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Abstract

Eleven derivatives of the fluorescent compound 3-hydroxyflavone (3HF) have been prepared for use as dopants in plastic scintillator applications. These compounds have been incorporated in a polystyrene matrix, and their fluorescence has been monitored as a function of temperature in the range from 5 K to room temperature. A strong correlation between structure and fluorescence has been observed. The *ortho*-substituted derivatives show a large increase in quantum yield as the temperature decreases, whereas the *para*-substituted derivatives exhibit only a minor increase.

1 Introduction

Certain materials emit light when charged particles or electromagnetic radiation interacts with them. Nuclear and high energy physics experiments often exploit this scintillation property by incorporating these materials into particle detection devices. Six types of scintillation materials are commonly being utilized: organic crystals, organic liquids, plastics, inorganic crystals, gases, and glasses [1]. Of those based on organic materials, plastic scintillators are currently the most widely used, because of their fast response and high light output. In addition, the development of high quality optical fibers has enabled plastic scintillating optical fibers to be manufactured, thus increasing the number of applications in which plastic scintillators can be of use.

Plastic scintillators consist of a polymer matrix, such as polystyrene, doped with one or two fluorescent organic compounds. In a system with two dopants, the compounds are referred to as the primary dopant and the secondary dopant, or wavelength shifter [2]. Plastic scintillators with a single dopant are referred to as intrinsic. In this type of scintillator, the single dopant functions as both primary and secondary dopant [3]. Until recently most plastic scintillators emitted light in the blue-violet region of the spectrum. However, this spectral region is strongly affected by radiation-induced damage in the polystyrene matrix, manifested by an absorption increase in the polymer. This absorption causes a decrease in the light yield of the scintillator after its exposure to ionizing radiation [4]. Plastic scintillators whose terminal fluorescence is in the green spectral region are less sensitive to radiation-induced degradation in the polymer.

In order to develop new plastic scintillators that emit in the green, we have focussed our study on the use of dopants that undergo an excited-state intramolecular proton transfer (ESIPT) when excited by UV or ionizing radiation, Figure 1. Compounds that exhibit ESIPT typically show a large separation between their absorption and emission spectra. The fluorescent organic compounds 3-hydroxyflavone (3HF) [5] and 2-(2'-hydroxyphenyl)-benzothiazole (HBT) [6] do undergo ESIPT upon excitation. The absorption maxima for 3HF and HBT are at approximately 350 nm, and these compounds have a peak fluorescence at approximately 530 nm. The spectral distribution of their fluorescence makes them attractive candidates for green-emitting plastic scintillators. The first application of 3HF in plastic

scintillator was as a wavelength shifter [7, 8]. However, the large Stokes shift between the absorption and emission bands in 3HF and HBT makes intrinsic scintillators fabricated with these compounds ideal in the sense that their terminal fluorescence is in the green, and that they exhibit little self-absorption [3].

The disadvantage of using 3HF or HBT in plastic scintillators is their low quantum yield. In an attempt to improve this yield, several derivatives of both compounds were prepared, and a study of their structure-fluorescence relationships was performed [9, 10]. Here we report on measurements of fluorescence as a function of temperature for the 3HF derivatives. This study was motivated by the fluorescence results gathered at room temperature in which the 3HF derivatives exhibited a fluorescence dependence based on the position of the substituent in the phenyl ring of the 3HF molecule. For instance, all the *ortho*-substituted derivatives showed less light yield than the parent compound 3HF, whereas all the *para*-substituted derivatives had slightly larger quantum yield than 3HF. This pattern is a consequence of phenyl ring torsion, identified as an important deactivation mode in the 3HF molecule [11]. In addition, the *ortho*-substitution forces the phenyl ring to be out of plane, thus increasing the molecule deactivation through this mode instead of by fluorescence. Our low temperature studies verify the role of the phenyl ring torsion. The rotation of the phenyl ring becomes more restricted as temperature decreases, and the deactivation process favors fluorescence over radiationless relaxation.

