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Synthesis of Proton-Transfer Fluorescent Dyes: 2,5-Bis(2'-Benzazolyl)Hydroquinones and Related Compounds

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ABSTRACT

*The synthesis and efficient purification of the fluorescent dyes 2,5-bis(2'-benzimidazolyl)hydroquinone (***1***) and 2,5-bis(2'-benzoxazolyl)hydroquinone (***2***), in the quantities needed for laser work, are reported. Additionally, simple modifications of these procedures are described for obtaining the corresponding monoheterocyclic compounds 4-(2'-benzimidazolyl)- and 4-(2'-benzoxazolyl)-2,5-dihydroxybenzoic acids* **3** *and* **4**. *Methylation and/or acetylation of bisbenzoxazole* **2** *yielded the respective mono- and disubstituted derivatives, which are important model molecules for the photophysical study of the parent dye.*

1 INTRODUCTION

Several aromatic and heteroaromatic compounds show a fluorescent emission with a large Stokes shift that originates from an intramolecular

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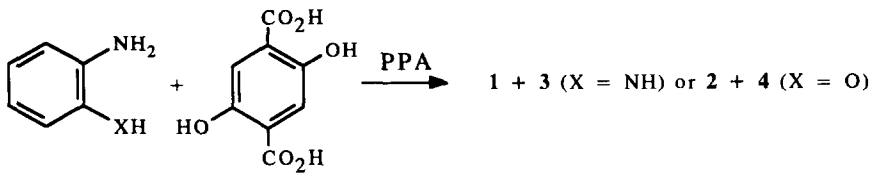
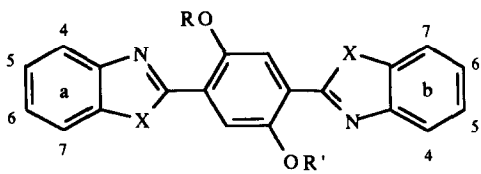
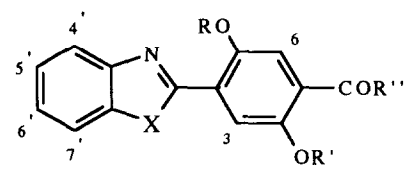
proton-transfer in the electronically excited state.[1,2] Since this process results in a phototautomer having zero concentration in the ground state, the reaction can generate stimulated emission,[3,4] provided that other kinetic and photophysical requirements are also satisfied.[5] We have previously reported that salicylamide,[6] sodium salicylate,[7] 2-(2'-hydroxyphenyl)-benzimidazole,[7] and several 5'-substituted derivatives of the latter,[8] can function as laser dyes through this mechanism.

As a continuation of this work, we were interested in finding new proton-transfer laser dyes covering the far-red and near-IR spectral ranges. In addition, there is also general interest in discovering proton-transfer derivatives where the very fast (femptoseconds–picoseconds) kinetics of the phototautomerization may be followed in detail. In this regard, it has been shown that, while 2,5-bis(2'-benzimidazolyl)-hydroquinone (**1**), 2,5-bis(2'-benzoxazolyl)hydroquinone (**2**) and a few of their derivatives show a single emission band in the far-red,[9] compound **2** and its *O*-methyl derivative **Me-2** present a *dual* fluorescence. This dual emission was ascribed to a rapid equilibration, in the excited state, between the species initially populated and the proton-transfer tautomer.[10–12] This unique behaviour facilitates considerably the study of the excited-state dynamics by ultra-fast spectroscopic techniques.[13]

