1) or $\gamma/(n+1)$. Except for the calculation of $\gamma/(n+1)$, the parameter a_3 was negligible; thus, the asymptotic values were obtained within the second order of $(n+1)^{-1}$.

The PM3 underestimates the dipole moments, since the SCF results are much more reliable. But, from the PM3 trend of the electrical properties with increasing chain length, we expect the similar trend for the SCF calculation. The asymptotic polarizabilities and second hyperpolarizabilities of the three polyene systems should have the same values. Thus, using different polyene systems, the asymptotic values can be better estimated than the case with one polyene system. We expect that the SCF and PM3 values of $\alpha/(n+1)$ are 61~63 and 47~50 a.u., respectively, while the PM3 values for $\gamma/(n+1)$ are 422~442 10^{-36} esu. If the parameter a_3 is neglected, the PM3 values of $\gamma/(n+1)$ for X/Y=H/H, F/CH_3, and NH_2/NO_2 are 304, 319, and 379 10^{-36} esu, respectively. Thus, in this case the second order approximation is not suitable. The PM3-predicted asymptotic values of β_μ for X/Y=F/CH_3 and NO_2/NH_2 are ~54 and ~382 10^{-30} esu, respectively. The corresponding SCF-predicted asymptotic values are 13 and 1189 10^{-30} esu., respectively. For these asymptotic values, the SCF results are more reliable due to the higher level of theory, while the PM3 results can give better trend with more data for polyene systems with longer chain length.

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Unusual Solvatochromic Behavior of the Open-Chain Merocyanine Forms of 5-chlorinated 1,3,3-spiro(2H-1-benzo-2,2'-indoline) Derivatives

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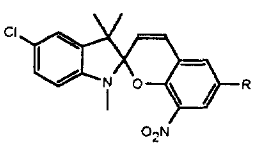
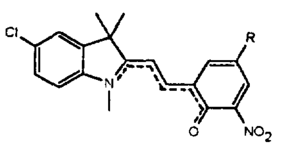
Thermo- and photochromic indolinobenzospiropyran dyes have attracted considerable attention in the last few decades, with regard to various practical applications such as recording, copying and displaying materials.[1,2] In addition, the open-chain merocyanine forms of spirobenzopyrans are of particular interest since merocyanine dyes are known to be used as empirical solvent polarity indicators.[3] Indolinobenzospiropyrans (I) are known to be in equilibrium with their metastable colored merocyanine forms (II) by UV-visible light, heat or spontaneously as we mentioned in previous papers.[4-6]



I



II

1; R=CH_3
2; =H
3; =Br

A number of studies[2,4-7] have reported important advances particularly towards understanding the backward spiro-ring formation processes in various solvents. The influence of solvents on the ring closure reaction rate could yield structural information of the ground state of open-chain merocyanine

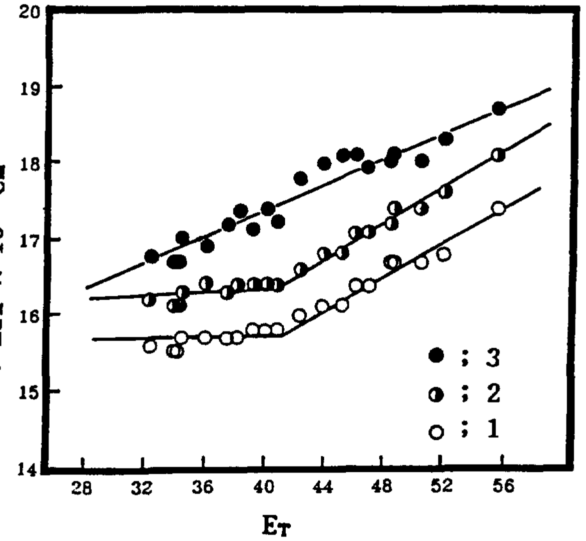
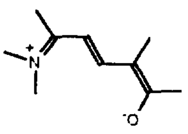


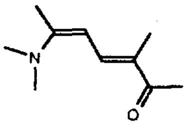
Figure 1. Plots of frequency $\nu_{max} \times 10^3$ *vs.* E_T for the open-chain merocyanine form of 5-chlorinated 1,3,3-trimethylindolinobenzospiropyrans; **1** (○); **2** (◐); **3** (●), in various solvents.

forms, and hence mechanistic information on the nature of the spiro-ring formation (II→I) process.

In a previous publication[4] we reported unusual solvatokinetic behavior of the spiro-ring formation from the open-chain merocyanine form of 5-chlorinated 1,3,3-spiro(2H-1-benzopyran-2,2′-indolines) (**1**-**3**). On plotting log (rate constant) versus the solvent polarity parameter E_T, an excellent linear plot was obtained for the compound **3**. However doubly branched linear plots were obtained for **1** and **2** unlikely to the non chlorinated cases,[2,5 7] in which no-branched linear plots had been obtained. Thus we suggested that the doubly branched solvatokinetics might be indicative of a structural change of the ring opened merocyanine, between polyene-like ionic structure IIa and the quinonoidal structure IIb in the ground state and hence alter the reaction mechanism for the spiro-ring formation. Dual mechanistic processes were thus suggested to be operating in the spiro-ring formations. Namely the ionic process *via* a charged transition state in polar solvent media and the concerted electrocyclic process *via* a uncharged transition state in nonpolar solvent media are operated for **1** and **2** in the spiro-ring formation. Whereas the ionic process is operated for **3** in the whole region of solvent polarity examined.



IIa



IIb

In this connection we have studied and found an abnormal solvatochromic behavior of the open-chain merocyanine form of 5-chlorinated 1,3,3-spiro(2H-1-benzopyran-2,2′-indolines) (**1**-**3**).

