "flat baseline" between absorption and fluorescence by allowing these molecules to undergo a process called "intra-molecular proton-transfer" (IMPT), which is more accurately described as "excited state intra-molecular proton-transfer" (ESIPT), which is well-described in the literature [29]. As of this writing we believe that *only* ESIPT fluors will provide the long attenuation lengths desired in scintillating fibers and in light guides as well as *all* the other desired properties. All the new fluors described in this report are ESIPT fluors.

Among the other desirable properties of shifters are fluorescence emission at 480-600 nm [3], quantum yield (Φ)

≥ 0.4 (preferably 1.0), scintillation decay time (τ) of ≤ 5 nsec (preferably 2.0 nsec), and extreme thermal, chemical, photochemical, and radiolytic stability, as well as sufficient solubility in both styrene and polystyrene [5].

Rational selection of a fluor with fast response time can be made because of the relation of fluorescence lifetime or "decay time" (τ) and extinction coefficient (ϵ). By 1970, Berlman had shown that τ for non-ESIPT fluors is inversely proportional to their extinction coefficients (ϵ) [6]. Paul Cahill, Sandia Laboratories, re-examined experimental data on fluorescence lifetimes and found that the minimum lifetime was a linear function of emission wavelength, not a quadratic function as had been reported. Therefore, even red-emitting fast ($\tau \leq 5$ nsec) fluors with unit Φ are not prohibited by theory [7].

Two related ESIPT fluors with satisfactory chemical, photochemical, and thermal stability are 2-(2'-hydroxyphenyl)benzoxazole (HBO, **1**, Table 1) and 2-(2'-hydroxyphenyl)benzothiazole (IBT) [8]. Both have low Φ , low ϵ (13,000 for HBO [9]) and slow τ , properties we decided to address by increasing the size of the fluorophore in HBO.

The compound 2,5-bis(2-benzoxazolyl)hydroquinone (**2**), now known to be an ESIPT fluor, was originally reported to have fluorescence emission in the solid state at $\lambda > 600$ nm [10,11]; neither ϵ or Φ values nor any absorption or emission wavelengths in solution were reported. Its melting point is $> 380^\circ$ and its solubility in aromatic solvents is very low. Mordzinski with various co-workers studied **2** and its derivatives **4** and **5**, and found that for **2**, $\Phi = 0.05$ and $\tau = 0.8$ nsec at 293 K [12]; and that **4** has the highest quantum yield we have seen for any hydroxyphenylbenzazole ($\Phi = 0.35$ -0.50 at room temperature, depending on solvent), as well as a satisfactorily high extinction coefficient (25,000) and $\tau = 4.6$

Table 1
Photophysical Properties of HBO and Related 2,5-Dibenzoxazolyhydroquinones

No.	Structure	λ maxabs (ε)	λ max fl	ESIPT Φ
1		330 nm (13,000) [a] [a,b]	490 nm	0.017 [b]
2		417 (20,000) [d] 408 (26,000) [f]	540 [c] 580 [d] 590 [f]	0.05 [c] 0.085 [f]
3		410 (25,300) [e]	540 [f]	0.03 [9]
4		385 (25,000)	580	0.36 [h] 0.50 [i]
5		377 (23,000) 364 (22,000)	402	0.0[j]

[a] In ethanol [9]. [b] In methylcyclohexane at 23° [27]. [c] In heptane at 27° [12]. [d] In 2-methyltetrahydrofuran at room temperature [13]. [e] In chloroform. [f] In toluene (this work). [g] In toluene at 22°; F = 0.02 when 343 nm absorption band was used (this work). [h] In 3-methylpentane at room temperature [13]. [i] In 2-methyltetrahydrofuran at room temperature [13]. [j] Has only non-ESIPT fluorescence In 2-methyltetrahydrofuran at room temperature [13].

nsec; and that **5** has no ESIPT fluorescence at all, since there is no transferable proton [13]. The reported synthesis of **4** by monomethylation of **2** required purification by hplc, while no melting point, elemental assays, or ir and pmr spectra were presented. We attempted to prepare **4** by another route with results discussed below.

The reported syntheses of **2** involved the condensation in polyphosphoric acid of 2-aminophenol and 2,5-dihydroxyterephthalic acid. The latter was available commercially when Orlando and Mordzinski did their work; it was not available when we began ours. Nor was its precursor, 2,5-dibromoterephthalic acid, which requires a high-pressure reactor for a practical yield [14]. Therefore, we used the available bromoterephthalic acid to prepare hydroxyterephthalic acid, which was condensed with various 2-aminophenols to prepare the series of 2,5-dibenzoxazolyphenols and related compounds **6-14** in Table 2. Their photophysical properties were strikingly different from those of the 2,5-bis(2-benzoxazolyl)hydroquinones **2** and **4** and will be discussed below. Later we prepared the hydroquinone **3** to confirm some of these differences.

With benzimidazoles the tosylamido group as a proton donor gave much higher values of Φ at room temperature than the phenolic hydroxyl group [15], ranging from 0.1 to 0.25 in toluene. Some tosylamidophenyl monobenzoxazoles were reported without Φ values [16]. We therefore synthesized the methanesulfonamidophenyl dibenzoxazole **8** in order to compare proton donors. (We will report

on the benzimidazole analogs separately).

Discussion and Results.

Syntheses.

The 2-aminophenols required for dibenzoxazoles **4**, **6**, and **9-14** were available commercially. Reduction of 4-ethyl-2-nitrophenol (**15**, Figure 1) by means of the palladium-catalyzed decomposition of sodium borohydride gave 2-amino-4-ethylphenol **16** in up to 90% yield.

The hydroxyterephthalic acid for dibenzoxazoles **6-7** and **9-14** was prepared from bromoterephthalic acid by copper-catalyzed displacement of bromine [14] similar to the 2,5-

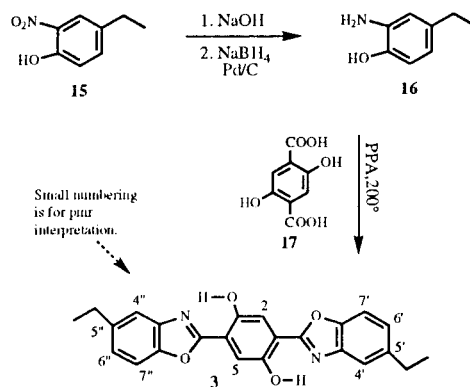


Figure 1. Synthesis of 2,5-Bis(5-ethyl-2-benzoxazolyl)hydroquinone **3**

Table 2
Photophysical Properties of New 2,5-Dibenzoxazoylphenols and Related Compounds

No.	Structure	λ max abs (ϵ) [a]	λ max Φ [a]	ESIPT Φ [b]
6		355 nm (52,000)	495 nm	0.48g
7		355 (57,000)	492	0.39
8		358 (48,000)	517	0.38
9		359 (53,000)	505	0.21
10		359 (57,000)	491	0.34
11		357 (58,000)	492	0.41
12		356 (49,400)	517	0.35
13		362 (60,000)	498	0.39
14		382 [c]	524	0.16 [d]

[a] In Chloroform on Perkin-Elmer LS-5B, uncorrected. [b] In toluene. [c] Excitation max. in toluene, corrected. [d] Plus non-ESIPT $\Phi = 0.05$ at 419 and 447 nm.