On the other hand, although the photophysics of **2** has been addressed in previous publications, details on its synthesis are sparse, and a complete structure analysis of this compound, and of its derivatives with photophysical interest, is almost non-existent. Obviously, a full knowledge of the structure of the dyes in the ground state is of great utility for the correct assignment of the emitting species. In addition, the published synthetic procedures lead to only minute amounts of the dyes having the ultrapure quality required for the spectroscopic research.[10] These procedures are based on the application of some of the general ways of access to the related 2-arylsubstituted monoheterocyclic compounds. Thus, 2-arylbenzimidazoles have been obtained[14] by condensation in different media of *o*-phenylenediamine with aromatic acids,[15–18] esters, amides, nitriles[18] or aldehydes (as bisulphite adducts),[19] and 2-arylbenzoxazoles from *o*-aminophenol and aromatic acids,[15,20,21] esters, amides, nitriles[18] or acid chlorides.[22] Photo-Fries rearrangement of 2-aryloxybenzimidazoles or 2-aryloxybenzoxazoles produces, with fair to low yields, mixtures of the corresponding 2-(2'-hydroxyaryl)- and 2-(5'-hydroxyaryl)benzazoles.[23] Orlando *et al.* have claimed that compounds **1** and **2** can be obtained by condensation of *o*-phenylenediamine with 2,5-dihydroxyterephthaldehyde (bisulphite adduct) in dimethylformamide (DMF), and of *o*-aminophenol with 2,5-dihydroxyterephthalic acid in polyphosphoric acid (PPA), respectively,[9,24,25] by procedures used formerly for obtaining derivatives







	X	R	R'
1	NH	H	H
2	O	H	H
Ac-2	O	H	Ac
DiAc-2	O	Ac	Ac
Me-2	O	H	Me
DiMe-2	O	Me	Me
AcMe-2	O	Ac	Me

	X	R	R'	R''
3	NH	H	H	OH
DiMe-3	NH	H	Me	OMe
4	O	H	H	OH
Cl-4	O	H	H	Cl
Me-4	O	H	H	OMe

Scheme 1

with two 2'-benzazolyl groups connected through an unsubstituted *p*-phenylene bridge.[26–28]

In the present communication we report more efficient methods for the synthesis and purification of compounds **1** and **2**, as well as of several mono- and disubstituted derivatives of **2**, in the quantities needed for laser work. The same syntheses can be directed to obtaining the corresponding monoheterocyclic compounds **3** and **4**. The structures of all the products have been elucidated by the usual spectroscopic methods.

2 RESULTS AND DISCUSSION

Dibenzimidazole **1** and dibenzoxazole **2** were obtained by condensation of 2,5-dihydroxyterephthalic acid[10] with *o*-phenylenediamine or *o*-aminophenol, respectively, in the presence of polyphosphoric acid (PPA), essentially as described for the synthesis of the corresponding 2-arylsubstituted monoheterocyclic compounds.[16–18] Dibenzimidazole **1**,

obtained in yields up to 81%, was easily purified by crystallization, but the crude product isolated in the synthesis of the dibenzoxazole **2**, following typical experimental conditions[10] could not be readily purified (11% yield). However, its acetates **Ac-2** and **DiAc-2**, obtained in the reaction of **2** with acetic anhydride, were readily purified by column chromatography, and their hydrolysis yielded pure **2**, with total yield up to 74%. A trace of an impurity with maximum absorption at 348 and 477 nm was eliminated by recrystallization or sublimation. Compound **2** also reacted with dimethyl sulfate, giving rise to mixtures of mono- and dimethylated **2**, **Me-2** and **DiMe-2**, respectively. Compound **Me-2** yielded the acetylated derivative **AcMe-2** by reaction with acetic anhydride. Similar assays, directed to the synthesis of the corresponding acetylated or methylated derivatives of **1**, were unsuccessful.

Spectroscopic data confirmed the assigned structures. Symmetrically substituted hydroquinones **1**, **2**, **DiAc-2** and **DiMe-2** show in their ^{1}H NMR spectra a singlet, assigned to the two equivalent protons ortho to the phenolic hydroxy groups. In the non-symmetrical 2,5-bis(2'-benzoxazolyl)-hydroquinones **Ac-2**, **Me-2** and **AcMe-2** these protons appear as two singlets, and were assigned on the basis of the expected electronic effects of the substituents. Protons H-4 and H-7 or H-5 and H-6 in the benzimidazole groups of **1** produce only one signal, due to the fast prototropic equilibrium of the NH proton between positions 1 and 3. Mass spectra of all the bis-benzazoles show the corresponding molecular ions. The main fragmentation route in the acetylated derivatives **Ac-2**, **DiAc-2** and **AcMe-2** is by the loss of ketene fragments, giving rise to the base peak, whilst the main fragmentation in the methyl derivatives **Me-2** and **DiMe-2** is the loss of methyl groups. All bis-benzoxazoles produce in their mass spectra common signals of variable intensity at *m/z* 315, 287 and 144.

