Synthesis and Photophysical Properties of Fluorescent 2-Aryl-1,3-dialkylbenzimidazolium Ions and a 1-Alkyl-2-arylbenzimidazole with Excited State Intramolecular Proton-Transfer

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To improve the solubility, photostability and fluorescence quantum yield (Φ) of 2-arylbenzimidazolium ions the N-1 hydrogen was replaced by an alkyl group before N-3 was quaternized; this substitution did not reduce Φ, proving the absence of steric inhibition to attainment of coplanarity in the excited state. A related symmetrical 2,2'-arylenebis(1,3-dimethyldibenzimidazolium ion) had $\Phi = 0.86$. The related 2,5-bis(1-methyl-2-benzimidazolyl)phenol had $\Phi = 0.38$ at 22° as well as a very large Stokes' shift due to proton-transfer. These findings supported a new insight into the electron distribution of the first excited singlet state of oligophenylenes. The compounds are of interest as laser dyes and scintillation fluors.

Introduction.

The 2-(2-furyl)benzimidazolium ion **1** (Figure 1) performed well as a xenon chloride excimer pumped laser dye [1], showing moderate light output and surprisingly good service lifetime. In its first excited singlet state ion **1** would be expected to have electron density transferred from the chlorine atom to N3 of the benzmidazole moiety in the manner described for some fluorescent pyridinium salts prepared as laser dyes [2]. This transfer requires that all the aromatic rings become coplanar. Because both furan and imidazole are 5-membered rings with 108° internal angles, and no hydrogen atom projects from the oxygen atom, there is little steric interference to attainment of coplanarity between the furan ring and the two *N*-methyl groups in **1**. We wanted to replace the photochemically unstable furan ring with a benzene ring in order to gain more service lifetime as a laser dye for a compound such as **2** [3], while retaining the 1,3-dialkylbenzimidazolium ion as the electron-attracting auxofluor. The two *ortho* hydrogens on the benzene ring in the general dye structure **2** might have some serious repulsions from the *N*-methyl groups; this would reduce the extinction coefficient (ε) and the fluorescence quantum yield (Φ), and thus the light output as a laser dye. Certainly, in oligophenylenes in which all the rings are 6-membered, this sort of repulsion reduces ε and Φ seriously [4]. Structure **2**, in which a 5-membered ring abuts a 6-membered ring, is intermediate between oligophenylenes and structure **1** in probable steric interference with attainment of planarity in the lowest excited singlet (S_1) state. We wanted to determine the extent of this interference.

Major parts of the particle detectors envisioned for the Super-conducting Super Collider (SSC) are to be fabricated from bundles of scintillating polystyrene fibers several meters long [5-7]. The scintillation fluor or the shifter, if a primary fluor is to be used, must have a number of prop-

erties that were not available in any fluor when this work was begun [8]. Among these properties are fluorescence emission at 500-600 nm, $\Phi \geq 0.4$ (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 [9]. Transparency of the fluor to its own emission wavelengths is a crucial property, a requirement now believed to be obtainable, along with all the other desirable properties, only from an organic molecule which displays excited-state intramolecular proton-transfer (ESIPT) fluorescence.
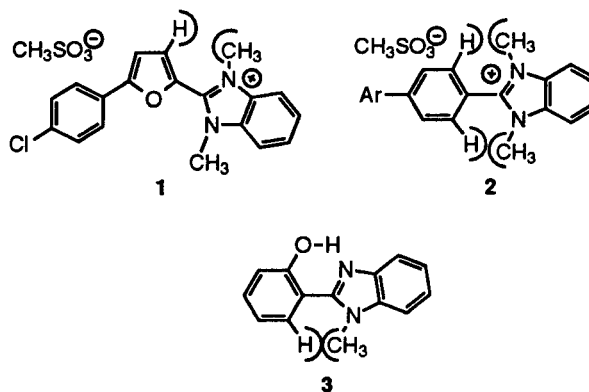

Figure 1. Steric interactions in 2-aryl-1,3-dimethylbenzimidazolium ions and 2-(2-hydroxyphenyl)-1-methylbenzimidazole.

For several years the benchmark compound for scintillation counting in polystyrene fibers has been the ESIPT fluor 3-hydroxyflavone (3HF), [10] which has, in polystyrene, an emission peak at 530 nm, $\Phi = 0.3$ (too low), and $\tau = 8.8$ nsec (much too slow). It is too reactive chemically, and also is not sufficiently soluble in polystyrene ($\approx 1\%$ w/w) to be used as a sole fluor. In the course of this

work we prepared flavones with greatly improved photophysical properties [11], but their chemical reactivity would be expected to remain the same.

The compound 2,5-bis(2-benzimidazolyl)hydroquinone, now known to be an ESIPT fluor, was reported to have fluorescence emission in the solid state at $\lambda > 600$ nm [12-13]; no ε or Φ values nor any absorption or emission wavelengths in solution were reported. Its melting point is $> 380°$ and its solubility in aromatic solvents is very low. Some 2-(2-hydroxyaryl)-1H-naphth[2,3-d]imidazoles had ESIPT emission in solution at 485-545 nm; these were also poorly soluble compounds melting $> 330°$ [14]. The N-hydrogen atoms are a potential point of free-radical reactivity [15] as well as the cause of intermolecular hydrogen bonding which decreases solubility in polystyrene. To remove this unwanted reactivity as well as to increase solubility in non-polar solvents, we decided to prepare a corresponding dibenzimidazole with N-methyl groups in place of N-hydrogens. The same sort of steric inhibition of excited state planarity which might have affected benzimidazolium ions such as 2 would also affect the hypothetical ESIPT benzimidazole 3. In related work on 2,5-bis(2-benzoxazolyl)hydroquinone [16] we found that the omission of one of the hydroxyl groups raised the Φ from 0.03 to 0.4, as well as raising ε from 25,000 to 58,000; therefore, after we observed the photophysical properties of the model compounds described below, we decided to prepare 2,5-bis(1-methyl-2-benzimidazolyl)-phenol (26 in Scheme 5).

To test for methyl-hydrogen repulsions, we prepared two model compounds (16a and 16b in Table 1) which incorporated N-propyl groups in both cases, but differed in that 16a bore a hydrogen atom and 16b bore an N-methyl group, and we compared their Φ values. In another modification of dye 1, we used methoxy as the electron-releasing auxofluor instead of chlorine, because this group was so effective with certain pyridinium salts evaluated as laser dyes [17], in which the pyridinium moiety was the electron-attracting auxofluor. Besides, it is well-known that a chloro group is more likely to quench fluorescence than a methoxy group [18-19].