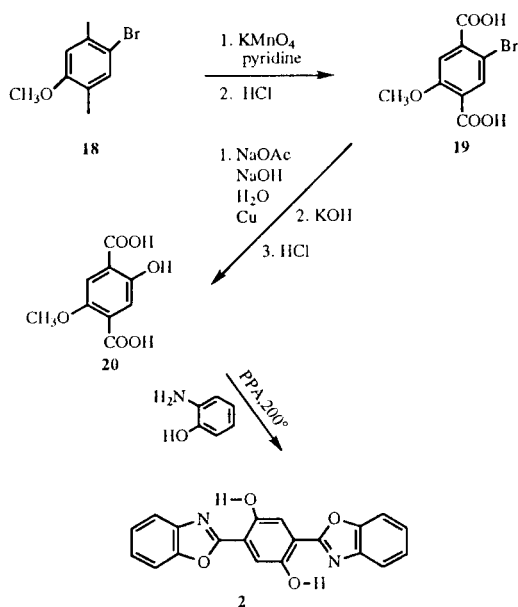


Figure 2. Attempted Synthesis of 2,5-Di-benzoxazolyl-3-methoxyphenol 4

dihydroxyterephthalic acid needed for dibenzoxazole 3.

The 2-hydroxy-5-methoxyterephthalic acid needed for dibenzoxazole 4 proved more of a challenge. Bromination of the disodium salt of hydroxyterephthalic acid in water decolorized the bromine, but only hydroxyterephthalic acid was recovered after acidification. The inexpensive dimethyl aminoterephthalate was subjected to diazotization and heating in the manner described [17] for the conversion of methyl anthranilate to methyl salicylate. Decomposition of the diazonium salt at 70° did not give any phenolic product. The dimethyl ester of hydroxyterephthalic acid was soluble in 1 *M* potassium hydroxide, but this phenoxide salt did not react with methyl methanesulfonate to give an ether. Bromination of the dimethyl ester of hydroxyterephthalic acid in methylene chloride gave no reaction, further demonstrating the electron-withdrawing power of the terephthalate system. Finally, the permanganate oxidation of 4-bromo-2,5-dimethylanisole (18, Figure 2) in pyridine gave the diacid 19 in 9% yield. Displacement of bromine to give 2-

hydroxy-5-methoxyterephthalic acid **20** was accomplished in 76% yield.

The 2-methanesulfonamidoterephthalic acid (**23**, Figure 3) needed for dibenzoxazole **8** was prepared from dimethyl aminoterephthalate **21**. Tosyl chloride forms a sulfonamide easily with methyl anthranilate [18], but not, as we found, with dimethyl aminoterephthalate **21**. The second ester function drastically reduces the reactivity of the amino group. A black tar formed on treatment of **21** with methanesulfonyl chloride, as has been observed with carbohydrates [19]. However, methanesulfonic anhydride gave sulfonamide **22** in 78% yield. Selective hydrolysis of the ester groups in **22** was accomplished with 4 moles of potassium hydroxide at 22° to give diacid **23**.

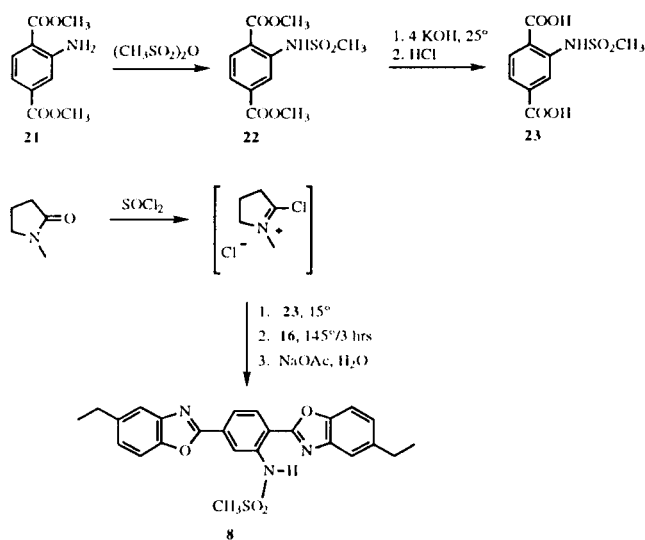


Figure 3. Synthesis of *N*-[2,5-bis(5-ethyl-2-benzoxazolyl)-phenyl]methanesulfonamide **3**

Three main methods of oxazole formation were investigated: (1) use of polyphosphoric acid (PPA) at 200° for 16-24 hours [11]; (2) preparation of the terephthaloyl chloride, followed by its reaction with the 2-aminophenol in pyridine or by Scha's method using *N*-methyl-2-pyrrolidinone (NMP) [20]; and (3) reaction of the diacid and the 2-aminophenol in dibutyl carbitol [21,22].

The PPA method succeeded with dibenzoxazoles **3**, **6**, **7**, and **9-14**. Nitroterephthalic acid with 2-aminophenol was decomposed. The 2-hydroxy-5-methoxyterephthalic acid **20** was demethylated leading to dibenzoxazole **2** rather than to **4**. The methanesulfonamidoterephthalic acid **23** was decomposed. The *t*-butyl group in 2-amino-4-*t*-butylphenol was decomposed, as was the ethoxy group in 2-amino-4-ethoxyphenol.

The NMP method was successful with dibenzoxazole **8**, obtained in 2% yield, and dibenzoxazole **11**, obtained in 17% yield in NMP by Scha's method, vs. only 4% by reaction of the diacid chloride in pyridine, showing the

utility of Scha's method with *t*-butyl and methanesulfonamido groups. Nitroterephthalic acid with 2-amino-4-*t*-butylphenol gave the 1,4-dibenzoxazolyl-2-nitrobenzene **11a** in 2% yield. (An attempt to reduce the nitro group with tin(II) chloride in 12 *M* hydrochloric acid failed.)

