The marginal upward trend of solvation forces in the relatively larger pore systems of $\lambda<0.4$ is primarily due to the increasing influence of particle-particle interactions. The amount of reversible cavity work required to accommodate a particle of size λ in the pore fluid increases with increasing λ. Under these conditions the size-exclusion structural effect leads to the enhancement of solvation forces. One of the most striking features exhibited in this figure is the oscillatory behavior of solvation forces for higher concentrations. The apparent local peaks are clearly displayed in the case of $n_B^*=0.55$ and the GCEMC curve for the resulting solvation force passes through the maximum peak near λ-0.4 and the minimum peak near λ-0.5.

For the systems of hard-sphere fluids restricted in the hard-wall pore, the degree of solvation forces corresponds to the local pore density in the vicinity of the acting pore wall. In the range $0.4<\lambda<0.5$, where the particle diameter is approximately half the size of the pore, the solvation force decreases dramatically due to density inhomogeneities in the pore fluid. In this transition regime between $\lambda=0.4$ and $\lambda=0.5$, the pore density profiles calculated during GCEMC runs indicate that the pore fluid particles formed a predominantly monolayer structure extending two particle diameters across a spherical pore. This suggests that the actual configurations in the pore phase are rapidly changed from three-dimensional to pseudo two-dimensional behavior. In the range $0.5<\lambda<1.0$ the accessible pore region can be occupied only by zero or one particle and there is a uniform probability of finding the center of one particle in the pore volume. Beyond $\lambda=0.5$ concentration effects are obviously more profound since configurations occupied by one particle become more probable state in the grand canonical ensemble. For higher concentration systems the oscillation of the solvation force is directly related to such local pore density variations, namely, the structural reordering in the pore phase.

The above observations are not restricted to a spherical pore system. Similar results obtained in this work have heen shown to exist in slit-shape pores[7] and further simulation studies in cylindrical pores[8] have also confirmed the existence of oscillatory solvation forces. It is noted that the magnitude of solvation forces for non-interacting hard-sphere fluids[8a] is qualitatively close to those for adsorbing Lennard-Jones systems.[8b,8d] In fact, the hard-sphere fluid model combined with sterically exclusive hard-wall potentials is a reasonable approximation to describe spherical molecules trapped in geometrically well-defined pores, for example, compact rigid proteins or enzymes inside cylindrical pores employed in track-etched membranes.[9] It would be of interest to investigate more realistic spherical models such as zeolite pore systems in order to verify a number of the conclusions observed in our GCEMC simulations. Confirmation of this possibility will be reported in the near future.

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A Simple and Convenient Synthetic Route to the Bis-Indolinospirobenzopyrans

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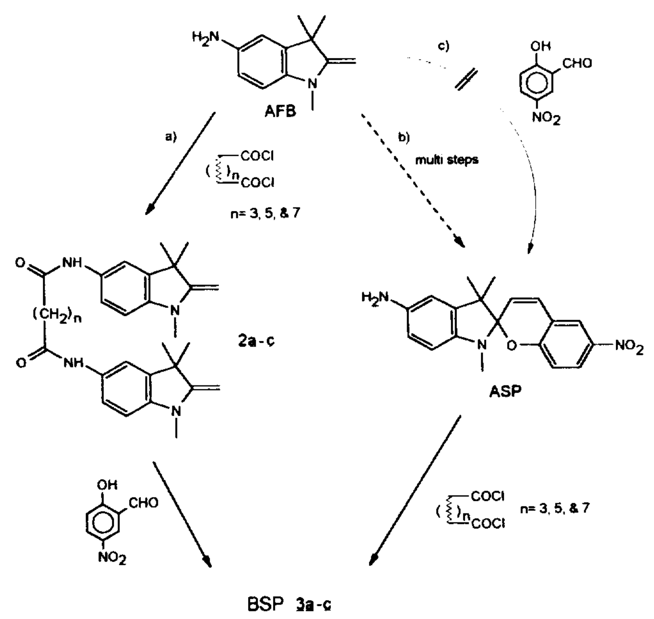
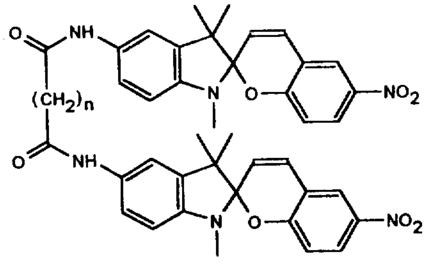
During the last decade, a large number of works[1-4] have been published on the behavior of thermo- and photochromic indolinospirobenzopyran dyes. Interest in these compounds is connected with their reversibility between the colorless spiro forms and the merocyanine colored forms. Structural modification of these dyes has been an active area research since the compounds were found to be useful for practical applications[3-7] that these dyes possess, including their use in recording, copying and preparation of display materials. It has been reported[5-6] as well that the merocyanine dyes are capable of giving "giant" molecular aggregates, including spiropyran-merocyanine complexes. In order to control the aggregate growth and hence to prepare a novel dimer, we thus undertook synthetic work on bis analogues of indolinos-