In the conventional picture of an oligophenylene in its S_1 state, two resonance forms with charge separation (4a and 4b in Figure 2) are shown [18]. It is hard to see how a given part of the molecule can be both positively and negatively charged at the same time. A better qualitative picture of the S_1 state is needed. Since carbanions are not stabilized by allylic resonance and carbocations are, as shown by the single curved arrow in 4a, we thought that both ends of this fluorophore would become negative in the S_1 state, while the entire center portion would become positively charged as in 4c. Typical electron-attracting auxofluors that might stabilize this sort of charge separa-

tion, such as halogen, carbonyl, or nitro, quench fluorescence by triplet formation [18-19], so they are misleading in testing this theory. The 1,3-dialkylbenzimidazolium ion is unusual in being both strongly electron-attracting and devoid of either unshared electron pairs prone to undergoing n-π* transitions, or heavy atoms; thus it was thought likely to be an excellent auxofluor to test the theory. The photophysical properties of the model compounds 16a and 16b showed that potential steric repulsions that could have diminished Φ were shown to be absent. However, since 16a and 16b contain push-pull auxofluors, we attempted to prepare the symmetrical di-quaternary salts of the N,N'-dialkyldibenzimidazoles 19 (Scheme 3) and 22 (Scheme 4) to find whether use of electron-attracting auxofluors at both ends of this fluorophore would increase Φ and ε to values higher than those possible with conventional auxofluors. High Φ and ε would be evidence for the contribution of resonance form 4c to the S_1 state of oligophenylenes and related symmetrical fluorophores. The ionic groups would confer good solubility in polar solvents for these potential laser dyes.
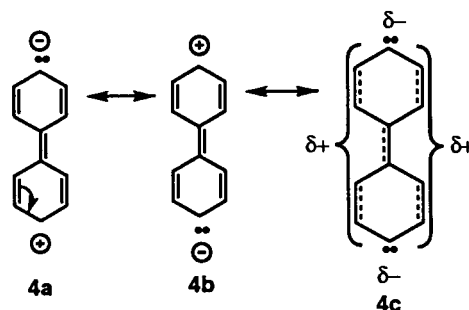

Figure 2. A new view of symmetrical charge distribution in the first excited singlet state of a symmetrical fluorophore — biphenyl.

Discussion and Results.

Syntheses of Fluorescent Quaternary Salts of 2-Aryl-1-propylbenzimidazoles.

Making the key intermediate, benzimidazole 12 (Scheme 1) proved to be surprisingly difficult. The report of a clean preparation of N-methyl-o-phenylenediamine 5 by methylation of o-phenylenediamine 6 [20] could not be repeated by us with 1-iodopropane to make the homologous N-propyl-o-phenylenediamine. The N-allyl-o-phenylenediamine 8 [21] was extremely unstable, thus we were unable to reduce it by means of Raney Nickel and hydrazine to give 7. Alkylation of o-chloronitrobenzene 9 with propylamine to the nitroamine went well, and reduction to diamine 7 with sodium dithionite was satisfactory [21], but the rapid oxidation of 7 in air led, on reaction

Synthesis and Photophysical Properties of Fluorescent
2-Aryl-1,3-dialkylbenzimidazolium Ions and a 1-Alkyl-2-arylbenzimidazole

with p-bromobenzoic acid 11 in polyphosphoric acid, to a poor yield of benzimidazole 12. The similar reaction of *o*-phenylenediamine 6 with 11 gave benzimidazole 13 in 60% yield. Alkylation of 13 with 1-iodopropane was difficult, with use of sodium hydroxide in aqueous acetone proving most effective, to give benzimidazole 12 in 55% yield.

chemically activated magnesium [23]; starting materials were isolated. Using ultrasound led to formation of the "dimer" of 12, which was not characterized or pursued because it was thought to have too short a fluorophore to be an effective laser dye. The well-known effectiveness of arylzinc compounds in coupling [24] and the compatibility of arylzinc compounds with functional groups reactive

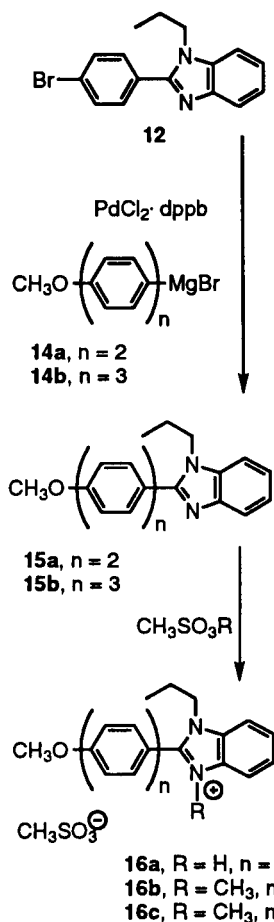Scheme 1. Synthetic Approaches to 1-Propyl-2-(4-bromophenyl)benzimidazole
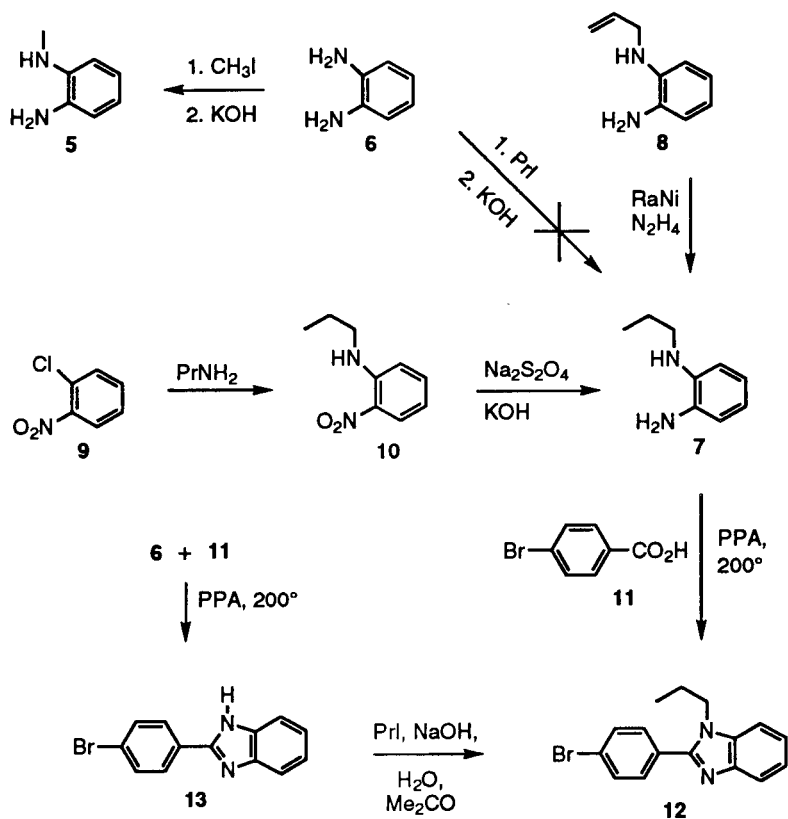
Palladium catalyzed coupling of the Grignard Reagents 14a and 14b from anisole and 4-bromo-4'-methoxybiphenyl (prepared by bromination of 4-biphenylyl benzoate followed by basic hydrolysis; and then ether formation details to be reported elsewhere) gave 80% and 40% yields, respectively, of the 2-(2-methoxyaryl)-1-propylbenzimidazoles 15a and 15b (Scheme 2). The acid salt 16a and the quaternary salts 16b and 16c were prepared by conventional methods.