The dibutyl carbitol method gave dibenzoxazole **7** in 28% yield vs. 69% with PPA. This method gave dibenzoxazole **12** in 6% yield (impure) vs. 70% (pure) with PPA, and failed with 2-amino-4-*t*-butylphenol and 2-amino-4-ethoxyphenol. That our technique was sound was shown by achieving an 81% yield of 9,9-dipropyl-2,7-bis(5-ethyl-2-benzoxazolyl)fluorene (to be reported in this journal at a later date). This seems to show that the hydroxyl group in hydroxyterephthalic acid is not compatible with this method.

The identity of the dibenzoxazoles rests on the method of preparation, on elemental assays (in all cases except **11a** for which an infrared spectrum was confirmatory), and on high field pmr spectra, which were determined for dibenzoxazoles **2**, **6**, **7**, **10**, **11** and **11a**. A particularly well-resolved pmr spectrum was obtained for the 2,5-bis(5-*t*-butyl-2-benzoxazolyl)phenol **11** (Figure 4) because of its high solubility. The chemical shifts of the phenolic hydrogens and their line widths indicate tight hydrogen bonding with slow exchange (Table 3) for most of the phenols. (Silverstein *et al.* list $\delta = 5.4$ -12.6 ppm for intramolecularly hydrogen-bonded phenols [23].) This is in contrast to the chemical shift of the phenolic proton in 3-hydroxyflavones ($\delta = 7.1$ ppm, broadened singlets) indicating loose hydrogen bonding [24], and to the extreme deshielding of the phenolic proton ($\delta = 14.1$ ppm) in a completely non-fluorescent 2-(2-hydroxyphenyl)pyridine [25], indicating hydrogen transfer in the ground state.

Photophysical Properties.

Absorption of light by HBO (**1**) is feeble ($\epsilon = 13,000$ at the longwave peak of 330 nm [9]). All four of the dibenzoxazolylhydroquinones or ethers **2-5** had about twice the extinction coefficient of HBO ($\epsilon = 20,000$ - 26,000 at $\lambda_{\max}$ 364-417 nm), showing that much of the molecule is involved in the electron transfer of the S_0 - S_1 transition. The hydroquinone **2** was reported to have, in addition to the broad bands at longer wavelengths than 350 nm, narrow bands at shorter wavelengths ($\epsilon = 42,000$ at 333 and 35,000 at 317 nm) [13]. Our work corroborates this by showing similar bands for the new hydroquinone **3** ($\epsilon = 39,000$ at 341 and 36,000 at 324 nm). In sharp contrast the dibenzoxazolylphenols have 4 closely spaced narrow bands with high extinction coefficients as in **7**, which is typical ($\epsilon = 50,000$ at 375, 57,000 at 355, and 39,000 at 330 nm). This pattern is quite similar to that of 1,4-dibenzoxazolylbenzene, which has no phenolic hydroxyl (0-0

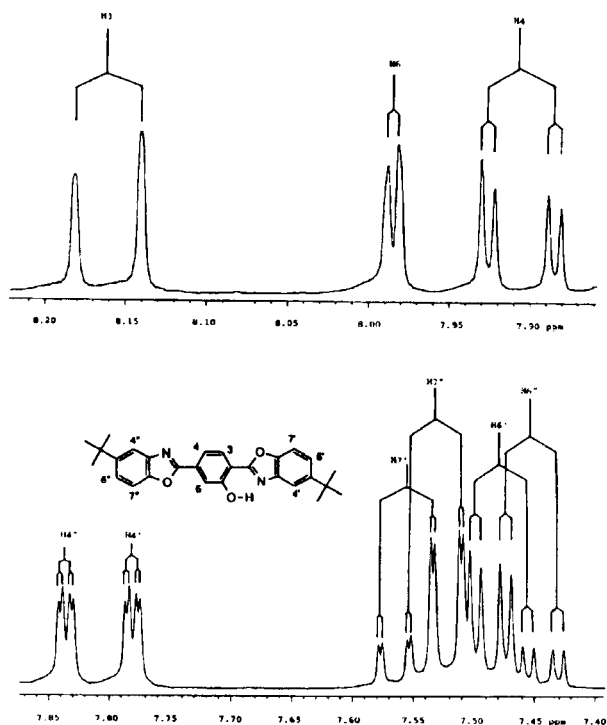


Figure 4. Aromatic region of the 200 MHz PMR spectrum of 2,5-bis(5-*tert*-butyl-2-benzoxazolyl)phenyl **11** with assignments of peaks

Table 3

PMR Data on Phenolic Protons
in Certain Dibenzoxazoles

No.	δ (ppm)	Line Width (Hz)
2	11.07	10
6	11.66	42
7	11.68	102
10	11.76	400
11	11.68	200
12	11.41	30

band 360, 0-1 band 341 nm with $\epsilon = 53,000$) [26]. Thus there is some resistance to attainment of coplanarity in the S_1 state, probably steric, in all of the hydroquinones, but not in the phenols. The effect of chloro (in **12**) and phenyl (in **13**) substituents on the benzo moiety is minor. Therefore, we suggest the electron flow shown in Figure 5 for the S_0 - S_1 transition in phenol **6**, where the outer substituents are not directly involved in the π electron movement.

The ESIPT fluorescence of HBO (**1**, peak 490 nm) is very feeble at room temperature ($\Phi = 0.017$) and increases at lower temperatures [27]. The ESIPT fluorescence of

2,5-dibenzoxazolylhydroquinones (**2-3**, peak 540-590 nm) is nearly as weak (Table 1). The monomethyl ether **4** has ESIPT fluorescence with $\Phi = 0.36$ in hydrocarbon solvent and non-ESIPT fluorescence with $\Phi = 0.11$ [13]. The new 2,5-dibenzoxazolylphenols **6-13** have ESIPT fluorescence at wavelengths from 492-517 nm with $\Phi = 0.21$ -0.48 in toluene. Only the naphthoxazole **14** had both

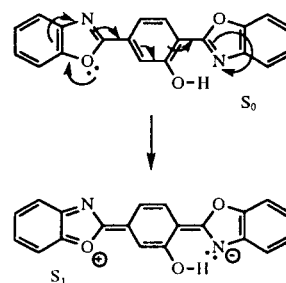


Figure 5. Hypothesized Electron Flow in S_0 - S_1 Transition of Dibenzoxazolylphenol **6**

weak ESIPT emission ($\Phi = 0.16$, peak 524 nm) and measurable non-ESIPT fluorescence ($\Phi = 0.05$). The characteristic fine structure of absorption is echoed by the fluorescence excitation spectrum of **12** in toluene, as are the sharp drop at the longwave side of the absorption, the flat baseline from 400-455 nm, and the broad asymmetrical emission (Figure 6). Note that dibenzoxazolylphenols **8** and **12** have larger Stokes' shifts than the other dibenzoxazolylphenols by virtue of redder emission, peaking at 517 nm. This might be explained by noting that a chloro substituent may decrease the basicity of an amine such as pyridine by 1-2 pKa units [28], and that the sulfonamide may be 1-2 pKa units less acidic than the corresponding phenol. In these two cases there would be a smaller energy difference in the S'_1 - S'_0 transition [29] of the proton-

