

Hydrogen bonding and cooperativity effects on the assembly of alkyl- and perfluoroalkyl-sulfonyl naphthols: F...F non-bonded interactions†

Janusz Kowalik,* Donald VanDerveer, Caroline Clower and Laren M. Tolbert

School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332-0400, USA.
E-mail: janusz.kowalik@chemistry.gatech.edu.

Received (in Corvallis, OR, USA) 16th July 1999, Accepted 24th August 1999

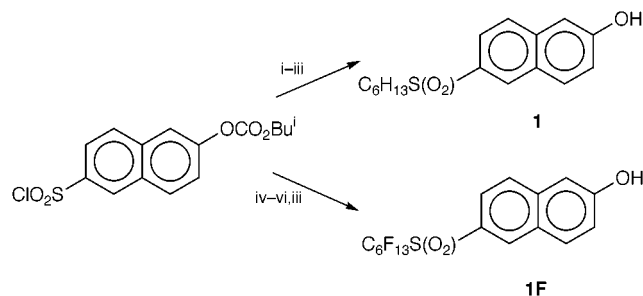
Important differences in the crystal packing of 6-perfluoroethylsulfonyl-2-naphthol (1F) including π - π stacking aromatic interactions and F...F non-bonded contacts, in contrast to its nonfluorinated analog (1), appear to translate into differences between their photophysical properties both in the solid state and in solution.

Photoacid generators produce acids upon irradiation. They are important in the field of polymeric photosensitive systems, as initiators for polymerizations,¹ for crosslinking of oligomers and polymers,² for polymer degradation,³ and for conversion of acid-sensitive functional groups attached to the polymers.⁴ Especially important technological applications involve manufacturing of photoresists and UV curing materials.⁵ A drawback to common (ionic) photoacid generators is that once incorporated, they usually remain within the polymeric structure, degrading the long-term stability of the polymers.

A less widely explored approach lies with generators that produce acids only for the duration of the photochemical event, thus allowing for a better control of the ensuing chemistry. Our interest in photoacids stems from the observation that hydroxy aromatics, weakly acidic in the ground state, become strong acids upon photoexcitation.⁶ We have established that naphthol derivatives strategically substituted with electron-withdrawing substituents yield significantly stronger acids ('enhanced photoacids') in the excited state.⁷ The electron withdrawing efficiency of substituents⁸ seems to have a similar effect on the ionization in the excited state, rendering systems substituted with functionalities of large positive Hammett constant (σ_p) values better photoacids (proton donors).

Since the σ_p value for the pentafluoroethylsulfonyl group is 1.08,⁹ versus 0.66¹⁰ for the cyano functionality, we synthesized and tested the 6-perfluoroethylsulfonyl-2-naphthol (1F), and its nonfluorinated analog (1) for comparison. Scheme 1 illustrates our synthetic approach.

The 6-(isobutoxycarbonyloxy)naphthalene-2-sulfonyl chloride, a starting material for both reaction avenues leading to 1 and 1F, was obtained in a two-step process involving masking of the hydroxy group in 6-hydroxynaphthalene-2-sulfonic acid



Scheme 1 Reagents and conditions: i, Zn, NaOH, H₂O-dioxane; ii, C₆H₁₃Br, DBU, DMF; iii, LiOH, 50% H₂O-THF; iv, PPh₃, PhH; v, NaOEt, C₆F₁₃I, DMF; vi, MCPBA, EtOAc, reflux.

† Atomic numbering schemes and stereoviews for 1 and 1F are available from the RSC web site. See <http://www.rsc.org/suppdata/cc/1999/2007/>

by allowing it to react with isobutyl chloroformate under Schotten-Baumann conditions,¹¹ followed by a reaction with POCl₃.¹² Reduction of the acid chloride with zinc metal yielded the corresponding zinc salt of the sulfinic acid, which was alkylated without isolation of the sulfinic acid with *n*-hexyl bromide, using a modified procedure of Mal.¹³ The hydroxy group protection in the obtained sulfone was then removed by hydrolysis with LiOH in THF-water to yield 1. Since heteroatom alkylations with perfluoroalkyl iodides proceed *via* a radical-ion chain mechanism,¹⁴ an alternative procedure was developed for the synthesis of 1F. Reduction of the sulfonyl chloride with PPh₃¹⁵ yielded the corresponding thiol, which then reacted smoothly with perfluorohexyl iodide to provide the aryl perfluorohexyl thioether. Oxidation with MCPBA and subsequent deprotection of the hydroxy functionality led to sulfone 1F.