Taking into account the observation that most classes of the most effective laser dyes are symmetrical along the long axis of the fluorophore [22], we attempted to prepare dibenzimidazole 19 (Scheme 3) with the intention of making the diquaternary salt of 19 with methyl methanesulfonate. The Grignard Reagent from 12 would not form under any conditions we tried, including the use of

with Grignard Reagents led us to try to form the aryllithium by reaction of *t*-butyllithium with 12, followed by anhydrous zinc chloride to make the arylzinc compound 17. Not knowing for certain whether arylzinc compound 17 had formed, conditions for coupling with 2,7-dibromo-9,9-dipropylfluorene [25] were employed, but no coupling occurred, probably because of reaction of the intermediate aryllithium with the C=N bond in another molecule. The direct formation of arylzinc compounds from highly reactive zinc [24] was reported too late for this work, but appears promising.

We elected to make the diquaternary salt 23 (Scheme 4) from the dibenzimidazole 22 by oxidation of the Schiff base 21 by means of lead tetraacetate. This followed the procedure of Stephens and Bower who prepared 1,4-bis-(1-methyl-2-benzimidazolyl)benzene [26]. Accordingly,

**Scheme 2. Syntheses of Fluorescent
2-Aryl-1-propylbenzimidazoles,
Methyl Methanesulfonate Salt and Quaternary Salts**

**Scheme 3. Attempted Synthesis of an
Arylene-2,2'-dibenzimidazole (19)**

shifts of absorption and fluorescence [4, 28]. In a series of progressively more methylated quaterphenyls the relative pulse heights in scintillation counting were measured, rather than the Φ values, and they dropped significantly.

**Scheme 4. Synthesis of an Arylene-2,2'-dibenzimidazole
and Its Diquaternary Salt**

the bis-Grignard reagent from 2,7-dibromo-9,9-dipropyl-fluorene **18** was formylated with DMF [27]. The dialdehyde **20** with the diamine **5** gave the Schiff base **21**, which, without purification was oxidized to the dibenzimidazole **22**, and quaternized with methyl methanesulfonate to make the diquaternary salt **23**.
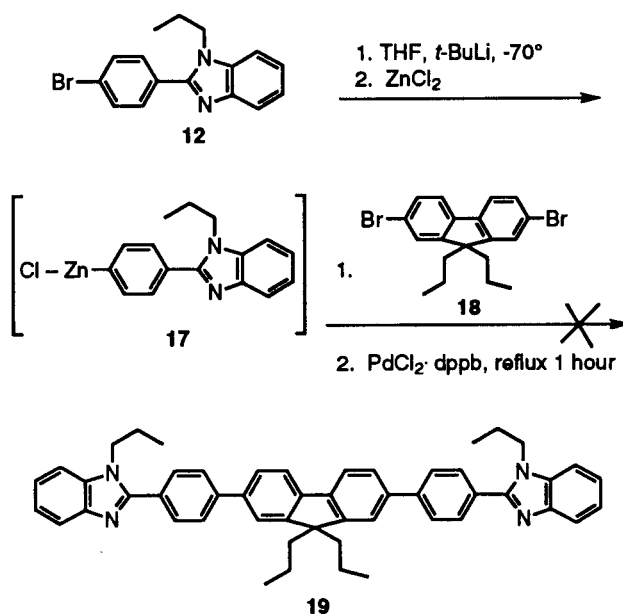
Synthesis of Fluorescent Dibenzimidazole **26**.

Hydroxyterephthalic acid **24** (Scheme 5) was converted to the diacid chloride **25** with thionyl chloride in the presence of a catalytic amount of dimethylformamide. Without isolation, reaction of **25** with *N*-methyl-*o*-phenylenediamine **22** in dimethylformamide gave the dibenzimidazole **26** in 20% yield. Excellent assays for C, H, and N support the structure, as well as the pmr spectrum, in which the two slightly different *N*-methyl groups appear as singlets with slightly different chemical shifts.
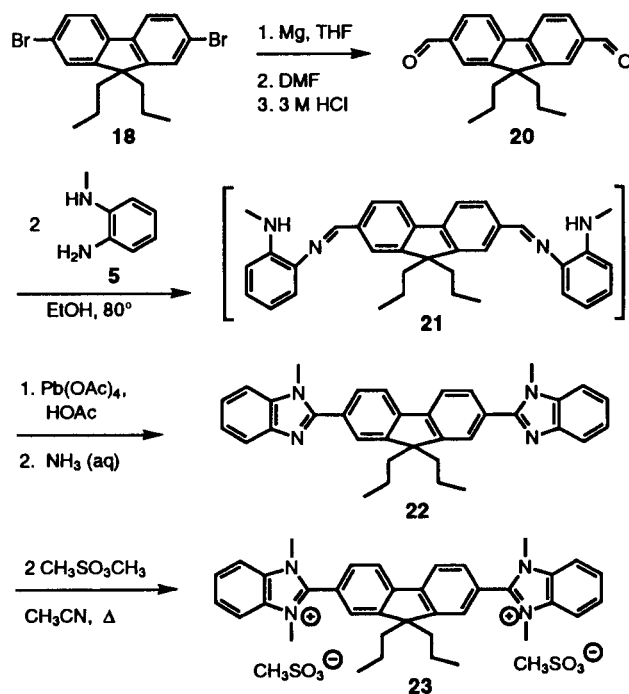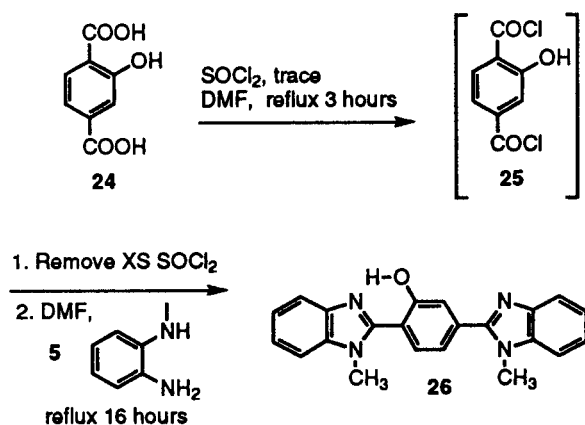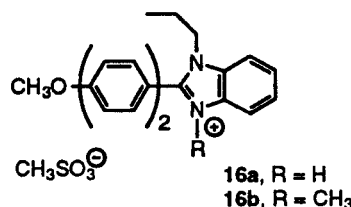
Photophysical Properties.