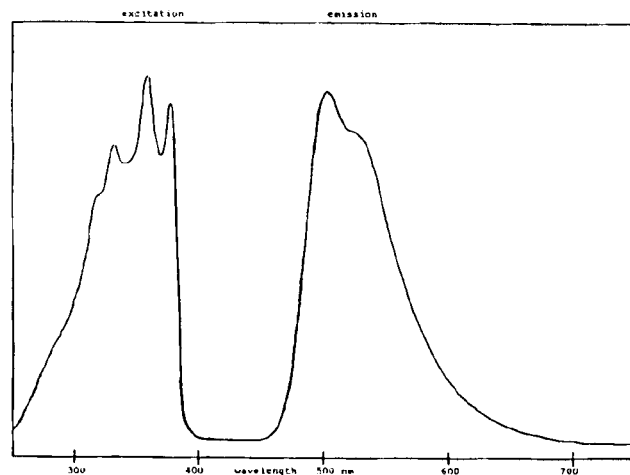


Figure 6. Fluorescence Spectrum of 2,5-Bis(5-chloro-2-benzoxazolyl)phenol **12**.

transferred species due mainly to higher energy in the S'_0 state, leading to the emission of lower energy photons.

Conclusions.

The well-known condensation of hydroxy- and dihydroxyterephthalic acids with 2-aminophenols in PPA at 200° proved the best method for formation of the oxazole ring in this work; however, PPA was incompatible with nitro, *t*-butyl, ethoxy, and methanesulfonamido groups. Scha's method, reaction of the diacid chloride with 2-aminophenols in NMP gave low yields when these groups were present (methoxy was not tried). Condensation in dibutyl carbitol gave a low yield when ethyl and chloro substituents were present, and no product with ethoxy, thus this method was not useful.

The ESIPT fluorescence efficiency ($FE = \Phi \cdot \epsilon$) of HBO is 221 at room temperature. For the hydroquinone **2** using ϵ for the 408 nm peak absorption, the ESIPT $FE = 2210$. For the monoether **4**, using the 385 nm peak absorption, the ESIPT $FE = 8750$ in hydrocarbon solvent. For the dibenzoxazolyphenol **6**, the ESIPT $FE = 25,000$, an unusually high value for this type of compound. Thus it is possible to make fluors which show solely ESIPT emission that are as efficient absorbers as the related fluors without the proton donor. Only the best of the newly reported 3-hydroxyflavones have comparable values of FE [24]. All these oxazoles show fluorescence in the solid state with the emission wavelengths bathochromically shifted from the peak wavelengths in solution.

These dibenzoxazolyphenols show exceptionally good thermal stability; **14**, for example, melts without decomposition in air at 458°. The radiolytic stability of **6** has been reported and is excellent [2]. These compounds are more soluble in aromatic hydrocarbons than the higher-melting hydroquinones. Potential uses include: fluors and shifters for scintillation counting; uv-sensitive, daylight-insensitive dyes and pigments, and additives for uv-protective lenses that could indicate the presence of uv photons by fluorescence emission near the peak response of the human eye.

EXPERIMENTAL

General.

All melting points were determined in unsealed capillary tubes in a heated oil bath (Thomas-Hoover Unimelt, Arthur H. Thomas Co.) using 76 mm immersion thermometers and needed no correction. Most stirring in round-bottomed flasks was done with teflon-coated magnets of prolate spheroid shape. Evaporations were carried out with a rotary evaporator at a final pressure of 15-30 torr. Most solids were dried in a vacuum oven at 15-30 torr. Thin-layer chromatography was carried out with Whatman MK6F silica 1 x 3 inch plates, and visualized with short- and long-wave ultraviolet light. Chromatographic purification by extraction from an "Ace-Kau" means that boil-

ing solvent was allowed to fall on a solid sample and pass thorough a column of adsorbent in a special apparatus (an Ace-Kauffman Column, Ace Glass Co.) [30]. Elemental analyses were done by Oneida Research Services, Rensselaer, NY. Infrared spectra were determined in potassium bromide pellets (unless noted otherwise) with a Perkin-Elmer 1600 series FTIR using a diffuse reflectance cell. Ultraviolet spectra were determined with a Shimadzu UV 265 unless noted otherwise. The dilute solution method was used to determine Φ with a Farrand Spectrofluorometer Mk. I, rebuilt to produce corrected spectra from 250 to 750 nm by Optical Technology Devices, Elmsford, NY. The reference standard was the oxazole "Ox 2" of $\Phi = 0.73$ in absolute ethanol [32]. The working equation was:

$$\Phi_{\text{spl.}} = (\Phi_{\text{std.}}) (\text{Area}_{\text{spl.}}) (\text{Absorbance}_{\text{std.}}) / (\text{Area}_{\text{std.}}) (\text{Absorbance}_{\text{spl.}})$$

The pmr spectra were determined at Villanova University by Walter J. Boyko on a Varian XL200 in deuteriochloroform unless noted otherwise. The numbering used for assignments for the dibenzoxazolyhydroquinones is shown for **3** in Figure 1, for the dibenzoxazolyphenols is shown for **7** and **8** in Table 2, and for **11** in Figure 4. The assignments for **7** and **11** were aided by COSY.

The polyphosphoric acid (PPA) was obtained from Aldrich (20,821-3) and was usually pre-heated to $\approx 60^\circ$ and measured by estimating the volume delivered to a round-bottomed flask. The 1-methyl-2-pyrrolidinone (NMP) was obtained from Aldrich (27,045-8) as were the alumina (Br. I. neut., Aldrich 19,997-4) and the Silica Gel (Merck Gr. 60, Aldrich 22,719-6). The 2-aminophenol was purified by extraction from a Soxhlet for 2 weeks with 4 ml/g of benzene, 9-10 years before use.

Attempted Synthesis of 2,5-Di-2-benzoxazoly-4-methoxyphenol **4** Leading to 2,5-Di-2-benzoxazolyphenol **2**.