2 Results and Discussion

The 3HF derivatives were prepared through substitution at the *ortho*- and *para*-positions of the phenyl ring. Figure 2 and Table 1 present the series of derivatives studied and the corresponding substitution pattern. The concentration of the dopant in the prepared polystyrene samples ranged from 0.6%–1% by weight, which is similar to the concentration of a primary dopant in standard plastic scintillators. The sample under study was placed in a cryostat, and the temperature was decreased to 5 K. The temperature was then increased in 25 K intervals to 300 K, and a fluorescence spectrum was recorded at each temperature. Before each measurement, the sample was allowed to equilibrate for half an hour. The fluorescence yield at each tem-

perature was calculated by integration of the fluorescence distribution over all wavelengths. The experimental data for each compound were normalized to its fluorescence yield at 300 K. The results are presented in Figures 3–5. The position of the substituent plays a more important role than its electronic character. The *para*-substituted derivatives have a performance very similar to the parent compound, 3HF. As the temperature decreases, their light yield slightly increases. However, a very different effect is observed in the *ortho*-substituted derivatives, whose light yield increases substantially as the temperature decreases. The *ortho*-substituents bring a large steric hindrance to the molecule which was non-existent in the unsubstituted compound. In the *ortho*-substituted derivatives, the phenyl ring is not coplanar with the rest of the molecule. These derivatives are very different from the original compound, 3HF. The *para*-substituents incorporated into the 3HF molecule do not significantly alter the initial geometry of 3HF. Thus the characteristics of the *para*-substituted compounds resemble those of 3HF. These results verify the role of the phenyl ring torsion as a deactivation mode and the importance of the planarity of the molecule in designing a compound with larger light yield than 3HF. In addition, these changes in relative quantum yield as a function of temperature indicate an upper limit for the absolute quantum yield of each compound in polystyrene. The absolute quantum yield of 3HF at room temperature in polystyrene is not available, but it can now be estimated using these data. (The quantum yield of 3HF in solution had been measured to be 42% in toluene [7] and 36% in ethanol [12].) The room temperature quantum yield of 3HF in polystyrene cannot be higher than 38–40% in order to be consistent with the data acquired at low temperature. A higher quantum yield value at 25 °C for 3HF would imply quantum yields larger than unity for some derivatives at 5 K.

3 Experimental Section

All melting points were determined with a Fisher-Johns apparatus and are uncorrected. Absorbance spectra were recorded using a Hewlett-Packard 8451A Diode Array spectrophotometer. All absorbance measurements used undoped polystyrene as the reference. Fluorescence measurements were performed using the diode array spectrophotometer as a fluorimeter. Collection and analysis of the raw data was accomplished using computer programs

developed at Fermi National Accelerator Laboratory [13]. Studies of fluorescence at low temperatures were performed using an Oxford Instruments CF1204 Cryostat placed in the spectrophotometer sample cavity. A broad-band filter (Melles Griot SB-300) was utilized to select the excitation wavelength at approximately 300 nm. Liquid helium was purchased from Linco. ^1H NMR spectra were determined for solutions in CDCl_3 (Me_4Si internal reference, J values given in Hz) on a Bruker WP200SY spectrometer. Elemental analyses (C, H) were performed on a Perkin-Elmer 240 Analyzer by Paulanne Ryder.

3.1 Fluorescent compounds

3-Hydroxyflavone (**1**) was purchased from Kodak, recrystallized as needed from a mixture of methylene chloride and hexane, and kept under vacuum in a desiccator. All 3HF derivatives were synthesized following the procedure outlined by Smith *et al.* [14], which is a modification of the Algar-Flynn-Oyamada method for preparation of flavonols [15].

2-Chloro-3-hydroxyflavone (**2**) was prepared, using the method mentioned above, from 2-hydroxyacetophenone (6 g, 0.04 mol) and 2-chlorobenzaldehyde (6.2 g, 0.04 mol) in 95% ethanol (60 mL) in a 42% yield. The crude was recrystallized from cyclohexane-methylene chloride, m.p. 181–183 °C, λ_{max} (ϵ) 335 nm ($6000 \text{ L mol}^{-1} \text{ cm}^{-1}$), λ_{em} 532 nm, δ_{H} 8.30 (1H, d, J_{H} 8), 7.8–7.3 (7H, m), 6.77 (1H, s) (Found: C, 66.07; H, 3.18. Calc. for $\text{C}_{15}\text{H}_9\text{ClO}_3$: C, 66.07; H, 3.33%).

4-Chloro-3-hydroxyflavone (**3**) was prepared using the method mentioned above in a 45% yield and recrystallized from methylene chloride, m.p. 202–204 °C (lit. [14] 203–205 °C).