The reaction of equimolar amounts of 2,5-dihydroxyterephthalic acid and *o*-phenylenediamine or *o*-aminophenol, yielded the corresponding monoheterocyclic compounds **3** and **4**, with a free carboxylic group. Variable proportions of the respective bis-derivatives were always present. The possibility of covalently binding these products to a polymeric frame through alcoholic groups makes these compounds of special interest, because they can be used for the preparation of polymeric intramolecular proton-transfer (IPT) dyes with new photophysical and laser properties, as well as improved light stability. On this basis, we also prepared the methyl esters **DiMe-3** and **Me-4**, which might serve as models of polymeric molecules with pendant IPT dyes. The ether-ester **DiMe-3** was obtained by methylation of **3** with methanol in the presence of acids, and its structure, with a 2-methoxy group, was assigned on the basis of

its spectroscopic data: the chemical shift increments of H-3 and H-6, with regard to the positions of the same protons in the non-methylated compound **3**, are in accordance with the expected electronic influences of the methylation of the carboxylic group and of the OH substituent in position 2; moreover, a differential NOE experiment under argon, irradiating the singlet at 3·39 ppm, showed that the corresponding methyl group is probably a CH_3OAr group, and not a CH_3N group, since no influence was observed on H-7' or on the other aromatic protons; irradiation of the CH_3 protons in 1-methyl-2-phenylbenzimidazole produces a clear NOE effect on its H-7' proton.[29] The structure assigned to **DiMe-3**, with a methoxy group in position 2, is also consistent with the observation of a fluorescence band at 570 nm in acetonitrile (quantum yield 0·20 ± 0·05, upon irradiation with light of 370 nm). The position of this proton-transfer emission is within the range of those observed in 5'-substituted 2-(2'-hydroxyphenyl)benzimidazole dyes,[8] rather than in the range of the fluorescence of salicylate esters.[30] Finally, ester **Me-4** was prepared from the acid **4** via the corresponding acyl chloride **Cl-4**.

3 EXPERIMENTAL

3.1 General

Melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer (Norwalk, USA) 1430 spectrophotometer. ^1H NMR spectra (δ scale, TMS as internal reference) were run on Varian (Palo Alto, USA) models XL-300 or VXR-200; correlations of chemical shifts were obtained with homonuclear decoupling experiments and by comparison with the spectra of the model structures 2-(2'-hydroxyphenyl)benzimidazole and 2-(2'-hydroxyphenyl)-benzoxazole; assignment of the aromatic protons in non-symmetrical bis-benzoxazoles was carried out by comparison with the symmetrically substituted ones. Mass spectra (MS's) were determined on Hewlett-Packard (Palo Alto, USA) model 5988A or on VG-ZAB, in the electronic impact mode and with direct injection. UV-visible absorption spectra were recorded, on solutions in DMF, on a Perkin-Elmer Lambda 2 spectrophotometer with 1 nm resolution; absorption spectra of compounds **1** and **2** are shown in Fig. 1; absorption maxima and the logarithm of the molar absorption coefficients (ϵ, $l.mol^{-1}\ cm^{-1}$) for all the compounds are included in Table 1. Microanalyses were performed on a Perkin-Elmer 2400 model; correct data could not be obtained for the monoheterocyclic compounds, although all of them gave only one spot on thin layer chromatographic plates with several eluents.

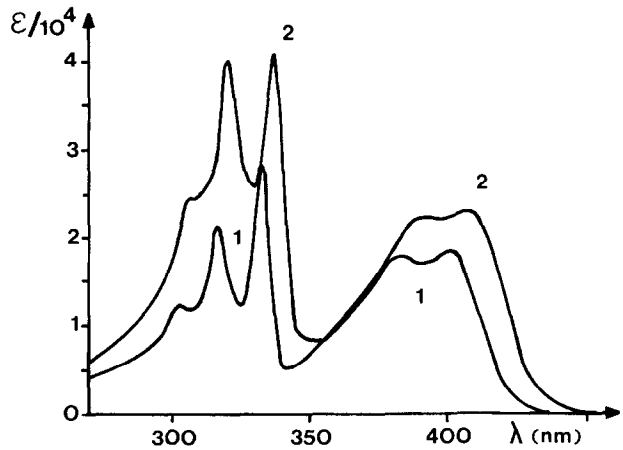


Fig. 1. Electronics spectra of bis-benzimidazole **1** and bis-benzoxazole **2** (3×10^{-5} M solutions in dimethylformamide).