The 2-aminophenol (1.68 g, 0.0154 mole) and 2-hydroxy-5-methoxyterephthalic acid (**20**, 1.48 g, 0.00700 mole) were ground together with mortar and pestle and added to ≈ 45 ml of PPA at $\approx 100^\circ$ with stirring. After 16 hours at 200° the mixture was allowed to cool to $\approx 110^\circ$ and quenched in 50 ml each ice and water. The reactor was rinsed with 50 ml of 95% ethanol, and the rinsings combined with the quench mixture, which was then neutralized to $pH = 6$ with 28% ammonia; a violent exotherm occurred. The mixture was filtered with suction, and the solid was dried 70°/20 torr/3 days to give 2.38 g of black solid which was sublimed at 250° bath temperature (Wood's metal), 0.03 torr, during about 4 hours to give 0.28 g of yellow solid, mp 379-385°, dec. This was recrystallized from 42 ml of *N,N*-dimethylacetamide to give 0.25 g (10%) of yellow needles of **2**, mp 389-391°, no dec, (lit [10,11] 376-378°); uv 5.44 x 10⁻⁵ M in chloroform: 306 nm ($\epsilon = 27,000$), 320 (50,000), 337 (54,000), 393 (br, 24,000), 408 (br, 26,000); pmr: 7.366-7.80 (8H, m, Hs 4'-7' and 4''-7''), 7.801 (2H, s, Hs 2 and 5), 11.07 ppm (2H, sl br s, -OHs).

Anal. Calcd. for $C_{20}H_{12}N_2O_4$: C, 69.76; H, 3.51; N, 8.14. Found: C, 69.27; H, 3.53; N, 8.11.

2,5-Bis(5-ethyl-2-benzoxazoly)hydroquinone **3**.

The 2-amino-4-ethylphenol (**16**, 6.93 g, 0.0505 mole) and 2,5-dihydroxyterephthalic acid (**17**, 5.00 g, 0.0253 mole [14]) were ground together in a mortar and added with stirring to ≈ 100 ml of PPA at $\approx 100^\circ$. After 22 hours at 200° the mixture was allowed to cool to $\approx 110^\circ$ and quenched in a mixture of 200

g of sodium acetate trihydrate and 500 ml each ice and water. The reactor was rinsed with 100 ml of 95% ethanol, and the rinsings combined with the quench mixture, which was then neutralized to $pH = 5$ with 19 *M* sodium hydroxide solution, stirred overnight, and filtered on polyester cloth 12.5 cm in diameter; this required 3 days. The solid was washed with water, then 1:1 methanol:water, and dried to give 20.0 g. This was extracted with 300 ml of toluene from a small Soxhlet overnight; the clear extract was diluted with 100 ml of 1-propanol and kept at 22° to crystallize; this gave 7.32 g of yellow solid, mp s. 293°, 301–307° with residue. This material was extracted from a 2 cm high column of alumina in a medium Ace-Kau with 200 ml of toluene overnight and the extract kept at 22° to give 5.56 g (55%) of yellow needles, mp 315–317°; uv 7.93×10^{-5} *M* in chloroform): 310 nm ($\epsilon = 21,200$), 324 (36,400), 341 (38,800), 392 (br, 24,100), 410 (br, 25,300).

Anal. Calcd. for $C_{24}H_{20}N_2O_4$: C, 71.99; H, 5.03; N, 7.00. Found: C, 71.82; H, 5.08; N, 6.94.

2,5-Di-2-benzoxazolylphenol 6.

The 2-aminophenol (0.0400 mole) and hydroxyterephthalic acid (0.0200 mole, [14]) were condensed in PPA as described for 3 above. The neutral ($pH = 6$) suspension could not be filtered; it was centrifuged at 4000 rpm for 10 minutes. The supernatant was decanted; the residue was mixed with 100 ml of 2 *M* hydrochloric acid and filtered (overnight) and the purple solid was dried to give 13.5 g. This was sublimed at 285° and 0.05 torr for 2 hours to give 4.89 g of pink solid, which was recrystallized from 200 ml of *N,N*-dimethylacetamide (the product was washed with 95% ethanol) to give 4.40 g (60%) of salmon-colored needles, mp 325–326°; uv (4.0×10^{-5} *M* in chloroform): 315 nm ($\epsilon = 32,000$), 327 (41,000), 353 (52,000), 372 (47,000); pmr: 7.38–7.48 (4H, m), 7.60–7.70 (2H, m), 7.73–7.86 (2H, m, together Hs 4'-7' and 4''-7''), 7.934 (1H, dd, H4, $J_{3,4} = 8.2$ Hz, $J_{4,6} = 1.6$ Hz, ABX pattern), 8.015 (1H, dd, H6, $J_{6,7} = 0.5$ Hz), 8.194 (1H, d, H3), 11.66 (1H, br s, -OH).

Anal. Calcd. for $C_{20}H_{12}N_2O_3$: C, 73.16; H, 3.68; N, 8.53. Found: C, 72.62; H, 3.66; N, 8.80.

2,5-Bis(5-ethyl-2-benzoxazolyl)phenol 7.

The 2-amino-4-ethylphenol (16, 0.56 mole) and hydroxyterephthalic acid (0.28 mole, [14]) were condensed in 800 ml PPA as described for 3 above. The quench mixture was filtered on Whatman #52 paper; the damp solid was slurried with 1000 ml of water, filtered, and then dried at 110°/20 torr/16 hours to give 183 g of gray powder. This was extracted from an extra large Soxhlet with 1500 ml toluene for 4 days. The extract was kept at -20° for 24 hours to deposit 89.4 g, mp 218–221°. This was extracted continuously from a 5 cm high, 6 cm diameter column of alumina with 1500 ml of benzene for 9 days, allowed to cool to 22° overnight, diluted with 500 ml of methanol, filtered and dried to produce 79.8 g of solid which still appeared to contain a colored impurity. The solid was dissolved in 780 ml of hot xylenes, treated with 4.5 g of Fisher C-170 carbon, filtered hot, and diluted hot with 800 ml of 2-ethoxyethanol. The resulting clear solution was kept at 22° overnight to give 72.97 g (69%) of pale yellow solid, mp 221.5–222.5°; uv (5.56×10^{-5} *M* in chloroform): 330 nm ($\epsilon = 39,000$), 355 (57,000), 375 (50,000); pmr: 1.313 (3H, t, 5''—CH₂CH₃, $J = 7.5$ Hz), 1.321 (3H, t, 5'—CH₂CH₃, $J = 7.6$ Hz), 2.797 (2H, q, 5''—CH₂CH₃), 2.804 (2H, q, 5'—CH₂CH₃), 7.228 (1H, dd, H6'', $J_{6',7'} = 8.4$ Hz,

$J_{4',6'} = 1.7$ Hz), 7.252 (1H, dd, H6', $J_{6',7'} = 8.3$ Hz, $J_{4',6'} = 1.7$ Hz), 7.508 (1H, dd, H7'', $J_{4'',7''} = 0.7$ Hz), 7.531 (1H, dd, H7', $J_{4',7'} = 0.6$ Hz), 7.579 (1H, dd, H4'), 7.619 (1H, dd, H4''), 7.899 (1H, dd, H4, $J_{3,4} = 8.3$ Hz, $J_{4,6} = 1.7$ Hz), 7.979 (1H, dd, H6, $J_{3,6} = 0.4$ Hz), 8.154 (1H, dd, H3), 11.68 (1H, br s, -OH).