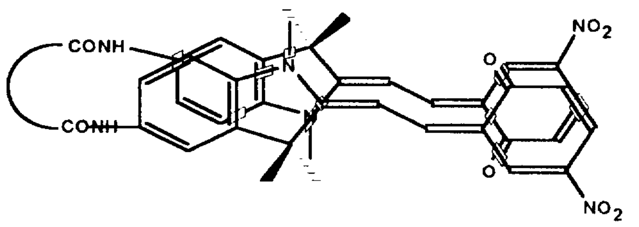
Scheme 1.

pirobenzopyrans by synthesizing a "dimeric" dye, **3**, which is obtained by connecting the 5-amino group of amino-Fischer base, **1c**, to the carbonyl group of diacid halide molecules, **2**.



3a n=3
3b =5
3c =7

A major goal of this research was to demonstrate that these dyes are capable of intra- and intermolecular π-stacking *via* medrocyanine units in nonpolar solvents.

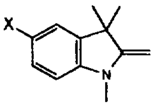


Intramolecular π-stacking

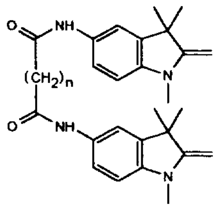
It is well established that substituted Fischer bases, 2-methylene-1,3,3-trimethylindoline, **1a**, react with various salicylaldehydes in 1 : 1 mole ratio to give the indolinobenzospiropyran derivatives (SP).[4b,7] One would hence expect that 5-amino-6′-nitro-1,3,3-trimethylspiro(indolino-2,2′-benzopyran) (ASP) would react with various diacid halides in the synthesis of a series of bis spiropyran dyes (BSPs), *i.e.*, bis[5-{1,3,3-trimethylspiro-(indolino-2,2′-benzopyranyl)}]-α,ω-dicarboxamides *via* route b in Scheme 1. It has been reported,[8] however, that ASP requires a multistep synthesis from 5-amino Fischer base, **1c**. Several tedious steps for blocking of the amino group and deblocking were needed in the reaction with salicylaldehydes since **1c** has an extra nucleophilic center in the amino group in addition to the methylene group of Fischer base. This may the reason why the route c in Scheme 1, that is the reaction of **1c** with nitrosalicylaldehyde, was not recommended for use to the synthesis of ASP.[8]

We thus undertook a synthetic study making use of diacid halides as both blocking group of the amino function and as carbon chains to make the connection between two spiropyranyl groups, as shown in route a in Scheme 1. Bis-Fischer bases (BFBs), [bis{5-(2-methylene-1,3,3-trimethylindoline)}-α,ω-dicarboxamides] were obtained from the reaction of diacid halides with 2-3 molar ratio of AFB, **1c**, which was prepared by adapting Gales' method.[9] The BFBs were then reacted with several salicylaldehydes to give the corresponding BSPs in good yields.

5-Nitro(and amino)-1,3,3-trimethyl-2-methyleneindolines (**1 b** and **1c**) were obtained from commercially available Fluka grade Fischer base (1,3,3-trimethyl-2-methyleneindoline, **1a**), according to a previously described procedure.[9] **1a** was nitrated with H_2SO_4/HNO_3 at 10℃. After the reaction was complete, the solution was neutrallized and kept in the refrigerator for 1 day. The solid was then filtered, dissolved in ether, washed with water and dried (anhdydrous Na_2SO_4). The crude product was recrystallized from methylene chloride-light petroleum ether to give **1b**, mp. 88-91℃ (lit[9]. 85-91℃), yield 60%. The red solid, **1b**, was boiled under reflux with stannous chloride dihydrate and concentrated hydrochloric acid for 2 h. On cooling the mixture was poured on to ice, made alkaline with aqueous sodium hydroxide solution and the resultant precipitate was extracted with diethylether. The crude material was recrystallized from methylene chloride/light petroleum ether to give colorless **1c**, mp. 98-100℃ (lit[9]. 98-100℃) in 77% yield.