2-Fluoro-3-hydroxyflavone (**4**) was prepared using the method mentioned above in a 66% yield and recrystallized from methylene chloride-hexane, m.p. 181–182 °C (lit. [16] 178–179 °C).

4-Fluoro-3-hydroxyflavone (**5**) was prepared using the method mentioned above in a 45% yield and recrystallized from methylene chloride-hexane, m.p. 153–154 °C (lit. [16] 150–151 °C).

2-Methyl-3-hydroxyflavone (**6**) was prepared using the method mentioned above in a 70% yield and recrystallized from methylene chloride-hexane, m.p. 192–193 °C (lit. [17] 191–192 °C).

4-Methyl-3-hydroxyflavone (**7**) was prepared using the method mentioned above in a 60% yield and recrystallized from methylene chloride-hexane, m.p. 195–197 °C (lit. [14] 196–198 °C).

2,5-Dimethyl-3-hydroxyflavone (**8**) was prepared using the method mentioned above in a 67% yield and recrystallized from hexane, m.p. 184–185 °C (lit. [17] 184–186 °C).

4-Phenyl-3-hydroxyflavone (**9**) was prepared using the method mentioned above in a 43% yield and recrystallized from methylene chloride-hexane, m.p. 220–222 °C (lit. [18] 222–223 °C).

2-Methoxy-3-hydroxyflavone (**10**) was prepared using the method mentioned above in a 46% yield and recrystallized from methylene chloride-ethyl acetate, m.p. 210–212 °C (lit. [19] 213–215 °C).

4-Methoxy-3-hydroxyflavone (**11**) was prepared using the method mentioned above in a 55% yield and recrystallized from methylene chloride-hexane, m.p. 230–232 °C (lit. [14] 231–232 °C).

4-Phenoxy-3-hydroxyflavone (**12**) was prepared, using the method mentioned above, from 2-hydroxyacetophenone (6 g, 0.04 mol) and 4-phenoxybenzaldehyde (8.8 g, 0.04 mol) in 95% ethanol (60 mL) in a 40% yield. The crude was recrystallized from methylene chloride, m.p. 183–184 °C, $\lambda_{max}(\epsilon)$ 350 nm (28000 L mol⁻¹ cm⁻¹), λ_{em} 538 nm, δ_H 8.25 (2H, d, J_{AB} 8), 7.75–7.65 (2H, dt, J_H 8), 7.58 (1H, d, J_H 8), 7.48–7.32 (3H, m), 7.22–7.09 (3H, m), 7.12 (2H, d, J_{AB} 8), 7.05 (1H, s) (Found: C, 76.19; H, 4.12. Calc. for C₂₁H₁₄O₄: C, 76.36; H, 4.27%).

3.2 Sample preparation

Glass polymerization tubes were cleaned with nitric and sulfuric acids, rinsed with distilled water, and then treated for about 4 hours with a 30% solution of dichlorodimethylsilane in chloroform. Finally, they were rinsed in turn

with chloroform, methanol, and distilled water. This treatment builds a hydrophobic Langmuir layer on the walls of the tube which enables the removal of the plastic after polymerization. The appropriate amount of 3HF or a 3HF derivative was then added to the polymerization tubes which were then filled with purified styrene [20]. The concentration of each 3HF derivative in polystyrene was based on their absorptivity coefficient at 320 nm compared to that of 3HF and knowing that the optimum 3HF concentration in an intrinsic scintillator has been determined to be 0.75% by weight [9]. The various solutions were degassed with repeated freeze-pump-thaw cycles. They were then polymerized in a silicone oil bath using the following temperature profile, 90 °C for 2 hours, 110 °C for 24 hours, 125 °C for 48 hours, 140 °C for 12 hours. The bath temperature was then ramped down to 90 °C at a rate of 10 °C/hour. When the temperature was raised to 125 °C, the solutions were backfilled with nitrogen to prevent them from boiling. At the end of the polymerization cycle, the test tubes were quenched in liquid nitrogen to facilitate the release of the polymer and avoid the formation of vacuum bubbles. The rods were cut into cuvettes (1.24 cm x 1.24 cm x 4 cm) and then polished.

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Figure Captions

Figure 1. Excited-state intramolecular proton transfer for 3-hydroxyflavone (3HF).

Figure 2. Substitution pattern in 3HF.