Anal. Calcd. for $C_{24}H_{20}N_2O_3$: C, 74.98; H, 5.24; N, 7.29. Found: C, 75.06; H, 5.26; N, 7.14.

N-[2,5-Bis(5-ethyl-2-benzoxazolyl)phenyl]methanesulfonamide 8.

Under argon methanesulfonamidoterephthalic acid (23, 13.04 g, 0.0500 mole) was dissolved in 100 ml of 1-methyl-2-pyrrolidone (previously dried with 4A Molecular Sieve). The solution was cooled to below 10° in an ice bath and thionyl chloride (8.76 ml, 14.3 g, 0.120 mole) was added below 15° during 30 minutes. Warm water was added to the bath to maintain 25°/15 minutes, then the 2-amino-4-ethylphenol (16, 15.07 g, 0.110 mole) was added, leading to an exotherm up to 45°. The mixture was heated in a mantle at 145°/3 hours, then held at 50° overnight, and quenched in a mixture of 17 g of sodium acetate trihydrate, 150 ml of water and 50 ml of ice. The solid was filtered, washed with water, then slurried in 250 ml of water, with addition of sodium acetate trihydrate to attain $pH = 8$; the solid was filtered again and dried, 10.8 g. This was recrystallized from 54 ml of 2-ethoxyethanol to give 1.16 g which was recrystallized from 11 ml of 2-ethoxyethanol to give 1.01 g. This was extracted from a 5 cm high column of Silica Gel in a small Ace-Kau with 70 ml of benzene (2 days). The solid obtained by cooling the extract was extracted as before with benzene; the hot extract was diluted with an equal volume of methanol and cooled at 0° to give 0.56 g (2.4%) of pale yellow powder, mp 275–278°; uv (chloroform): 342 nm ($\epsilon = 37,000$), 358 (48,000), 377 (40,000); pmr: 1.314 (3H, t, 5''—CH₂CH₃, $J = 7.6$ Hz), 1.324 (3H, t, 5'—CH₂CH₃, $J = 7.6$ Hz), 2.797 (2H, q, 5''—CH₂CH₃), 2.808 (2H, q, 5'—CH₂CH₃), 3.210 (3H, s, -SO₂CH₃), 7.245 (1H, dd, H6'', $J_{6',7'} = 8.3$ Hz, $J_{4',6'} = 1.7$ Hz), 7.278 (1H, dd, H6', $J_{6',7'} = 8.3$ Hz, $J_{4',6'} = 1.7$ Hz), 7.534 (2H, d, Hs 7' and 7''), 7.628 (1H, dd, H4''), 7.654 (1H, dd, H4'), 8.134 (1H, dd, H4, $J_{3,4} = 8.4$ Hz, $J_{4,6} = 1.6$ Hz), 8.376 (1H, dd, H6, $J_{3,6} = 0.5$ Hz), 8.674 (1H, dd, H3), 11.75 (1H, s, -NH).

Anal. Calcd. for $C_{25}H_{23}N_3O_4S$: C, 65.06; H, 5.02; N, 9.11. Found: C, 65.06; H, 4.98; N, 8.93.

2,5-Bis(6-methyl-2-benzoxazolyl)phenol 9.

The 2-amino-5-methylphenol (6.90 g, 0.0560 mole, Aldrich 14,491-6) and the hydroxyterephthalic acid (5.10 g, 0.0280 mole, [14]) were stirred by motor with an all-glass system in 80 ml of PPA for 16 hours at 190°. The mixture was allowed to cool to $\approx 100^\circ$ and quenched in a mixture of 150 g of sodium acetate trihydrate, 250 ml of water and 250 ml of ice. More base was added to attain a $pH = 2$ and 5 g of standard Celite was added. The mixture was filtered on polyester cloth and dried to give 23 g of solid which was extracted from a medium Soxhlet with 300 ml of benzene for 4 days to give 7.80 g of pale green powder, which was extracted from a 3 cm high column of alumina in a medium Ace-Kau with 300 ml of benzene for 7 days to give 6.26 g of yellow powder, mp 289–291°. This was recrystallized from 600 ml of xylenes to produce 5.88 g (59%); uv (3.11×10^{-5} *M* in chloroform): 330 nm ($\epsilon = 32,100$), 359 (50,000), 379 (45,300).

Anal. Calcd. for $C_{22}H_{16}N_2O_3$: C, 74.14; H, 4.53; N, 7.86.

Found: C, 74.43; H, 4.63; N, 7.63.

The solubility in xylenes at 22° was 0.63 g/l or 0.0018 *M*; at 120° it was 10 g/l or 0.028 *M*.

2,5-Bis(5,7-dimethyl-2-benzoxazoly)phenol 10.

The 2-amino-4,6-dimethylphenol (0.0364 mole, Aldrich 19,327-5) and hydroxyterephthalic acid (0.0182 mole, [14]) were condensed in 125 ml of PPA, then quenched as described for 7 above. The crude product was extracted from a small Soxhlet with 150 ml of benzene (3 days); the extract was diluted with an equal volume of cyclohexane, and the mixture was kept at 0° to deposit 4.29 g, mp 282-298°. This solid was recrystallized from 400 ml of 2-ethoxyethanol twice, 40 ml of *N,N*-dimethylacetamide, then 90 ml of xylenes to give 1.73 g of orange solid, mp 297-305°. Extraction from a 3 cm high column of alumina in a medium Ace-Kau with 160 ml of benzene for 2 days gave an extract of 75 ml which was diluted with an equal volume of absolute ethanol and cooled at 0° to give 0.63 g (9%), mp 303-305°; uv (2.9×10^{-5} *M* in chloroform): 331 nm ($\epsilon = 32,000$), 359 (57,000), 378 (50,000); pmr: 2.460 (3H, s, 7' or 7'' —CH₃), 2.467 (3H, s, 7' or 7'' —CH₃), 2.570 (3H, s, 5' or 5'' —CH₃), 2.586 (3H, s, 5' or 5'' —CH₃), 7.008 (1H, d, 6''H, $J_{4'-6''} = 1.7$ Hz), 7.032 (1H, d, 6'H, $J_{4'-6'} = 1.6$ Hz), 7.366 (1H, d, 4'H), 7.408 (1H, d, 4''H), 7.922 (1H, dd, H4, $J_{3,4} = 8.2$ Hz, $J_{4,6} = 1.6$ Hz), 7.994 (1H, dd, H6, $J_{3,6} = 0.4$ Hz), 8.176 (1H, dd, H3), 11.76 (1H, br s, —OH).