The presence of internal alkyl groups on oligophenylenes causes ε and Φ to drop, and produces hypsochromic

Scheme 5. Synthesis of Dibenzimidazole 26
with Hydroxyl Group as Proton Donor

Two similar pairs of pyridinium quaternary salts, each of which also had a methoxy auxofluor, and also differing by a phenylene group were recently reported by Hall *et al.*, to behave in the same manner; these are **11A** *vs.* **2B** and **11B** *vs.* **2J** [in 17]. These authors report still other examples.

Table 1
Steric Effect of a 1-Methyl Group *vs.* that of a 1-Hydrogen on
2-Aryl-3-propylbenzimidazoles as Shown by
Measurement of Fluorescence Quantum Yield (Φ)

16a, R = H
16b, R = CH$_3$

R	Solvent	Φ
H	ethanol	0.80
CH$_3$	ethanol	0.77
H	ethanol:water::1:1	0.78
CH$_3$	ethanol:water::1:1	0.78
H	water	0.56
CH$_3$	water	0.66

In our 1,3-dialkylbenzimidazolium ion (**16b** in Table 1) steric hindrance to attainment of coplanarity in the excited state might be more pronounced than for the acid salt of a 3-alkylbenzimidazole because a methyl group is significantly larger than the hydrogen atom in the acid salt **16a**. The Φ value is a most sensitive measure of interference with a molecule's ability to reach the planar excited state from which it can fluoresce. Table 1 shows that **16a**, whose planar S$_1$ state must suffer an N-H - - H-C repulsion, has a slightly higher Φ value in ethanol than **16b** whose planar S$_1$ state must suffer a potentially more severe N-H - - CH$_3$-C repulsion. They show the same Φ value in 1:1::ethanol:water (v/v), and **16a** has a lower Φ value in water. Thus there is no difference between the pair in steric hindrance to attainment of coplanarity in the excited state of these molecules in solution. Therefore, larger fluorophores which are quaternary salts of 1,3-dialkylbenzimidazoles and *N*-methylbenzimidazoles with proton transfer from an atom on the ortho position of a 2-phenyl group should be efficient fluors. The lower value for the acid salt **16a** in water may indicate that the small water molecule quenches fluorescence by collision with the N-H bond, but is kept away better by the hydrophobic methyl group in **16b**. The longwave absorption peak of **16b** (ε = 34,000 at 304 nm) shows that the 1,3-dialkylbenzimidazolium ion is an extremely effective auxofluor compared with the methyl group in 4,4'-dimethoxy-biphenyl (ε = 23,000 at 263 nm) [28].

Where **16a** and **-b** are biphenyls, **16c** (Scheme 2) is a terphenyl; however its absorption maximum was bathochromically shifted only 9 nm to 313 nm (ε = 40,000), and its emission was a weak green luminescence with a whitish overcast in contrast to the clean violet fluorescence of the shorter homologs. This indicates triplet state formation, which possibly results from limited interaction between the auxofluors at opposite ends of the fluorophore.

The bis(dialkylbenzimidazolium ion) **23** proved to be an efficient fluor indeed (Φ = 0.86, λem = 390 nm ε = 49,500 at 320 nm, in absolute ethanol). Compare these values with those we found for 9,9-dipropylfluorene (Φ = 0.36, ε = 12,700 at 304 nm, in cyclohexane) or for 2,7-di-*t*-butylfluorene (Φ = 0.70, ε = 13,100 at 308 nm, in cyclohexane). This result shows that at least one type of electron-attracting auxofluor attached to both ends of an oligophenylene fluorophore is more effective than the most effective electron-releasing auxofluors, such as alkoxy or amino groups (as judged by the values for the 4,4'-substituted biphenyls); and supports the idea that stabilizing the negative charges of an S$_1$ state (as shown in **4c**) improves fluorescence efficiency. This compound is of potential use as a laser dye.

Dibenzimidazole **26** with a hydroxy proton donor group had ε = 24,000 at 342 nm, somewhat higher than that of typical monobenzazoles such as 2-(4-cyano-2-hydrox-yphenyl)benzothiazole [8], and Φ = 0.38 in toluene, which is significantly higher that of the most efficient monobenzimidazoles at room temperature, higher than that of monobenzazoles in general [29], and comparable with values we found for the corresponding dibenzoxazoles [16]. Emission at 478 nm means that the Stokes' shift of **26** is 131 nm, a typical shift for ESIPT fluors. The low ε must indicate that the auxofluors are acting in push-pull mode as postulated for the dibenzoxazoles [16]. The low ε cannot be due to an N-H - - CH$_3$-C repulsion, as shown by

the results on the model compounds **16**. This compound was of potential use a waveshifter in scintillating fibers, but it has lower fluorescence efficiency (ε·Φ) than that of the flavone [11] or dibenzoxazoles cited above.