Preliminary studies of the emission spectroscopy of 1 and 1F in aqueous-organic solutions showed considerable differences in the relative intensities of the fluorescence.¹⁶ Emission of the perfluoroalkyl analog was quenched by 40 × in MeOH (Fig. 1).

Similar effects were observed qualitatively in the solid state, using 366 nm radiation from a hand-held laboratory UV-VIS lamp to produce a bright fluorescence of the nonfluorinated sulfone, in contrast with a very low intensity fluorescence of the perfluoroalkyl analog. It was shown, that intermolecular π - π interactions effectively quenched the solid state fluorescence, the degree of fluorescence quenching can be used as an indicator of intermolecular π - π interactions.¹⁷

Recent reports from Tung's laboratory indicate that perfluoroalkyl esters of naphthalenecarboxylic acid form aggregates of unknown structure in aqueous organic solvents, leading to formation of excimers upon excitation, and chemical dimerizations as a consequence.¹⁸ Hydrophobic attraction as well as other forces, such as hydrogen bonding,¹⁹ are powerful

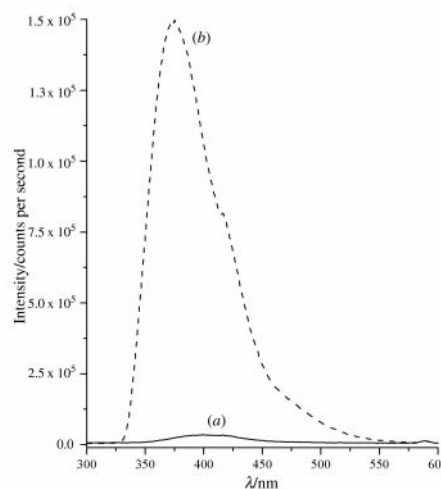


Fig. 1 Emission spectra of (a) 1F and (b) 1 in MeOH. Concentration = 4 × 10⁻⁵ M, λ_{ex} = 295 nm.

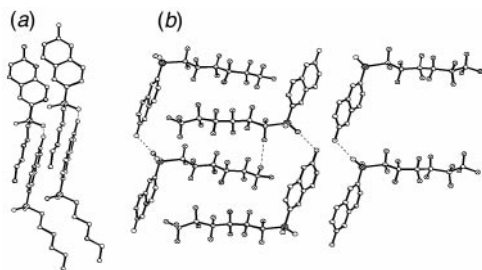


Fig. 2 Packing diagram of (a) **1** and (b) **1F**. For clarity, hydrogen atoms are omitted. The hydrogen bonds and F...F non-bonded interactions are specified by dotted lines.

tools in forming supramolecular assemblies both in solution and in the solid state. Molecular recognition leading to aggregation and nucleation may as a result become productive in generating crystals.²⁰ Although the dynamics of these systems remains complex, one might assume that the forces that play a role in molecular recognition in self-organized systems in solution would be reflected in the crystal. Following this assumption we determined the crystal and molecular structures of **1**† and **1F**‡ (see Fig. 2).