Figure 3. Changes in fluorescence yield as a function of temperature for 3HF, 2C3HF, 4C3HF, 2F3HF and 4F3HF relative to each yield at room temperature.

Figure 4. Changes in fluorescence yield as a function of temperature for 3HF, 25M3HF, 2M3HF, 4M3HF and 4P3HF relative to each yield at room temperature.

Figure 5. Changes in fluorescence yield as a function of temperature for 3HF, 2MO3HF, 4MO3HF and 4PO3HF relative to each yield at room temperature.

Table 1. List of 3-hydroxyflavone derivatives studied.

R_2	R_4	R_5	Compound	Description
H	H	H	3HF, 1	3-hydroxyflavone
Cl	H	H	2C3HF, 2	2'-chloro-3-hydroxyflavone
H	Cl	H	4C3HF, 3	4'-chloro-3-hydroxyflavone
F	H	H	2F3HF, 4	2'-fluoro-3-hydroxyflavone
H	F	H	4F3HF, 5	4'-fluoro-3-hydroxyflavone
Me	H	H	2M3HF, 6	2'-methyl-3-hydroxyflavone
H	Me	H	4M3HF, 7	4'-methyl-3-hydroxyflavone
Me	H	Me	25M3HF, 8	2',5'-dimethyl-3-hydroxyflavone
H	Ph	H	4P3HF, 9	4'-phenyl-3-hydroxyflavone
MeO	H	H	2MO3HF, 10	2'-methoxy-3-hydroxyflavone
H	MeO	H	4MO3HF, 11	4'-methoxy-3-hydroxyflavone
H	PhO	H	4PO3HF, 12	4'-phenoxy-3-hydroxyflavone