1a X=H
1b =NO_2
1c =NH_2



2a n=3
2b =5
2c =7

A portion of (4.83 mmole) of glutaryl dichloride ($n=3$) in 20 mL methylene chloride and triethylamine (10 mL) was added dropwise to a cold solution of **1c** (10.62 mmole) in 30 mL methylene chloride, which was stirred for 3 h at room temperature. The reaction mixture was washed with water and brine, dried, evaporated. The white solid which formed was then recrystallized from methylene chloride/hexane to give product **2a**, in 70% yield, mp. 182-184℃. For the synthesis of **2b** and **2c**, the same procedure was followed using pimeloyl dichloride ($n=5$) and azelaoyl dichloride ($n=7$), except that THF solvent was used in both cases. Yields and mps were 71 & 92% and 136-138 & 142-143℃, for **2b** & **2c**, respectively.

A portion (0.24 mmole) of bis-Fischer base, **2a-c**, in 50 mL ethanol was then added dropwise to a stirred solution containing 0.55 mmole 2-hydroxy-5-nitrobenzaldehyde (nitrosalicylaldehyde) in 50 mL ethanol. The solution was kept at

Table 1. Characterization Data for BSPs (**3a**, **3b** and **3c**)

Compound	mp. (℃)	Analysis C. H. N.	M. W.	Molecular ion	
				(m/z)	Rel. int. (%)
3a	172-173	calcd. 67.00, 5.49, 10.90 found. 67.01, 5.52, 10.68	770.88	771.1	100
3b	155-158	calcd. 67.65, 5.80, 10.52 found. 67.51, 5.64, 10.43	798.93	799.96	24.24
3c	155-156	calcd. 68.26, 6.09, 10.16 found. 68.57, 6.18, 9.98	826.98	827.0	8.80

*Electroscopy (ES) mass spectra were recorded on a VG Quattro mass spectrometer at Queen's University.

Table 2. UV-Visible Spectroscopic Data (λ_{max}, $1000\times\nu$) of Opened Forms of Bis-indolinobenzopyrans (**3a**-**3c**) in Various Solvents

Solvent	E_T	3a	3b	3c
Dioxane	36.0	596 (16.7)	587 (17.0)	591 (16.9)
CH_2Cl_2	40.7	589 (17.0)	587 (17.0)	588 (17.0)
Acetone	40.2	578 (17.3)	579 (17.3)	579 (17.3)
DMF	43.8	576 (17.4)	577 (17.3)	579 (17.3)
EtOH	51.9	547 (18.3)	546 (18.6)	548 (18.2)

40℃ for 1 day. The precipitates were purified by column chromatography using silica gel (100-200 mesh) with $CHCl_3$/EtOAc (9 : 1) as eluent. Recrystallization from methylene chloride/hexane gave pure **3a-c**. Yields were 70, 88, and 81%, for **3a**, **3b** & **3c**, respectively. The characterization data including microanalysis and electrospray (ES) mass spectral data are summerized in Table 1.

The synthesized BSPs exhibited strong photochromism, with very large molar extinction coefficients for the open chain merocyanines, as shown in Table 2. A negative solvatochromism[4b,4f,10] is observed, as discussed previously for general monoindolinospirobenzopyran dyes. As solvent polarity increased from dioxane (E_T=36.0) to ethanol (E_T=51.9), a hypsochromic shift (from 546 to 596 nm) was generally observed for **3a-b**. In the nonpolar solvent region (less than E_T=36), however, some precipitates were observed. This is assumed that there are intra- or intermolecular π-stacking (aggregation) *via* merocyanine units in nonpolar solvents. Further investigations on the intra- and intermolecular π-stacking behavior of the open form of these BSPs are currently underway.

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