X-Ray analysis reveals that both **1** and **1F** crystallize in monoclinic unit cells, containing four molecules of **1**, and eight molecules of **1F**. The common motif present in both structures is an infinite, intermolecular, linear network of hydrogen bonds OH...OS(O)-. It passes through the crystals in the direction of the *b* axis, making the molecular arrangement supramolecular in nature. Distances are typically 2.78 Å.²¹ The differences in the crystal packing are substantial. In the case of **1F** there is a distinct segregation of the well-ordered perfluoroalkane chains from the aromatic rings. The perfluoroalkyl chains are nearly parallel. There is a pronounced proximity between the fluorine atom attached to the α carbon (*vs.* sulfonyl group) and the terminal CF₃ group of the next molecule. The distance between the corresponding fluorine atoms is 2.85 Å, which positions them within the range of a non-bonded interaction (van der Waals radius for fluorine is 1.47 Å).²² We believe that the strong electron withdrawing character of the sulfonyl moiety renders the α fluorine atoms more positive than the terminal ones, effecting a dipolar interaction. This interaction along with the electrostatic repulsion between the π -electrons of the aromatic rings and the fluorine atoms,²³ substantially contribute to the crystal architecture of **1F**. The naphthol rings in **1F** partially overlap in layers 3.52 Å apart. This value relates well with 3.5 Å (interplanar distance in graphite)²⁴ and is still smaller than 3.81 Å, where the electronic interaction between the aromatic chromophores was found to exist.²⁵ The attractive π - π interaction is believed to be another element stabilizing the crystal structure of **1F**. By contrast, the planes of the aromatic rings that are positioned parallel to each other in the crystal of **1** are separated by 7.7 Å and are interdigitated with the alkyl chains. There is no interactive proximity between the hexyl chains, and the aromatic chromophores are removed beyond the limit of electron interactions between them.

In summary, three cooperative attractive interactions present in **1F** produce a crystal lattice where a strong chromophore interaction seems to effectively deactivate fluorescence in the solid state. In contrast, the more intense fluorescence of the non-fluorinated analog is attributed to the absence of that interaction. We therefore conclude that similar behavior in solution supports the notion that extensive aggregation of **1F** in MeOH and in water-organic solvent systems is caused by the same attractive interactions as those present in the solid state.

Support of this research from the NSF, grant no. CHE 9727157, is gratefully acknowledged.

Notes and references

† *Crystal data for 1*: C₁₆H₂₀O₃S, *M* = 292.38, monoclinic, *a* = 5.6190(2), *b* = 15.8672(6), *c* = 17.1890(7) Å, β = 96.581(2)°, *U* = 1522.4(1) Å³, *T*

= 173 K, space group *Cc* (No. 9), *Z* = 4, μ (Mo-K) = 0.217 mm⁻¹, 4774 reflections measured, 2387 unique (*R*_{int} = 0.049) which were used in all calculations. The final *wR*(*F*²) was 0.1335 (all data). Single crystals of **1** were recrystallised from PrOH, mounted on a glass fiber with stopcock grease and placed in the cold gas stream of the diffractometer. The structure was solved using direct methods and refined by full-matrix least-squares on *F*².

‡ *Crystal data for 1F*: C₁₆H₇F₁₃O₃S, *M* = 526.28, monoclinic, *a* = 33.291(1), *b* = 9.9469(2), *c* = 11.4174(3) Å, β = 99.187(1)°, *U* = 3732.3 (2) Å³, *T* = 173 K, space group *P2*₁/*c* (No. 14), *Z* = 8, μ (Mo-K) = 0.32 mm⁻¹, 18775 reflections measured, 6536 unique (*R*_{int} = 0.086), which were used in all calculations. The final *wR*(*F*²) was 0.284 (all data). The **1F** was recrystallised from PrOH, mounted on a glass fiber using stopcock grease and placed in the cold gas stream of the diffractometer. The structure was solved using direct methods and refined by full-matrix least-squares on *F*². CCDC 182/1393. See <http://www.rsc.org/suppdata/cc/1999/2007/> for crystallographic data in .cif format.

