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7-Amino-4-perfluoroheptylcoumarins: a novel class of perfluorocarbon-soluble fluorescent dyes*

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Abstract

Five examples of 7-amino-4-perfluoroheptylcoumarins (**3**), a novel class of perfluorocarbon-soluble dyes, have been prepared by the reaction of β-ketoesters containing a perfluoroheptyl group (**1a** and **b**) with 3-aminophenols (**2a**, **b** and **c**). All these dyes fluoresced brightly when irradiated with long-wavelength ultraviolet light.

Introduction

Dyes that are soluble in very non-polar solvents are of interest as possible leak-detecting agents in air-conditioning units utilizing HFCs (hydrofluorocarbons) as the refrigerant fluid. Previously, we prepared several dyes that possess excellent solubility in non-polar solvents [1, 2], but these dyes lacked the ability to fluoresce brightly when irradiated with long-wavelength ultraviolet light. The ability of a dye to fluoresce brightly would greatly aid in visually detecting small traces of dye that would be deposited at the leak site.

Aminocoumarin dyes, including three that contain a trifluoromethyl group in the 4-position of the coumarin ring [3, 4], are used as optical bleaches and laser dyes because of their fluorescent properties. However, these dyes are only sparingly soluble in very non-polar solvents such as perfluorohexane. Aminocoumarin dyes containing a perfluoroalkyl substituent substantially larger than the trifluoromethyl group would be expected to have a much greater solubility in non-polar solvents.

Results and discussion

Five new 7-aminocoumarin dyes (**3a–e**), each containing a perfluoroheptyl group in the 4-position, were prepared by the zinc chloride catalyzed condensation of a β-ketoester with a 3-aminophenol (Scheme 1). This same

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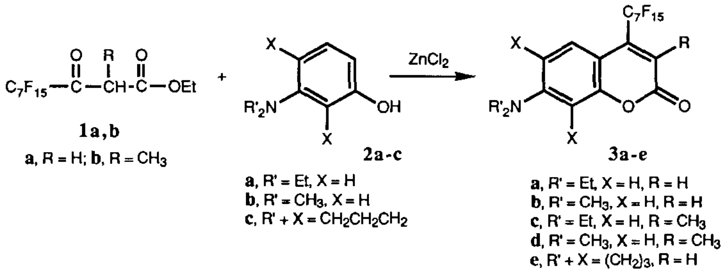
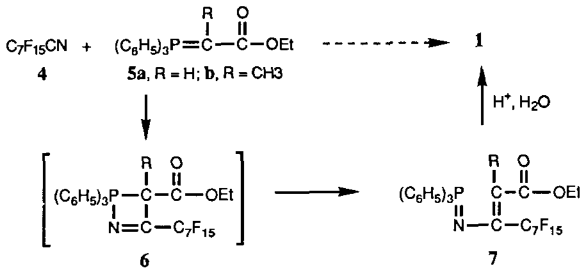


Scheme 1. Preparation of 7-amino-4-perfluoroheptylcoumarins.



Scheme 2. Preparation of β-ketoesters containing a perfluoroheptyl group.

method has been used previously to prepare aminocoumarins containing a trifluoromethyl group [3, 4].

Ethyl 2-perfluorooctanoylacetate (**1a**), the ketoester required for the preparation of coumarins **3a**, **3b** and **3e**, was prepared by a literature procedure [5]. A similar method was used to prepare the new ester, ethyl 2-perfluorooctyl propionate (**1b**), needed for the preparation of **3c** and **3d**; thus the phosphorous ylid **5b** was condensed with perfluorooctanonitrile (**4**) to give the phosphineimine **7** by the way of the cyclic intermediate **6**, and then **7** was hydrolyzed to give **1b** (see Scheme 2). Examination of the ^{1}H NMR spectrum of a neat sample of this ketoester indicates that it exists in a 50:50 equilibrium mixture with its enolic form.

The new coumarin dyes were all sufficiently soluble in perfluorohexane to give solutions that fluoresced intensely when irradiated with long-wavelength ultraviolet light. Their UV–vis absorption maxima in acetonitrile solution ranged from 389 nm for **3d** to 429 nm for **3e**. It is interesting to note that the coumarins containing a methyl group in the 5-position (**3c** and **3d**) absorbed at shorter wavelengths than the corresponding coumarins containing a hydrogen in same position (**3a** and **3b**), and the coumarins containing a diethylamino group (**3a** and **3c**) absorb at longer wavelength than the corresponding coumarins containing a dimethylamino group (**3b** and **3d**).

Experimental

General

The ^1H NMR spectra were obtained with a Varian EM-360 NMR spectrometer; chemical shifts are reported in parts per million (ppm) relative to TMS. The UV–vis spectra were obtained with a Varian Cary 1 UV–vis spectrometer using acetonitrile as the solvent; absorption maxima are given in nanometers. Electron impact mass spectra were obtained with a Hewlett-Packard GC/MSD (HP 5890 series gas chromatograph equipped with a HP 5971A mass selective detector). Compounds **1b** and **3a–e** are new.