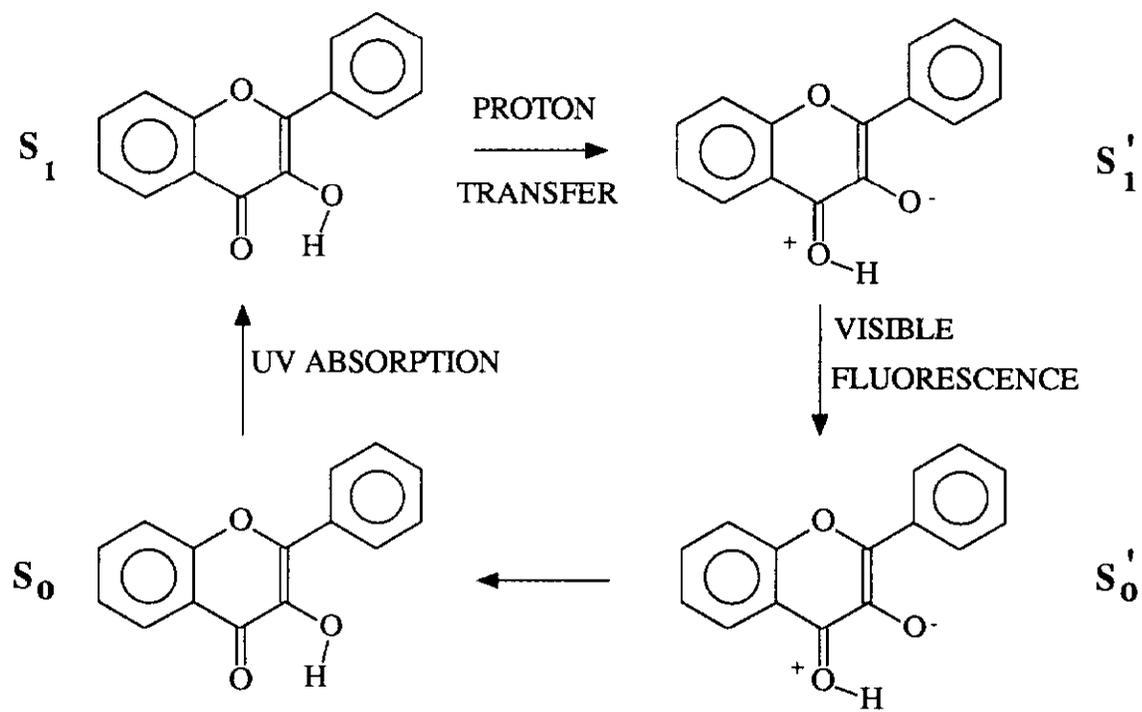


FIGURE 1

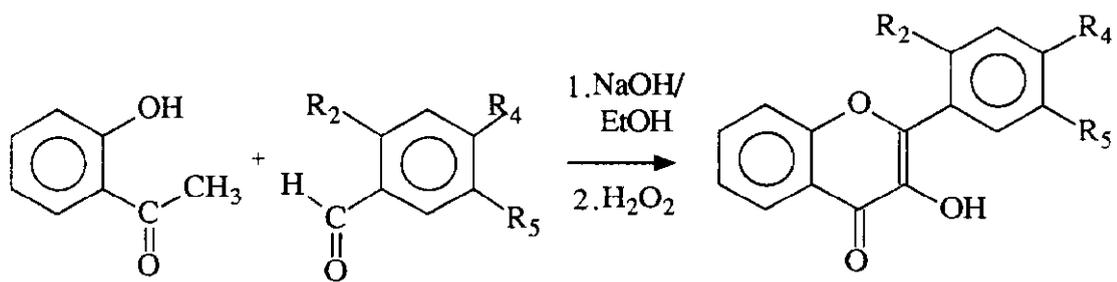