2,5-Dihydroxyterephthalic acid was obtained from 2,5-diethoxycarbonyl-1,4-cyclohexanedione (Aldrich, Milwaukee, USA) through oxidation (bromine, carbon disulfide, reflux) and hydrolysis (NaOH, ethanol–water 1:1 (v/v), reflux).[10] Polyphosphoric acid (PPA) (from BDH, Poole, England) had a P_2O_5 content of 82–85%.

3.2 2,5-Bis(2'-benzimidazolyl)hydroquinone (1)

A mixture of *o*-phenylenediamine (0·50 g, 4·6 mmol), 2,5-dihydroxyterephthalic acid (0·45 g, 2·3 mmol) and PPA (30 ml) was heated to 190–200°C with stirring. After 1 h the mixture was cooled, poured into 1 kg of ice-water, and the yellow precipitate was filtered, washed with

TABLE 1
Electronic Spectral Data in DMF Solution (*c.* 3×10^{-5} M)

Compound	λ_{max} *(nm) (log ε)*
1	303 (4·10), 317 (4·34), 333 (4·46), 383 (4·26), 401 (4 27)
2	307 (4·39), 320 (4 60), 337 (4·62), 391 (4·36), 407 (4·37)
Ac-2	321 (4·47), 326 (4·46), 336 (4·42), 358 (4·28), 377 (4·28), 409 (3·94)
DiAc-2	328 (4·53), 342 (4·49), 357 (4·41), 376 (4·22), 413 (3·59)
Me-2	319 (4·47), 381 (4 35)
DiMe-2	314 (4·39), 335 (4·27), 370 (4·35)
AcMe-2	315 (4·39), 328 (4·41), 356 (4·41), 403 (3·17)
3	302 (4·23), 314 (4·23), 332 (3·79), 373 (3·97)
DiMe-3	315, 325, 380
4	301 (4·36), 313 (4·22), 338 (3·57), 386 (4·00)
Me-4	308 (4·26), 323 (4·11), 384 (3·91)

water and dried at 60°C (yield 0·86 g). Soxhlet extraction of this with ethanol removed soluble impurities, yielding 0·7 g (81%) of **1**, which was further purified by recrystallization from ethanol or DMF; m.p. > 420°C. Calculated for $C_{20}H_{14}N_4O_2$: C, 70·19; H, 4·09; N, 16·36. Found: C, 69·83; H, 4·12; N, 16·14. MS, *m/z* (%): 342 (M+, 10), 341 (8), 327 (7), 326 (9), 281 (31), 270 (10), 207 (100), 192 (10), 168 (7). ^{1}H NMR (300 MHz, DMSO-d6, 60°C): δ 7·31 (m, 4H, 2 × H-5 and 2 × H-6), 7·67 (m, 4H, 2 × H-4 and 2 × H-7), 7·78 (s, 2H, 2 × H ortho-OH). IR (KBr): 3309s, 3233vs, 1556m, 1500vs, 1354s, 1317m, 1248s, 838m, 745m, 732m cm^{-1}.

3.3 2,5-Bis(2'-benzoxazolyl)hydroquinone (2)