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. Chromatographic purification by extraction from an "Ace-Kau" means that boiling solvent was allowed to fall on a solid sample and pass through a column of adsorbent in a special apparatus [30], (an Ace-Kauffman Column, Ace Glass Co.). The usual adsorbents were Silica Gel (Aldrich 24,217-9) or Brockmann I neutral alumina (Aldrich 19,997-4). Thin-layer chromatography was carried out with Whatman MK6F silica 1 x 3 inch plates visualized with short- and long-wave ultraviolet light. Elemental analyses were done by either Desert Analytics, Tucson AZ, Microanalysis, Wilmington DE, or Oneida Research Services, Rensselaer, NY. PMR spectra made use of tms as an internal standard, and were determined on the instruments indicated. 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 either a Perkin-Elmer MPF-44A with a Hitachi Corrected Spectra Unit, or a Farrand Spectrofluorometer Mk. I rebuilt to produce corrected spectra to 750 nm by Optical Technology Devices, Elmsford, NY (unless noted otherwise). The reference standard used with the MPF-44A was quinine bisulfate in 1 N sulfuric acid of Φ = 0.55 [31], and with the Mk. I was the oxazole "Ox 2" of Φ = 0.73 in absolute ethanol for **26** [32]. The working equation was:

$$\Phi_{spl.} = (\Phi_{std.}) (Area_{spl.}) (Absorbance_{std.}) / (Area_{std.}) (Absorbance_{spl.})$$

The two spectrometers, with different operators, gave Φ = 0.27 and 0.25, respectively, for 3-hydroxyflavone [11]; thus they were in excellent agreement for this type of measurement.

2-(4-Bromophenyl)benzimidazole (13).

A mixture of 4-bromobenzoic acid (**11**, 20.1 g, 0.100 mole, Lancaster 1974), o-phenylenediamine (**6**, 11.9 g, 0.110 mole, Eastman Practical Grade) and polyphosphoric acid (100 g, Aldrich 20,821-3) was stirred at 210° under nitrogen for 6 hours. After the mixture cooled down to 100°, it was poured onto 1 kg of crushed ice. After prolonged stirring, the solid was filtered, washed with 3 x 100 ml of water, slurried in 5% sodium carbonate solution, filtered again, and dried in air. This crude product was boiled in 1 ℓ of 95% ethanol with 3 g of carbon (Fisher C-170), filtered hot, and the clear filtrate concentrated to 0.5 ℓ. Keeping it at 20° gave 16.4 g (60%) of product as needles, mp

296-298° (lit [33] 299° for the chloro analog), single spot on tlc, R_f = 0.7 (1:9 ethyl acetate:chloroform). Its identity was confirmed by conversion to **12** below.

2-(4-Bromophenyl)-1-propylbenzimidazole (12).

A solution of 2-(4-bromophenyl)benzimidazole (**13**, 10.9 g, 0.0400 mole), 1-iodopropane (11.9 g, 0.0700 mole), 30 ml of 50% (w/v) aqueous sodium hydroxide, and 250 ml of acetone was refluxed with stirring for 14 hours. When cooled to 20°, the aqueous layer was extracted with 500 ml of chloroform. The extract was combined with the acetone layer and evaporated. To the oily residue was added 20 ml of acetone and 6 ml of 6N hydrochloric acid; the mixture was stirred, then cooled at 2° to give 10 g of the crude hydrochloride salt as a yellow powder, mp 210-212°. This salt, in 50 ml of chloroform, was neutralized by stirring with excess 5% sodium carbonate. The chloroform layer was washed with 50 ml of water, dried over magnesium sulfate, and evaporated. The residue was recrystallized from 50 ml of hexane to give 6.00 g (55%) of yellow crystals, mp 94-95°; single spot on tlc, R_f = 0.80 (1:1 hexane:ethyl acetate); pmr, 80 MHz Bruker, (2% in deuteriochloroform): δ 1.00 (t, J = 6 Hz, 3H, —CH$_2$CH$_2$CH$_3$), 2.05 (2 dt, J ≈ 6Hz, 2H, —CH$_2$CH$_2$CH$_3$), 4.45 (t, J = 6Hz, 2H, —CH$_2$CH$_2$CH$_3$); 7.2-8.0 ppm (m, 8H, ArH).

Anal. Calcd. for C$_{16}$H$_{15}$BrN$_2$: Br, 25.35; N, 8.89. Found: Br, 25.53; N, 8.97.

Extraction of the product of another run, mp 61-71°, 4.6 g, from 3 cm of alumina Brockmann I, neutral) over 3 cm of Silica Gel (Davison Grade 62) in a medium Ace-Kau with 125 ml of Freon TF for 2 days gave 3.9 g (85% rec) of white product, mp 89.0-91.5°, by cooling the extract at -20° for 2 days; pmr identical with that above.

2-(4'-Methoxybiphenyl-4-yl)-1-propylbenzimidazole (15a).

A 100 ml 3-necked flask was equipped with a nitrogen inlet, thermometer, reflux condenser, and a pressure-equalizing liquid addition funnel. Magnesium (0.300 g, 12.6 mmoles, Fisher M-11) was added. The flask was flame-dried and swept with nitrogen. After the flask cooled, a solution of 4-bromoanisole (2.4 g, 6.3 mmoles, Moore-Tec) in 10 ml of anhydrous tetrahydropyran (Aldrich 29,310-5) was added dropwise during 30 minutes with stirring and heating to maintain reflux. Reflux was continued for an hour after the last addition. To the mixture at 20° (containing Grignard **14a**) were added 2-(4-bromophenyl)-1-propylbenzimidazole (**12**, 2.0 g, 6.3 mmoles) and palladium(II) chloride 1,4-bis(diphenylphosphino)butane (70 mg, 0.13 mmoles); then heating at reflux was carried out for 3 hours, during which time the color changed from yellow to black. The mixture was evaporated, leaving a residue; the part soluble in 50 ml of chloroform was washed with 50 ml of water, dried over magnesium sulfate, and evaporated. The residue was recrystallized from 50 ml of hexane to give 1.75 g (80%) of white crystals, mp 109-110°; single blue fluorescent spot on tlc, R_f = 0.50 (1:1 hexane:ethyl acetate).

Anal. Calcd. for C$_{23}$H$_{22}$N$_2$O: C, 80.67; H, 6.47; N, 8.17. Found: C, 80.76; H, 6.46; N, 8.45.

2-(4'-Methoxybiphenyl-4-yl)-1-propylbenzimidazolium Methanesulfonate (16a).