Anal. Calcd. for C₂₄H₂₀N₂O₃: C, 74.98; H, 5.24; N, 7.29. Found: C, 74.73; H, 5.20; N, 7.16.

2,5-Bis(5-*t*-butyl-2-benzoxazoly)phenol 11.

Hydroxyterephthalic acid (0.0500 mole, [14]) and 2-amino-4-*t*-butylphenol (0.110 mole, Janssen 18,563.56) were subjected to Seha's method as described for 8 above. Quenching gave, after decantation, a glob of organic material, which was soaked in 100 ml of 2-propanol overnight, then heated in 100 ml of 2-ethoxyethanol and cooled to 22° overnight to give 4.25 g of granular material, mp 252-253°. This was extracted from a 6 cm high column of alumina in a medium Ace-Kau with 200 ml of cyclohexane. The extract was distilled down to a volume of ≈ 30 ml, diluted with 100 ml of absolute ethanol, and kept at 22° to give 3.65 g (17%) of pale yellow powder, mp 258-259°; uv (4.36×10^{-5} *M* in chloroform): 331 nm ($\epsilon = 37,000$), 357 (58,000), 377 (50,000); pmr: 1.410 (9H, s, 5' or 5'' —C(CH₃)₃), 1.419 (9H, s, 5' or 5'' —C(CH₃)₃), 7.452 (1H, dd, H6'', $J_{6'-7''} = 8.7$ Hz, $J_{4'-6''} = 1.9$ Hz), 7.476 (1H, dd, H6', $J_{6'-7'} = 8.7$ Hz, $J_{4'-6'} = 1.8$ Hz), 7.531 (1H, dd, H7'', $J_{4'-7''} = 0.7$ Hz), 7.555 (1H, dd, H7', $J_{4'-7'} = 0.7$ Hz), 7.779 (1H, dd, H4'), 7.834 (1H, dd, H4''), 7.906 (1H, dd, H4, $J_{3,4} = 8.2$ Hz, $J_{4,6} = 1.6$ Hz), 7.985 (1H, dd, H6, $J_{3,6} = 0.3$ Hz), 8.161 (1H, dd, H3), 11.68 (1H, br s, —OH).

Anal. Calcd. for C₂₈H₂₈N₂O₃: C, 76.34; H, 6.41; N, 6.36. Found: C, 75.96; H, 6.23; N, 6.27.

2,5-Bis(5-*t*-butyl-2-benzoxazoly)-1-nitrobenzene 11a.

Nitroterephthalic acid (0.0545 mole, Aldrich N2,690-3) and 2-amino-4-*t*-butylphenol (0.121 mole, Aldrich 19,328-3) were subjected to Seha's method as described for 8 above. The quench mixture was made strongly basic with sodium hydroxide to obtain filterable solid; this was slurried with 100 ml of 1:1 methanol:water for an hour, filtered and dried to give 3.47 g of brown dust. This was extracted from a 7 cm high column of alumina in a medium Ace-Kau with 150 ml of benzene for 4

days. The clear extract was diluted with 125 ml of methanol and kept at -2° to yield ≈ 2 g (10%), mp 301-302°; ir: 3430 (—OH free), 3320 (—OH intra. bonded), 2955 (Ar-H), 2901 and 2866 (Ar-CH₃), 1625 (C=N), 1561 and 1526 cm⁻¹ (Ar-NO₂); pmr: 1.43 (18H, s, 5' and 5'' —C(CH₃)₃), 1.60 (s, dissolved H₂O), 6.40 (2H, s, intramolecularly bonded H₂O), 7.42 (2H, d, H7' and H7'', $J_{6,7} = 8.7$ Hz), 7.51 (2H, d, H6' and H6''), 7.66 (1H, d, H4, $J_{3,4} = 8.7$ Hz), 7.70 (1H, s, H6), 7.78 (1H, d, H5'', $J_{5,7''} = 1.5$ Hz), 7.82 (1H, d, H5', $J_{5,7'} = 1.5$ Hz), 8.20 (1H, d, H3).

2,5-Bis(5-chloro-2-benzoxazoly)phenol 12.

The 2-amino-4-chlorophenol (0.400 mole, Aldrich C4,440-0) and hydroxyterephthalic acid (0.200 mole, [14]) were condensed in 60 ml PPA as described for 3 above. The quench mixture was filtered on Whatman #3 paper; the damp solid was washed with water and 95% ethanol, and then dried at 10°/20 torr/4 hours to give 24.8 g of purple solid. This was extracted from a medium Soxhlet with 300 ml toluene for 2 days. The extract was kept at 22° to give 6.50 g of salmon colored powder. This was extracted continuously from a 25 cm high column of alumina in a medium Ace-Kau with 300 ml of toluene for 2 days, allowed to cool to 22° to give 5.55 g (70%) of pink microcrystals, mp 321-321.5°; uv (2.47×10^{-5} *M* in chloroform): 330 nm ($\epsilon = 36,800$), 340 (32,400), 356 (49,400), 376 (45,500).

Anal. Calcd. for C₂₀H₁₀Cl₂N₂O₃: C, 60.48; H, 2.54; N, 7.05. Found: C, 60.65; H, 2.46; N, 7.05.

2,5-Bis(5-phenyl-2-benzoxazoly)phenol 13.

The 2-amino-4-phenylphenol (0.0160 mole, TCI A 0397) and the hydroxyterephthalic acid (0.00800 mole, [14]) were condensed in 50 ml of PPA as described for 3 above. After the quench and filtration the black solid, 4.95 g, was extracted from a small Soxhlet with 150 ml of benzene for a week. The buff solid obtained on cooling was recrystallized from 70 ml of *N,N*-dimethylacetamide, then from 80 ml of *p*-xylene to obtain 0.64 g (15%), mp 310-316°; uv (4.91×10^{-5} *M* in chloroform): 348 nm ($\epsilon = 40,000$), 361 (60,000), 381 (50,000).

Anal. Calcd. for C₃₂H₂₀N₂O₃: C, 79.99; H, 4.20; N, 5.83. Found: C, 79.71; H, 4.23; N, 5.70.

2,5-Bis(2-naphth[2,3-*d*]oxazoly)phenol 14.