*Ethyl 2-perfluorooctanoylpropionate (**1b**)*

Perfluorooctanonitrile (9.66 g, 0.028 mol) was added dropwise to a solution of (carbethoxyethylidene)triphenylphosphorane (10.0 g, 0.028 mol) in anhydrous ether (30 ml). The reaction mixture was stirred and heated to 30 °C overnight, and the ether was then removed by evaporation under reduced pressure. The residue was mixed with methanol (30 ml), water (30 ml) and conc. HCl (30 ml), and refluxed for 2 h. After cooling, the lower layer was separated and distilled to give **1b** (8.93 g, 64%) as a colorless liquid, b.p. 54–55 °C/1.0 mmHg. ^1H NMR ($CDCl_3$) δ: 1.33 (m, 4.5 H); 1.85 (s, 1.5H, vinyl CH_3); 2.15 (q, 2H); (0.5H, CH); 13.07 (s, 0.5H, OH) ppm. MS (EI 70 eV): 498 (M^+, 0.4); 453 ($M^+ - OCH_2CH_3$, 32); 129 ($M^+ - C_7F_{15}$, 100); 69 (CF_3^+, 50). Analysis: Calcd. for $C_{13}H_9F_{15}O_3$: C, 31.34; H, 1.82; F, 57.20%. Found: C, 31.64; H, 2.08; F, 56.80%.

*7-Diethylamino-4-perfluoroheptylcoumarin (**3a**)*

A solution of 3-diethylaminophenol (3.30 g, 0.02 mol), ethyl perfluorooctanoyl acetate (9.68 g, 0.02 mol) and zinc chloride (3.00 g) in 20 ml of ethanol was heated at reflux for 15 h, then cooled and poured into water (500 ml) containing conc. HCl (50 ml). The aqueous mixture was extracted with fluorotrichloromethane, and the extract was dried ($MgSO_4$) and evaporated to dryness to give 5.27 g (45%) of crude **3a** as a yellow-brown oil. An analytical sample was purified by chromatography over silica (hexane/ether). UV–vis (λ_{max}) (nm): 409. ^1H NMR ($CDCl_3$) δ: 1.10 (t, $J = 7$ Hz, 6H); 3.29 (q, $J = 7$ Hz, 4H); 6.48 (s, 1H); 6.69 (m, 2H); 7.70 (m, 1H) ppm. Analysis: Calcd. for $C_{20}H_{14}F_{15}NO_2$: F, 48.69; N, 2.39%. Found: F, 48.39; N, 2.23%.

*7-Dimethylamino-4-perfluoroheptylcoumarin (**3b**)*

Compound **3b**, prepared similarly to **3a** except that 3-dimethylaminophenol was used in place of 3-diethylaminophenol, was obtained as a yellow-brown oil. UV–vis (λ_{max}) (nm): 401. ^1H NMR ($CDCl_3$) δ: 3.61 (s, $J = 6$ Hz, 6H); 6.50 (s, 1H); 6.70 (m, 2H); 7.73 (m, 1H) ppm. Analysis: Calcd. for $C_{19}H_{12}F_{15}NO_2$: F, 57.20; N, 2.45%. Found: F, 56.80; N, 2.28%.

*7-Diethylamino-4-perfluoroheptyl-3-methylcoumarin (**3c**)*

Compound **3c**, prepared similarly to **3a** except that **1b** was used in place of ethyl perfluorooctanoyl acetate, was obtained as a yellow-brown oil.

UV–vis (λ_{max}) (nm): 393. ^{1}H NMR ($CDCl_3$) δ: 1.10 (t, $J=7$ Hz, 6H); 2.44 (s, 3H); 3.29 (q, $J=7$ Hz, 4H); 6.69 (m, 2H); 7.70 (m, 1H) ppm. Analysis: Calcd. for $C_{21}H_{16}F_{15}NO_2$: F, 47.55; N, 2.34%. Found: F, 47.25; N, 2.13%.

*7-Dimethylamino-4-perfluoroheptyl-3-methylcoumarin (**3d**)*

Compound **3d**, prepared similarly to **3c** except that 3-dimethylaminophenol was used in place of 3-diethylaminophenol, was obtained as a yellow-brown oil. UV–vis (λ_{max}) (nm): 389. ^{1}H NMR ($CDCl_3$) δ: 2.46 (s, 3H); 3.61 (s, $J=6$ Hz, 6H); 6.70 (m, 2H); 7.73 (m, 1H) ppm. Analysis: Calcd. for $C_{19}H_{12}F_{15}NO_2$: F, 49.88; N, 2.45%. Found: F, 49.66; N, 2.28%.

*2,3,6,7-Tetrahydro-9-(perfluoroheptyl)-1H,5H,11H-[1]benzopyrano[6,7,8-ij]quinolizin-11-one (**3e**)*

Compound **3e**, prepared similarly to **3a** except that 8-hydroxyjulolidine was used in place of 3-diethylaminophenol, was obtained as a dark orange oil. UV–vis (λ_{max}) (nm): 429. ^{1}H NMR ($CDCl_3$) δ: 1.93 (m, 4H); 2.81 (m, 4H); 3.28 (m, 2H); 6.20 (s, 1H); 6.97 (s, 1H) ppm. Analysis: Calcd. for $C_{22}H_{14}F_{15}NO_2$: F, 46.77; N, 2.30%. Found: F, 46.44; N, 2.08%.

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References

1 B. K. Freed and W. J. Middleton, *J. Fluorine Chem.*, *47* (1990) 219.
2 B. K. Freed, J. Biesecker and W. J. Middleton, *J. Fluorine Chem.*, *48* (1990) 63.
3 E. J. Schimitschek, J. A. Trias, M. Taylor and J. E. Celto, *IEEE J. Quantum Electron.*, *9* (1973) 781.
4 I. I. Grandberg, L. K. Denisov, L. M. Mel'nkova, O. A. Popova, G. P. Tokmakov, V. N. Drozd and V. N. Knyazev, *Izv. Timiryazevsk. S-kh., Akad.*, (1984) 149.
5 H. Trabelsi, E. Rouvier and A. Cambon, *J. Fluorine Chem.*, *31* (1986) 351.