A mixture of *o*-aminophenol (2·20 g, 20 mmol), 2,5-dihydroxyterephthalic acid (1·98 g, 10 mmol) and PPA (50 ml) was heated to 180–200°C with stirring. After 12 h the mixture was cooled, poured into 2 kg of ice-water and the dark green precipitate was isolated as before. A mixture of this crude product (3·4 g) with acetic anhydride (50 ml) and conc. sulfuric acid (1 ml) was stirred for 30 min at room temperature and then poured into ice-water, the precipitate was filtered, washed with water and dried. The separated solid (3·60 g) was a mixture of the mono and the diacetylated derivatives of **2**, **Ac-2** and **DiAc-2**. They were separated and purified by column chromatography (silica gel, chloroform), yielding 0·77 g and 2·33 g, respectively. The mixture of the two purified compounds was hydrolysed (50 ml conc. sulfuric acid, room temperature, stirring, 30 min); the reaction mixture was poured into ice-water, and the yellow solid **2** filtered and dried. Yield 2·53 g (74%). An analytical sample of **2** was obtained by recrystallization from DMF or chloroform and sublimation; m.p. >360°C. Calculated for $C_{20}H_{12}N_2O_4$: C, 69·77; H, 3·49; N, 8·14. Found: C, 69·62; H, 3·31; N, 7·85. MS, *m/z* (%): 344 (M+, 100), 315 (2), 287 (21), 259 (6), 172 (10), 144 (18). ^{1}H NMR (300 MHz, DMSO-d_6, 60°C): δ 7·48 and 7·52 (m, 4H, 2 × H-5 and 2 × H-6), 7·70 (s, 2H, two H *o*-OH), 7·85 and 7·89 (two m, 4H, 2 × H-4 and 2 × H-7); (200 MHz, CF_3CO_2H) δ 8·09 (m, 4H, 2 × H-5 and 2 × H-6), 8·24 (m, 4H, 2 × H-4 and 2 × H *o*-OH). IR (KBr): 3125b, 1564vs, 1496vs, 1448s, 1230vs, 1060m, 831s, 762s, 749 m cm^{-1}.

*2,5-Bis(2'-benzoxazolyl)-4-acetoxyphenol (**Ac-2**).* M.p. 275–277°C (from chloroform–cyclohexane). Calculated for $C_{22}H_{14}N_2O_5$: C, 68·39; H, 3·63; N, 7·25. Found: C, 68·00; H, 3·86; N, 7·16. MS, *m/z* (%): 386 (M^+, 2), 344 (100), 287 (11), 144 (7). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2·44 (s, 3H, CH_3), 7·37 (m, 4H, H-5a, H-5b, H-6a and H-6b), 7·53 (m, 2H, H-7a and H-7b), 7·71 (m, 2H, H-4a and H-4b), 7·81 (s, 1H, H ortho-OH), 7·96 (s, 1H, H ortho-OAc), 11·40 ppm (broad s, 1H, OH). IR (KBr): 3078b,

1764vs, 1558s, 1496s, 1448s, 1361m, 1246s, 1204vs, 1183vs. 1058s, 763m, 748s cm^{-1}.

*2,5-Bis(2'-benzoxazolyl)-1,4-diacetoxybenzene (**DiAc-2**).* M.p. 307–309°C. Calculated for $C_{20}H_{16}N_2O_6$: C, 67·31; H, 3·74; N, 6·54. Found: C, 67·01; H, 3·80; N, 6·72. MS, *m/z* (%): 428 (M^+, 8), 386 (8), 344 (100). ^1H NMR (200 MHz, $CDCl_3$): δ 2·49 (s, 6H, 2 × CH_3), 7·36 (m, 4H, 2 × H-5 and 2 × H-6), 7·51 (m, 2H, 2 × H-7), 7·73 (m, 2H, 2 × H-4), 8·12 (s, 2H, 2 × H ortho-OAc). IR (KBr): 1764vs, 1563m, 1496m, 1449s, 1365s, 1247s, 1204vs, 1164vs, 1053s, 763m, 747s cm^{-1}.

3.4 2,5-Bis(2'-benzoxazolyl)-4-methoxyphenol (Me-2) and 2,5-bis(2'-benzoxazolyl)-1,4-dimethoxybenzene (DiMe-2)

A mixture of **2** (0·5 g, 1·45 mmol), sodium hydroxide (0·25 g, 6·25 mmol), dimethyl sulfate (0·2 ml, 2·13 mmol, for **Me-2**, or 0·40 ml, 4·26 mmol, for **DiMe-2**) and tetrahydrofurane (100 ml) was heated under reflux for 1 h, with stirring. The cooled reaction mixture was acidified with 10% HCl (20 ml), the organic solvent was removed *in vacuo* and the separated solid was filtered, washed with water, dried and purified by column chromatography (silica gel, chloroform) and crystallization from DMF or by sublimation. Yield 156 mg (30%) of **Me-2** or 270 mg (50%) of **DiMe-2**.