Methanesulfonic acid (70 mg, 0.70 mmole, Aldrich M880-6) was added to a stirred and refluxing solution of 2-(4'-methoxy-

biphenyl-4-yl)-1-propylbenzimidazole (**15a**, 220 mg, 0.70 mmole) in 10 ml of anhydrous benzene, followed by an hour at reflux. After cooling to 20° the solid was filtered, washed with 10 ml of ether, and dried at 100° to yield 170 mg (59%) of white crystals, mp 181-183°.

Anal. Calcd. for $C_{24}H_{26}N_2O_4S$: C, 65.73; H, 5.97; S, 7.31. Found: C, 66.46; H, 5.93; S, 7.59.

2-(4'-Methoxybiphenyl-4-yl)-1-methyl-3-propylbenzimidazolium Methanesulfonate (16b).

A stirred mixture of 2-(4'-methoxybiphenyl-4-yl)-1-propyl-benzimidazole (**15a**, 205 mg, 0.60 mmoles) in 10 ml of 2-propanol was warmed to 60° to obtain a solution, then methyl methanesulfonate (60 mg, 0.60 mmoles, Aldrich 12,992-5) was added, and the mixture was boiled under reflux for 1 hour. When at 20° the mixture was filtered, the filtrate was diluted with 50 ml of anhydrous ether, and the precipitate was filtered, washed with 10 ml of anhydrous ether and dried at 100° to give 170 mg (70%) of white crystals, mp 171-172°; uv (ethanol): λmax = 212 nm (ε = 40,000), λmax = 304 nm (ε = 34,000).

Anal. Calcd. for $C_{25}H_{28}N_2O_4S$: S, 7.09. Found: S, 7.09.

2-(4''-Methoxyterphenyl-4-yl)-1-propylbenzimidazole (15b).

A solution of 1,2-dibromoethane (1.4 ml, 3.8 g, 0.020 mole) in 10 ml of anhydrous tetrahydropyran was added dropwise during 3 hours to a stirred solution of 4-bromo-4'-methoxybiphenyl (3.76 g, 0.010 mole) in 10 ml of anhydrous tetrahydropyran containing magnesium (720 mg, 0.030 mole) under nitrogen at reflux. The resulting Grignard Reagent (**14b**) was transferred under nitrogen to a 3-necked flask containing 2-(4-bromophenyl)-1-propylbenzimidazole (**12**, 3.15 g, 0.010 mole) and palladium(II) chloride 1,4-bis(diphenylphosphino)butane (70 mg, 0.13 mmoles) in 10 ml of anhydrous tetrahydropyran. The resulting mixture was stirred under nitrogen at reflux for 2 hours. After evaporation of the solvent, the residue was dissolved in 100 ml of chloroform, and this solution was stirred with 20 ml of 6*N* hydrochloric acid. The chloroform solution was neutralized by stirring with saturated aqueous sodium carbonate, washed with water, dried over magnesium sulfate, and evaporated. The residue was triturated with butyl ether. The yellow crystals which formed were extracted with heptane from a Soxhlet extractor for 6 hours. The *residue* in the Soxhlet was recrystallized from 2-ethoxyethanol to give 1.66 g (40%) of yellow crystals, mp 240-243°; single blue fluorescent spot, R_f = 0.8 (9:1 chloroform:ethyl acetate); pmr, 80 MHz, Bruker (deuteriochloroform): δ 1.0 (t, J = 6 Hz, 3H, —$CH_2CH_2CH_3$), 2.05 (dt, J $\approx$ 6 Hz, 2H, —$CH_2CH_2CH_3$), 3.9 (s, 3H, —OCH_3), 4.45 (t, J = 6 Hz, 2H, —$CH_2CH_2CH_3$), 7.0-8.2 ppm (m, 16H, Ar*H*). Its identity was further confirmed by conversion to the salt below.

2-(4''-Methoxyterphenyl-4-yl)-1-methyl-3-propylbenzimidazolium Methanesulfonate (16c).

To a stirred solution of 2-(4''-methoxyterphenyl-4-yl)-1-propylbenzimidazole (**15b**, 209 mg, 0.500 mmole) in 7.5 ml of toluene at reflux was added methyl methanesulfonate (0.10 ml, 1.0 mmole). Reflux was maintained for 1 hour. After cooling to 20° the mixture was filtered, and the white crystals were washed with hot ethyl acetate, and dried at 150° to give 420 mg (80%), mp 245-247°; pmr, 80 MHz, Bruker (deuteriochloroform): δ 1.0 (t, J = 6 Hz, 3H, —$CH_2CH_2CH_3$); 2.05 (dt, J $\approx$ 6 Hz, 2H, —$CH_2CH_2CH_3$); 2.5 (s, 3H, CH_3S), 3.9 (s, 3H, —OCH_3), 4.2

(s, 3H, CH_3N), 4.5 (t, J = 6 Hz, 2H, —$CH_2CH_2CH_3$), 7.0-8.2 ppm (m, 16H, Ar*H*); uv (ethanol): λ max = 211 nm (ε = 43,000), λ max = 313 nm (ε = 40,000).

Anal. Calcd. for $C_{31}H_{32}N_2O_4S$: S, 6.00. Found: S, 5.78.

9,9-Dipropylfluorene-2,7-dicarboxaldehyde (20).

A 30 ml portion of a solution of 24.49 g (0.060 mole) of 2,7-dibromo-9,9-dipropylfluorene (**18** [25]) dissolved in 150 ml of dry tetrahydrofuran was added to 2.92 g (0.120 mole) of magnesium metal, which was heated to 100° under a blanket of nitrogen and then cooled to 75° prior to addition, and gently boiled under reflux. The formation of the Grignard reagent did not begin immediately, and a few drops of 1,2-dibromoethane were added as an entrainer, after which the solution turned purple and the remainder of the bromide was added over 25 minutes. The mixture was boiled under reflux for an additional 1 hour, cooled to 0°, and 9.29 ml (0.120 mole) of dimethylformamide dissolved in 150 ml of tetrahydrofuran was added over the next half hour, giving a thick precipitate. After this the mixture was stirred overnight at room temperature, 60 ml of 3*M* hydrochloric acid was added, resulting in an exotherm to 45° and the dissolution of most of the precipitate. The mixture was poured into 1600 ml of water, giving an oil at first, which solidified to a gummy yellow solid, which was filtered, dissolved in 250 ml of methylene chloride, washed with 150 ml of water, dried over magnesium sulfate, and the solvent removed, to give 19.9 g of solid. A 10% solution of the solid in toluene was passed through 200 g of Silica Gel with toluene as the solvent to give 9.4 g of solid. After recrystallization from 75 ml of heptane recovered 6.85 g (37%) of solid, mp 106.5-109°; tlc: R_f (toluene) = 0.23.