FIGURE 2

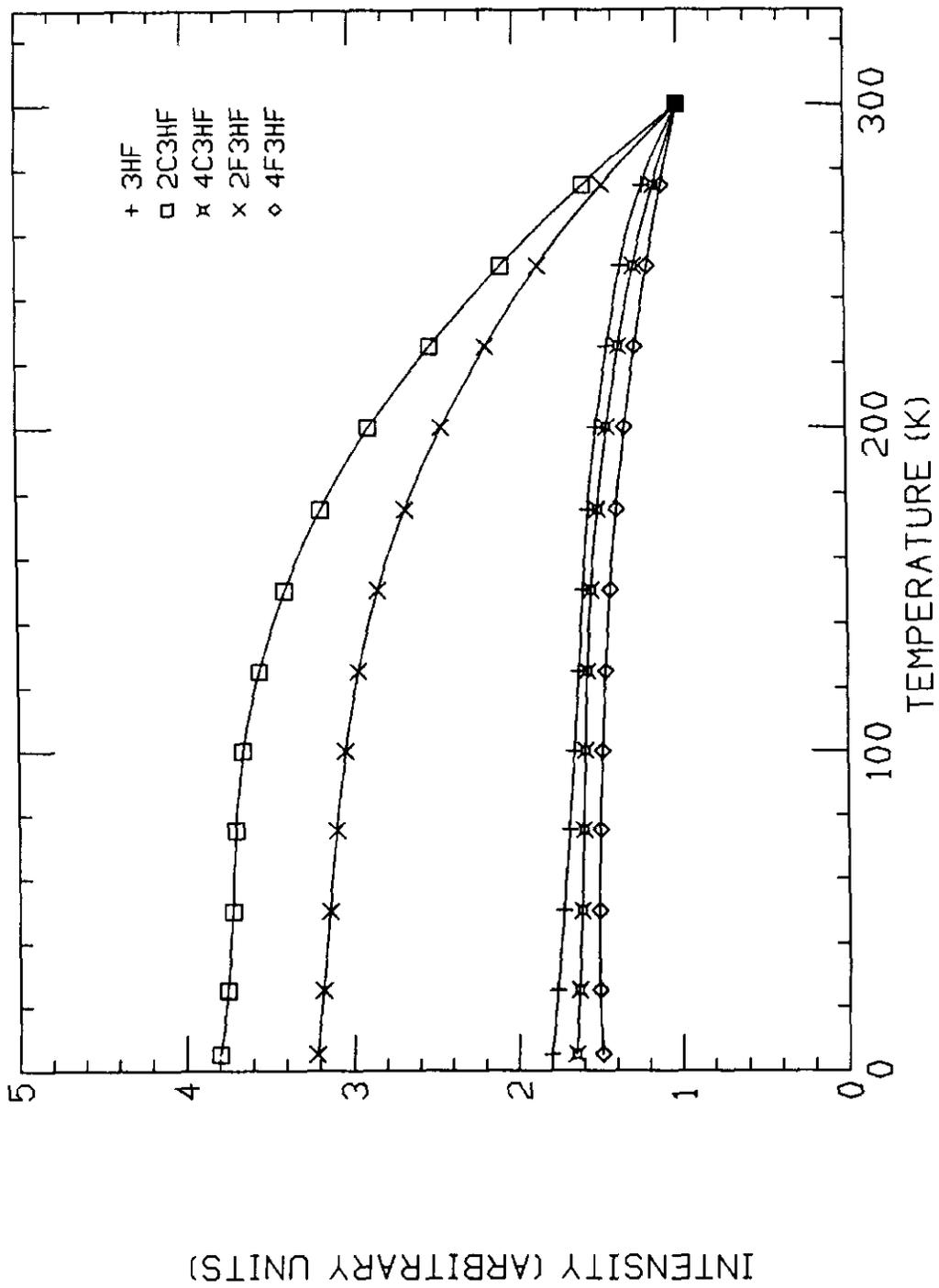


FIGURE 3