Me-2. M.p. 271–272°C. Calculated for $C_{21}H_{14}N_2O_4$: C, 70·39; H, 3·94; N, 7·82. Found: C, 70·72; H, 4·29; N, 7·63. MS, *m/z* (%): 358 (M^+, 100), 357 (56), 343 (35), 329 (40), 315 (15), 313 (14), 287 (21), 211 (31), 144 (22). ^1H NMR (200 MHz, $CDCl_3$): δ 4·07 (s, 3H, CH_3), 7·38 (m, 4H, 2 × H-5 and 2 × H-6), 7·60 (m, 2H, 2 × H-7), 7·62 (s, 1H, H ortho-OH), 7·72 (m, 1H, H-4a), 7·82 (m, 1H, H-4b), 7·89 (s, 1H, H ortho-OMe), 11·10 (broad s, 1H, OH). IR (KBr): 3177b, 1557m, 1535s, 1500s, 1449vs, 1246vs, 1216m, 1182m, 827s, 763m, 751s cm^{-1}.

DiMe-2. M.p. 323–324°C. Calculated for $C_{22}H_{16}N_2O_4$: C, 70·96; H, 4·33; N, 7·52. Found: C, 70·95; H, 4·38; N, 7·76. MS, *m/z* (%): 372 (M^+, 100), 371 (4), 357 (21), 343 (21), 329 (7), 315 (2), 313 (8), 287 (2), 251 (17), 225 (43), 144 (10). ^1H NMR (200 MHz, $CDCl_3$): δ 4·09 (s, 6H, 2 × CH_3O), 7·38 (m, 4H, 2 × H-5 and 2 × H-6), 7·63 (m, 2H, 2 × H-7), 7·85 (m, 2 × H-4), 7·87 (s, 2H, 2 × H ortho-OMe). IR (KBr): 1550s, 1480m, 1448vs, 1410vs, 1225vs, 1034s, 821m, 763m, 749s cm^{-1}.

3.5 2,5-Bis(2'-benzoxazolyl)-4-acetoxy-1-methoxybenzene (AcMe-2)

A mixture of **Me-2** (100 mg, 0·28 mmol), conc. sulfuric acid (0·2 ml) and acetic anhydride (15 ml) was stirred at room temperature for 30 min. Subsequent work-up yielded 80 mg (69%) of **AcMe-2**. M.p. 225–227°C.

MS, *m/z* (%): 400 (M^+, 8), 358 (100), 343 (21), 329 (30), 315 (10), 287 (14), 144 (26). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2·47 (s, 3H, CH_3CO), 4·15 (s, 3H, CH_3O), 7·36 (m, 4H, 2 × H-5 and 2 × H-6), 7·57 (m, 1H, H-7a), 7·74 and 7·75 (two m, 2H and 1H, respectively, H-4a, H-4b and H-7b), 7·94 and 8·03 (two s, 2H, H ortho-OMe and H ortho-OAc). IR (KBr): 1761vs, 1535m, 1447m, 1244m, 1214vs, 1194vs, 1023s, 761m, 749s cm^{-1}.

3.6 4-(2'-Benzimidazolyl)-2,5-dihydroxybenzoic acid (3)

An equimolar mixture of *o*-phenylenediamine (0·25 g, 2·3 mmol) and 2,5-dihydroxyterephthalic acid (0·45 g, 2·3 mmol) in PPA (30 ml) was reacted using the same experimental conditions to those for the diheterocyclic compound **1**. Soxhlet extraction with ethanol of the resulting solid yielded, after solvent elimination, almost pure **3**. It was crystallized from a large volume of water (1 mg/100 ml). Yield 0·19 g (30%). M.p. 350°C (decomp.). MS, *m/z* (%): 270 (M^+, 63), 252 (57), 224 (45), 168 (100), 143 (46). ^{1}H NMR (300 MHz, DMSO-d_6, 60°C): δ 7·44 (m, 2H, H-5' and H-6'), 7·55 and 7·61 (two s, 2H, H-3 and H-6), 7·71 (m, 2H, H-4' and H-7'). IR (KBr): 3050b, 1677m, 1618s, 1561m, 1501m, 1408m, 1239s, 1198vs, 1180s, 792m, 751m cm^{-1}.