- 1 Y. Wei, W. Wang, J. M. Yeh, B. Wang, D. C. Yang and J. K. Murray, *Adv. Mater.*, 1994, **6**, 372.
- 2 J. M. Harvard, M. Yoshida, D. Pasini, N. Vladimirov, J. M. J. Frechet, D.R. Medeiros, K. Patterson, S. Yamada, C. G. Willson and J. D. Byers, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 1225; H. S. Yu, T. Yamashita and K. Horie, *Macromolecules*, 1996, **29**, 1144; K. H. Chae, I. J. Park and M. H. Choi, *Bull. Korean Chem. Soc.*, 1993, **14**, 614.
- 3 S. G. Moon, K. Naitoh and T. Yamaoka, *Chem. Mater.*, 1993, **5**, 1315.
- 4 S. T. Kim, J. B. Kim, C. M. Chung and K. D. Ahn, *J. Appl. Polym. Sci.*, 1997, **66**, 2507; J. P. Chen, J. P. Gao and Z. Y. Wang, *J. Polym. Sci., Part A: Polym. Chem.*, 1997, **35**, 9; H. K. Kim and C. K. Ober, *Polym. Bull.*, 1992, **28**, 33.
- 5 For a recent review see: M. Shirai and M. Tsunooka, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 2483 and references cited therein.
- 6 L. G. Arnaut and S. J. Formosinho, *J. Photochem. Photobiol. A: Chem.*, 1993, **75**, 1; L. G. Arnaut and S. J. Formosinho, *J. Photochem. Photobiol. A: Chem.*, 1993, **75**, 21.
- 7 K. M. Solntsev, D. Huppert, L. M. Tolbert and N. Agmon, *J. Am. Chem. Soc.*, 1998, **120**, 7981; E. Pines, D. Pines, T. Barak, B.-Z. Magnes, L. M. Tolbert and J. E. Haubrich, *Ber. Bunsenges. Phys. Chem.*, 1998, **102**, 511; D. Huppert, L. M. Tolbert and S. Linares-Samaniego, *J. Phys. Chem.*, 1997, **101**, 4602; I. Carmeli, D. Huppert, L. M. Tolbert and J. E. Huppert, *Chem. Phys. Lett.*, 1996, **260**, 109.
- 8 K. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165.
- 9 N. V. Kondratenko, V. I. Popov, A. A. Kolomeitsev, E. P. Saenko, V. V. Prezhdo, A. E. Lutskii and L. M. Yagupol'skii, *Zh. Org. Khim.*, 1980, **16**, 1049.
- 10 D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420
- 11 P. Karrer and P. Leiser, *Helv. Chim. Acta*, 1944, **27**, 678.
- 12 S. Fujita, *Synthesis*, 1981, 423.
- 13 G. Biswas and D. Mal, *J. Chem. Res. (S)*, 1988, 308.
- 14 V. N. Boiko and G. M. Shchupak, *J. Fluorine Chem.*, 1994, **69**, 207.
- 15 S. Oae and H. Togo, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 3802.
- 16 J. Kowalik, C. Clower and L. M. Tolbert, to be published.
- 17 K. Shirai, M. Matsuoka and K. Fukunishi, *Dyes Pigm.*, 1999, **42**, 95.
- 18 C.-H. Tung and H.-F. Ji, *J. Phys. Chem.*, 1995, **99**, 8311; C.-H. Tung and H.-F. Ji, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 2761.
- 19 M. C. Calama, R. Hulst, R. Fokkens, N. M. M. Nibbering, P. Timmerman and D. N. Reinhoudt, *Chem. Commun.*, 1998, 1021; K. A. Jolliffe, M. C. Calama, R. Fokkens, N. M. M. Nibbering, P. Timmerman and D. N. Reinhoudt, *Angew. Chem., Int. Ed.*, 1998, **37**, 1247; C. J. Kepert, D. Heseck, P. D. Beer and M. J. Rosseinsky, *Angew. Chem., Int. Ed.*, 1998, **37**, 3158; M. Mascari, J. Hansen, P. S. Fallon, A. J. Blake, B. R. Heywood, M. H. Moore and J. P. Turkenburg, *Eur. Chem. J.*, 1999, **5**, 381.
- 20 A. Gavezzotti and G. Filippini, *Chem. Commun.*, 1998, 287; A. Gavezzotti, *Eur. Chem. J.*, 1999, **5**, 567.
- 21 W. C. Hamilton and J. A. Ibers, *Hydrogen Bonding in Solids*, W. A. Benjamin, New York, Amsterdam, 1968, p.16.
- 22 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
- 23 N. Hayashi, T. Mori and K. Matsumoto, *Chem. Commun.*, 1998, 1905.
- 24 G. Pimentel and R. Spratley, *Chemical Bonding Clarified Through Quantum Mechanics*, Holden-Day, San Francisco, California, 1969, p. 256.
- 25 H. Langhals, T. Potrawa, H. Nöth and G. Linti, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 478.