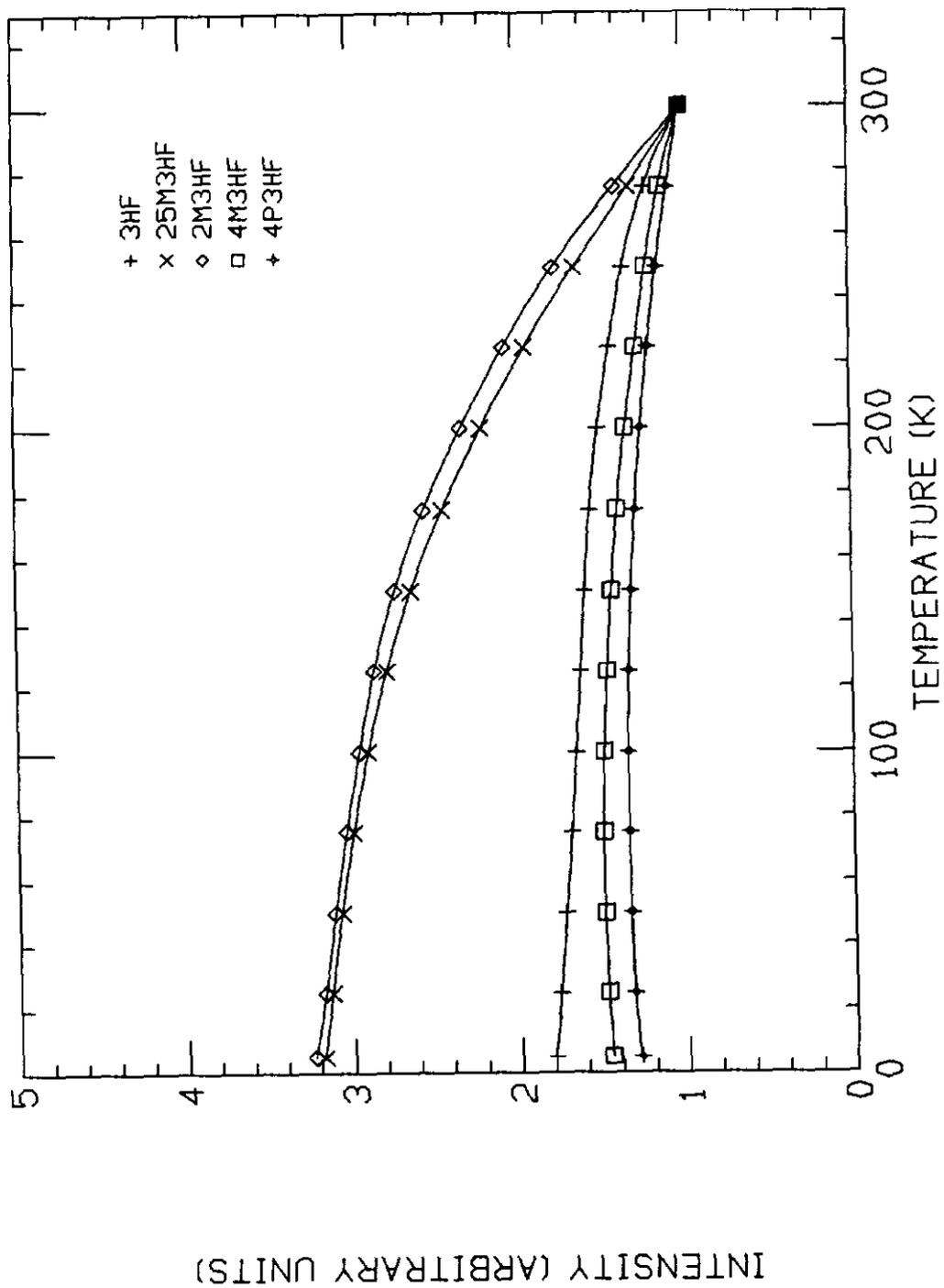


FIGURE 4

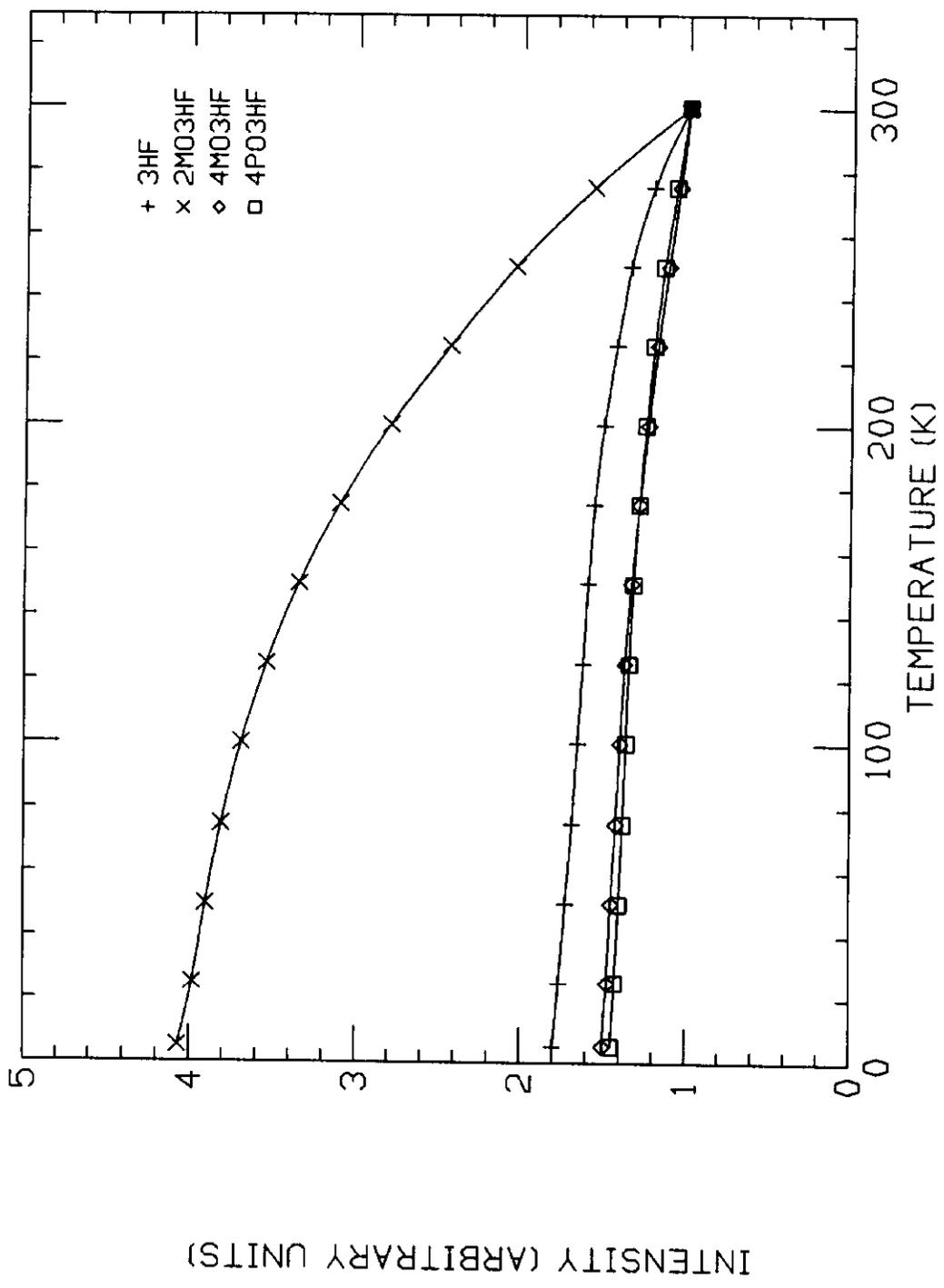


FIGURE 5