An analytical sample was prepared by passing a portion through another Silica Gel column with toluene as the eluent and recrystallization from ethanol/water to give yellow plates, mp 111-112°; pmr, Varian EM 360L, (deuteriochloroform): δ 0.67 (10H, s, —$CH_2CH_2CH_3$), 2.00 (4H, m, —$CH_2CH_2CH_3$), 7.98 (6H, s, Ar*H*), 10.15 ppm (2H, s, aldehyde *H*).

Anal. Calcd. for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.22; H, 7.32.

2,7-Bis(1-methyl-2-benzimidazolyl)-9,9-dipropylfluorene (22).

A solution of 7.17 g (58.8 mmoles) of *N*-methyl-1,2-phenylenediamine (**5**) in 40 ml of absolute ethanol (prepared by neutralization of the dihydrochloride (Eastman 1291848) with sodium carbonate and dried over sodium hydroxide pellets) was heated to reflux under nitrogen and 6.00 g (19.6 mmoles) of the dialdehyde **20** dissolved in 30 ml of absolute ethanol was added and the mixture boiled under reflux for an additional 10 minutes. The solution was cooled, diluted with water until cloudiness persisted, and cooled to -20°, resulting in the formation of a gummy semi-solid. The liquid was decanted and additional semisolid obtained by further dilution of the supernatant with water and cooling to -20°. The semisolid was dissolved in absolute ethanol and concentrated by rotary evaporation to give 7.5 g (15 mmoles) of the intermediate Schiff's base **21**, which was then dissolved in 50 ml acetic acid and 6.50 g (15 mmoles) of lead tetraacetate was added, resulting in an exotherm and the appearance of a blue fluorescence. The mixture was diluted with water and made basic with concentrated ammonia, resulting in the precipitation of solid and the formation of an oil. The solid was collected by vacuum filtration, while the oil was dissolved in methanol, diluted with water, resulting in the formation of an oil,

which solidified upon drying to give 5.0 g of total solid. The solid was passed through a medium Ace-Kau col with 5 cm Silica Gel over 3 cm alumina with toluene as the solvent. After cooling to -20°, 1.57 g (16%) of pale yellow solid was collected by filtration, mp 260 - 261.5°, s. 258; tlc: Rf (ethyl acetate) = 0.65; pmr, Varian XL200, (deuteriochloroform): δ 0.73 (br s, 10H, Ha), 2.12 (m, 4H, Hb), 3.98 (s, 6H, Hc), 7.40 (m, 6H, Hd), 7.81 (d, J_{e-g} = 8 Hz, 2H, He), 7.92 (s, 2H, Hf), 7.95 (m, 4H, Hg).

22
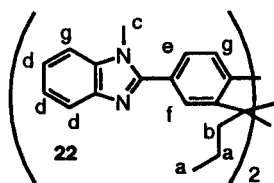
Anal. Calcd. for $C_{35}H_{34}N_4$: C, 82.32; H, 6.71; N, 10.97. Found: C, 82.30; H, 6.92; N, 10.87.

2,7-Bis(1,3-dimethyl-2-benzimidazolyl)-9,9-dipropylfluorene Dimethanesulfonate Monohydrate (**23**).

A mixture of 1.50 g (2.94 mmoles) of the dibenzimidazole **22** and 0.77 g (7.00 mmoles) of methyl methanesulfonate in 25 ml of acetonitrile was boiled under reflux for 16 hours. The solution was cooled, filtered, and the precipitate washed with 10 ml acetonitrile, to give 2.04 g (95%) of solid after drying, mp 400-415° dec, starts to decompose at ~380°; uv (ethanol): λ max 211 nm (ε = 55,600), 320 nm (ε = 49,500); Fl. Em., Farrand Mk. I, ethanol: λ max = 390 nm; Φ = 0.86 (ref. std. 9,10-diphenylanthracene, Φ = 0.86 in N_2- sat'd. cyclohexane [34]; pmr, Varian XL200, (dimethyl sulfoxide-d_6): δ 0.69 (br s, 10H, Ha), 2.16 (m, 4H, Hb), 2.28 (s, 6H, Hc), 3.32 (s, HOD), 3.98 (s, 12H, Hd), 7.76-7.86 (high-order m, 4H, He), 8.0 (dd, J_{f-g} = 1.17 Hz, J_{f-i} = 7.94 Hz, 2H, Hf), 8.16 (sl br s, 2H, Hg), 8.12-8.23 (high-order m [35], 4H, Hh), 8.46 (d, 2H, Hi).

23

CH$_3$SO$_3^{\ominus}$
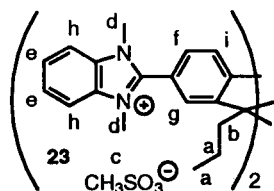
Anal. Calcd. for $C_{39}H_{46}N_4O_6S_2 \cdot H_2O$: C, 62.54; H, 6.46; N, 7.48. Found: C, 62.55; H, 6.44; N, 7.57.

2,5-Bis(1-methyl-2-benzimidazolyl)phenol (**26**).

Into a 100 ml round-bottomed flask fitted with a magnetic stirrer and condenser was placed hydroxyterephthalic acid (**24**, 2.0 g, 0.011 mole, [36]) and then 20 ml of thionyl chloride was added. The contents were stirred gently for 2-3 minutes and then 2-3 drops of dimethylformamide was added as a catalyst. After this, the reaction mixture was heated under reflux for 3 hours in an atmosphere of dry nitrogen. The mixture was cooled and the thionyl chloride removed completely by means of a rotary evaporator for 3 hours at 50°. A tan gelatinous mass was obtained, to which was added 30 ml of dry dimethylformamide, followed by warming to obtain a yellow solution of diacid chloride **25**. Then

N-methyl-*o*-phenylenediamine (**5**, 2.8 g, 0.023 mole, liberated from the dihydrochloride, Eastman 129 1848, within a day before use) dissolved in 10 ml of dry dimethylformamide was added all at once at room temperature. The contents were heated under reflux for 25 hours under nitrogen, cooled to room temperature, and then kept at 0° for one week. A green mass was obtained which was removed by filtration and dried to afford 0.80 g (20%) of **26**, mp 250-253°.