3.7 Methyl 4-(2'-benzimidazolyl)-5-hydroxy-2-methoxybenzoate (DiMe-3) (tentative)

A mixture of **3** (50 mg, 0·18 mmol) and conc. sulfuric acid (0·1 ml) in methanol (50 ml) was refluxed for 24 h with stirring. The reaction mixture was poured into ice-water, and the precipitate was filtered, washed with water and dried. Yield 20 mg (38%); m.p. 251–253°C. MS, *m/z* (%): 298 (M^+, 1), 283 (63), 252 (52), 224 (54), 168 (100), 143 (45). ^{1}H NMR (300 MHz, DMSO-d_6, 80°C): δ 3·39 (s, 3H, CH_3OAr), 3·93 (s, 3H, CO_2CH_3), 7·31 (m, 2H, H-5' and H-6'), 7·38 (s, 1H, H-6), 7·67 (m, 2H, H-4' and H-7'), 7·73 (s, 1H, H-3), 9·84 and 10·10 (two broad s, 2H, OH + NH). IR (KBr): 3260b, 1720s, 1605m, 1551m, 1501s, 1329s, 1232s, 1192s, 1000m cm^{-1}.

3.8 4-(2'-Benzoxazolyl)-2,5-dihydroxybenzoic acid (4)

A mixture of *o*-aminophenol (0·55 g, 5 mmol), 2,5-dihydroxyterephthalic acid (1·0 g, 5 mmol) and PPA (30 ml) was heated to 180–200°C for 2 h with stirring. The cooled mixture was poured into 1 kg of ice-water, and the precipitate was filtered, washed with water, dried and soxhlet-

extracted with chloroform. Compound **4** was isolated from the solvent. Yield 0·40 g (29%); m.p. 312°C (decomp.). MS, *m/z* (%): 271 (M^+, 87), 257 (88), 225 (86), 169 (100), 144 (93). ^{1}H NMR (300 MHz, DMSO-d_6, 80°C): δ 7·51 and 7·68 (two m, 2H, H-5' and H-6'), 7·51 and 7·73 (two s, 2H, H-3 and H-6), 7·86 and 7·89 (two m, 2H, H-4' and H-7'); (200 MHz, CF_3CO_2H): δ 8·17 (m, 2H, H-5' and H-6'), 8·26 (m, 2H, H-4' and H-7'), 8·32 and 8·58 (two s, 1H each, H-3 and H-6). IR (KBr): 3075b, 1674s, 1635m, 1562m, 1491s, 1446vs, 1203vs, 1180vs, 840m, 763s, 747m cm^{-1}.

3.9 4-(2'-Benzoxazolyl)-2,5-dihydroxybenzoyl chloride (Cl-4)

A mixture of **4** (150 mg, 0·55 mmol) and thionyl chloride (50 ml) was heated to 50°C with stirring. After 4 h the thionyl chloride was vacuum-evaporated and the resulting solid was dried *in vacuo* and used without further purification. Yield 136 mg (85%); m.p. 145°C (decomp.). ^{1}H NMR (300 MHz, DMSO-d_6, 90°C): δ 7·47 and 7·51 (two m, 2H, H-5' and H-6'), 7·49 and 7·54 (two s, 2H, H-3 and H-6), 7·82 and 7·86 (two m, 2H, H-4' and H-7'). IR (KBr): 3400b, 1775m, 1726s, 1688s, 1485vs, 1447m, 1290m, 1235m, 1179s, 1150vs, 1030s, 822m, 758m, 747s cm^{-1}.

3.10 Methyl 4-(2'-benzoxazolyl)-2,5-dihydroxybenzoate (Me-4)

This was obtained from **Cl-4** (100 mg, 0·34 mmol) by treatment with methanol (50 ml) at room temperature. It was purified by column chromatography (silica gel, chloroform). Yield 80 mg (85%), m.p. 225–226°C. MS, *m/z* (%): 285 (M^+, 84), 253 (80), 225 (64), 169 (100), 144 (43). ^{1}H NMR (300 MHz, DMSO-d_6, 60°C): δ 3·91 (s, 3H, CH_3), 7·43 and 7·58 (two s, 2H, H-3 and H-6), 7·47 and 7·51 (two m, 2H, H-5' and H-6'), 7·84 and 7·87 (two m, 2H, H-4' and H-7'), 9·88 and 10·50 (two s, 2H, two OH). IR (KBr): 3284b, 1688s, 1500s, 1474m, 1444s, 1345s, 1227s, 1203vs, 789m, 737m cm^{-1}.

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