The 3-amino-2-naphthol (0.0300 mole, Aldrich 16,426-7) and hydroxyterephthalic acid (0.0150 mole, [14]) were condensed in 125 ml of PPA as described for 3 above. After the quench and filtration the black solid, 8.96 g, was ground in a mortar and slurried overnight in a mixture of 50 ml of water, 50 ml of 95% ethanol, and excess sodium bicarbonate, filtered, dried; extracted from a small Soxhlet with 150 ml of chloroform for 10 days to obtain 1.52 g of chartreuse powder; this was extracted with chloroform from a 1 cm high column of alumina in a medium Ace-Kau for 10 days to obtain 0.54 g (8%), mp 455-458°. It was too insoluble to determine ϵ .

Anal. Calcd. for C₂₈H₁₆N₂O₃: C, 78.49; H, 3.76; N, 6.54. Found: C, 78.69; H, 3.84; N, 6.42.

2-Amino-4-ethylphenol 16.

Based on the procedure in Vogel [32] for 2-aminophenol, a solution of 2-nitro-4-ethylphenol (15, 150.3 g, 0.900 mole [33]) in 4500 ml of 1 *M* sodium hydroxide solution was added with stirring during 45 minutes to a mixture of sodium borohydride (70.2 g, 1.86 moles) and 0.5 g of 10% palladium on carbon in 900 ml of water under argon at 20-30°, cooling by means of an

ice bath. After 90 minutes of stirring the product was filtered, washed with water and dried at 60°/15 torr/44 hours to give 111 g (90%), mp 139-141° (lit. [34] 139.5°). Some sublimate that appeared on drying had mp 140.5-142°.

2-Bromo-5-methoxyterephthalic Acid 19.

In a 2000 ml 3-necked flask in a heating mantle, with magnetic stirrer, were placed 4-bromo-2,5-dimethylanisole (**18**, $d = 1.3773$ g/ml at 18°, 28.0 g, 0.130 mole [35]), 800 ml of pyridine and 80 ml of water. At the boiling point, potassium permanganate was added in ten 10 g portions; this was followed by 130 ml of water and 50 g of potassium permanganate, 140 ml of water and 24 g of potassium permanganate, 140 ml of water and 29 g of potassium permanganate, and 65 ml of water. The mixture was held just at the boiling point overnight, and filtered on a steam-heated Büchner funnel. The lower layer *only* of the filtrate (≈ 100 ml) was diluted with 100 ml of water and acidified with 6 *M* hydrochloric acid. The crude precipitated product, 3.82 g after drying, was recrystallized from 34 ml of *N,N*-dimethylformamide diluted hot with 180 ml of water to obtain 3.15 g (9%), mp 288.5-291.5° (lit [36] mp 265-268°); pmr (10% in DMSO- d_6): Varian EM 360L, 3.82 (3H, s, $-\text{OCH}_3$), 7.43 (1H, s, H6), 7.88 (1H, s, H3), 13.2 (2H, v br s, $-\text{COOH}$).

Anal. Calcd. for $\text{C}_9\text{H}_7\text{BrO}_5$: C, 39.30; H, 2.57. Found: C, 39.39; H, 2.60.

2-Hydroxy-5-methoxyterephthalic Acid 20.

The 2-bromo-5-methoxyterephthalic Acid (**19**, 2.75 g, 0.0100 mole) was subjected 3 times to the hydrolytic conditions employed by Field and Engelhardt [14] for hydroxyterephthalic acid. The disappearance of the pmr peak at 7.88 ppm was used to monitor the purity of the product, which was 45% the first time, 90% the second time, and $\approx 100\%$ the third time; 1.61 g (76%) was obtained, mp 263-266° sl dec; pmr (10% in DMSO- d_6): Varian EM 360L, 3.75 (3H, s, $-\text{OCH}_3$), 7.15 (1H, s, H3), 7.40 (1H, s, H6), 9.78 (3H, br s, all $-\text{OH}$).

Anal. Calcd. for $\text{C}_9\text{H}_8\text{O}_6$: C, 50.95; H, 3.80. Found: C, 50.67; H, 3.77.

Dimethyl Methanesulfonamidoterephthalate 22.

In a 100 ml round bottomed flask fitted with a magnetic stirrer and a condenser topped with a calcium chloride tube was placed methanesulfonic anhydride (10 g, 0.057 mole, Aldrich 26,919-0). This was heated in an oil bath to 100-150° (bath temp.) until a clear melt was obtained. Then dimethyl aminoterephthalate (**21**, 5.0 g, 0.024 mole, Aldrich 20,537-0) was added over a period of 2-3 minutes and the mixture was heated at 100-110° for 1.5 hours. The contents were allowed to cool to $\approx 60^\circ$ and quenched with 50 ml of cold water over a period of 10 minutes, and then stirred for 30 minutes; a dark yellow precipitate formed. It was removed by filtration, and dried under vacuum to give 5.3 g (78%), mp 118-120°. Recrystallization from 60 ml of methanol afforded 5.1 g (75%), mp 120-122°; pmr: Varian EM360L, δ 3.10 (3H, s, $-\text{SO}_2\text{CH}_3$), 3.95 (3H, s, $\text{CH}_3\text{O}-$), 3.98 (3H, s, $\text{CH}_3\text{O}-$), 7.68-8.50 (3H, m, *ArH*), 10.30-10.62 ppm (1H, br s, *NH*).

Anal. Calcd. for $\text{C}_{11}\text{H}_{13}\text{NO}_6\text{S}$: C, 45.99; H, 4.53; N, 4.88. Found: C, 45.99; H, 4.58; N, 4.87.

Methanesulfonamidoterephthalic Acid 23.

A solution of potassium hydroxide (8.0 g, 0.14 mole) in 50

ml of water was added to dimethyl methanesulfonamidoterephthalate (**22**, 10 g, 0.035 mole) in a 150 ml round-bottomed flask fitted with a magnetic stirrer. The flask was stoppered, stirred overnight at 22°, and then acidified by adding 6 *M* hydrochloric acid to reach pH 2. The resulting thick white precipitate was filtered, washed with 3 x 10 ml of water, and dried in vacuum at 80° for 24 hours to give 8.8 g (98%) of **26** which melted at 300-301°.

Anal. Calcd. for $\text{C}_9\text{H}_9\text{NO}_6\text{S}$: C, 41.70; H, 3.47; N, 5.41. Found: C, 41.57; H, 3.39; N, 5.37.

For its pmr spectrum, the diacid was converted to its tripotassium salt; 245 mg was suspended in 3 ml of water, and then 190 mg of potassium hydroxide was added. The mixture was stirred for 15 minutes, when a clear solution was obtained, which was washed with 15 ml of benzene, then with 50 ml of benzene, and then evaporated until a solid mass was obtained; pmr (deuterium oxide): Varian EM360L, spectrum showed signals at the following δ -values downfield from internal DDS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate), 2.81 (3H, s, $-\text{SO}_2\text{CH}_3$), 7.03-7.73 ppm (3H, m, *ArH*).

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