The analytical sample was obtained by recrystallization from dimethylformamide, mp 254-255°; pmr, Varian EM360L, (deuteriochloroform): δ 3.98 (s, 3H, N-CH_3), 4.14 (s, 3H, N-CH_3), 7.27-8.10 ppm (m, 12 H, ArH and OH located by D_2O-exchange); uv (chloroform): λ max = 342 nm (ε = 24,000); Fl. Em., Perkin-Elmer LS5B, uncor., (chloroform): λ max = 478 nm; Φ = 0.38 (toluene).

Anal. Calcd. for $C_{22}H_{18}N_4O$: C, 74.56; H, 5.12; N, 15.81. Found: C, 74.46; H, 5.19; N, 15.74.

REFERENCES AND NOTES

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   **   Present address: University of Tehran, Tehran, Iran.
  [1]   M. Rinke, Doctoral Dissertation, Universität Karlsruhe and Research Report KfK 3810, Kernforschungszentrum Karlsruhe, 1984.
  [2]   J. M. Kauffman and J. H. Bentley, *Laser Chem.*, **8**, 49 (1988).
  [3]   P. A. Fleitz, C. J. Seliskar, R. N. Steppel, J. M. Kauffman, C. J. Kelley and A. Ghiorghis, *Laser Chem.*, **11**, 99 (1991).
  [4]   H. O. Wirth, F. U. Herrmann, G. Herrmann and W. Kern, *Mol. Cryst.*, **4**, 321 (1968).
  [5]   D. Adams, A. Bambaugh, F. Bird, R. Chaney, C. Collins, W. Gall, K. Hess, D. Koltick, A. Odette and R. Ruchti, eds, Conceptual Design, Scintillating Fiber Outer Tracker, Draft Presented to the SDC

Collaboration Tracking Review Committee, Purdue University, 12 November, 1991.

[6]   S. Majewski and C. Zorn, Fast Scintillators for High Radiation Levels, in Instrumentation in High Energy Physics, Fabio Sauli, ed, World Scientific Publishing Co. Pte., Ltd, 1992.

[7]   J. Proudfoot, *Radiat. Phys. Chem.*, **41**, 1 (1993).

[8]   J. M. Kauffman, *Radiat. Phys. Chem.*, **41**, 365 (1993).

[9]   S. W. Moser, W. F. Harder, C. R. Hurlbut and M. R. Kusner, *Radiat. Phys. Chem.*, **41**, 31 (1993).

[10]   D. McMorrow and M. Kasha, *J. Phys. Chem.*, **81**, 2253 (1984).

[11]   J. M. Kauffman and M. A. Aziz, *J. Heterocyclic Chem.*, **30**, 1549 (1993).

[12]   C. M. Orlando, Jr., J. G. Wirth and D. R. Heath, *Chem. Commun.*, 1551 (1971).

[13]   C. M. Orlando, J. G. Wirth and D. R. Heath, US 3,673,202, 27 June (1972).

[14]   C. M. Orlando, J. G. Wirth and D. R. Heath, *J. Heterocyclic Chem.*, **7**, 1385 (1970).

[15]   J. M. Kauffman, Design of Radiation-Hard Fluors, Proc. Workshop on Scint. Fiber Detector Development for the SSC, 14-16 November, 1988, Fermilab, Vol II, Batavia, IL, 1988, p 677.

[16]   J. M. Kauffman and G. S. Bajwa, *J. Heterocyclic Chem.*, **30**, 1613 (1993).

[17]   (The Late) J. H. Hall, J. Y. Chien, J. M. Kauffman, P. T. Litak. J. K. Adams, R. A. Henry and R. A. Hollins, *J. Heterocyclic Chem.*, **29**, 1245 (1992).

[18]   H. H. Jaffe and M. Orchin, Theory and Applications of Ultraviolet Spectroscopy, John Wiley & Sons, New York, 1962.

[19]   N. J. Turro, Modern Molecular Photochemistry, Benjamin/Cummings, Menlo Park, CA, 1978.

[20]   H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.* **75**, 24 (1953).

[21]   B. W. Ashton and H. Suschitzky, *J. Chem. Soc.*, 4559 (1957).

[22]   T. G. Pavlopoulos and P. R. Hammond, *J. Am. Chem. Soc.*, **96**, 6568 (1974).

[23]   R. D. Rieke, S. E. Bales, P. M. Hudnall, T. P. Barns and G. S. Poindexter, *Org. Synth.* Coll Vol **6**, 845 (1988).

[24]   L. Zhu, R. M. Wehmeyer, and R. D. Rieke, *J. Org. Chem.*, **56**, 1445 (1991).

[25]   J. M. Kauffman, C. J. Kelley, A. Ghiorghis, E. Neister and L. Armstrong, *Laser Chem.*, **7**, 343 (1987).

[26]   F. F. Stephens and J. D. Bower, *J. Chem. Soc.*, 1722 (1950).

[27]   D. Comins and A. I. Meyers, *Synthesis*, 403 (1978).

[28]   I. B. Berlman, Handbook of Fluorescence Spectra of Aromatic Molecules, 2nd ed, Academic Press, New York, NY, 1971.

[29]   L. Sh. Afanasiadi, I. N. Tur and B. M. Bolotin, Khim. Geterosikl. Soedin., 390 (1980).

[30]   J. M. Kauffman and C. O. Bjorkman, *J. Chem. Ed*, **53**, 33 (1975).

[31]   W. H. Melhuish, *J. Phys. Chem.*, **65**, 229 (1961).

[32]   R. F. Kubin, R. A. Henry, M. E. Pietrak and D. E. Bliss, *Laser Chem.*, **10**, 247 (1990).

[33]   H. F. Ridley, R. G. W. Spickett and G. M. Timmis, *J. Heterocyclic Chem.*, **2**, 453 (1965).

[34]   J. V. Morris, M. A. Mahaney and J. R. Haber, *J. Phys. Chem.* **80**, 969 (1976).

[35]   The exact equivalence of the nitrogen atoms in **23** as *ortho* substituents is shown by the high-order pmr patterns; M. Zanger, *Org. Magn. Reson.*, **4**, 1 (1972).

[36]   L. Field and P. R. Engelhardt, *J. Org. Chem.*, **35**, 3647 (1970).