The UV-Vis spectral data of the open form of spiropyrans, **1**-**3** in various solvents are collected in Table 1 and the results are plotted as frequency (ν) versus the solvent polarity parameter (E_T) in Figure 1.

Table 1. UV Data λ_{max} (ν) of The Open Chain Merocyanine Forms of 5-chlorinated 1,3,3-spiro(2H-1-benzopyran-2,2′-indolines), **1**-**3** in Various Solvents

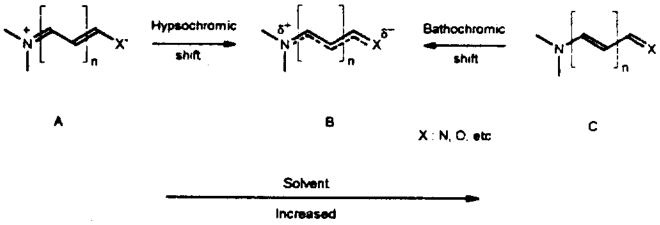
No. solvent	E_T	**1**	**2**	**3**
		$\lambda_{max}(\nu_{cm^{-1}})$	$\lambda_{max}(\nu_{cm^{-1}})$	$\lambda_{max}(\nu_{cm^{-1}})$
1 CCl_4	32.4	640(15600)	619(16200)	596(16800)
2 Toluene	33.9	646(15500)	622(16100)	599(16700)
3 Benzene	34.3	645(15500)	622(16100)	600(16700)
4 Ether	34.5	637(15700)	615(16300)	588(17000)
5 1,4-Dioxane	36.0	637(15700)	611(16400)	589(16900)
6 THF	37.4	638(15700)	614(16300)	581(17200)
7 Et-acetate	38.1	635(15700)	608(16400)	576(17400)
8 $CHCl_3$	39.1	634(15800)	608(16400)	586(17100)
9 Me-acetate	40.0	634(15800)	611(16400)	575(17400)
10 CH_2Cl_2	40.7	634(15800)	608(16400)	582(17200)
11 Acetone	42.2	624(16000)	601(16600)	563(17800)
12 DMF	43.8	622(16100)	595(16800)	557(18000)
13 DMSO	45.1	622(16100)	594(16800)	553(18100)
14 Acetonitrile	46.0	608(16400)	584(17100)	552(18100)
15 Cyclohexanol	46.9	611(16400)	584(17100)	560(17900)
16 2-Propanol	48.4	600(16700)	583(17200)	555(18100)
17 Isobutyl-OH	48.6	600(16700)	576(17400)	553(18100)
18 $PhCH_2OH$	50.4	598(16700)	575(17400)	557(18000)
19 EtOH	51.9	595(16800)	569(17600)	546(18300)
20 MeOH	55.4	576(17400)	553(18100)	536(18700)

The results show that an excellent linearity is obtained for the compound **3** and branched linear plots are however obtained for the compounds **1** and **2**. A marked solvatochromism[3] is exhibited by the merocyanines derived from the spiropyran **1** and **2** in polar solvent region (E_T>40) and from spiropyran **3** in whole region of solvent examined. Branched linear plots with zero slopes are exhibited by the merocyanines derived from the compounds **1** and **2** were obtained in the less polar-solvent region (E_T<40). Figure 1 shows that there is a fairly good relationship between ν_{max} and the solvent polarity parameter E_T for the solvent dependent region, with the following relationship:

[1] Compound **1** : $\nu_{max} = 1.04 \times 10^{-1} E_T + 11.6$, $r = 0.972$, $n = 10$
[2] Compound **2** : $\nu_{max} = 1.10 \times 10^{-1} E_T + 12.0$, $r = 0.985$, $n = 10$
[3] Compound **3** : $\nu_{max} = 8.58 \times 10^{-2} E_T + 14.0$, $r = 0.956$, $n = 20$

The striking feature about the present results, as displayed in Table 1 and Figure 1, is the followings; 1) the marked hypsochromic shift is exhibited with increasing solvent polarity (*i.e.*, negative solvatochromism) for the compound **3** in the whole region of solvent polarity examined and for the compound **1** & **2** in the polar solvent region (E_T>40) and 2) the branched linear plots with zero slope (solvent independent linear plots) are shown in the less polar-solvent region (E_T<40) for the compound **1** and **2**. Similar situation, but not exactly same, has been reported by Jacques[8] in the study of the solvatochromic merocyanine dye, 4-[-2-(1-methyl-4-4-pyridino)ethyl]phenolate which exhibits both batochromic (E_T<40) and hypsochromic shift (E_T>40) of long wavelength π-π* absorption band as the solvent polarity increases.

It is known that the nature of the observed solvent effect for a given dye molecule, *i.e.*, bathochromic or hypsochromic shift with increasing solvent polarity, depends largely on the change in polar characteristics between ground and exited states.[3a] For a weakly polar molecule, with low polarity in the ground state and increased polarity in the excited state, a bathochromic shift results. Conversely, for a highly polar molecule in the ground state and reduced polarity in the excited state, a hypsochromic shift is observed. In principle, a merocyanine dye could exhibit either a bathochromic or a hypsochromic shift since the ground state could have an electronic configuration corresponding largely to the nonpolar quinoid IIb, or to the dipolar, zwitterionic form IIa, or an inbetween character. In general terms, we may represent the ground state of the merocyanines as a polyene-like structure A and the excited state as a plyamethine-like structure B, a situation which will result in a hypsochromic shift. Conversely, a bathochromic shift would have results if the ground state had the quinoid structure C and the excited state the dipolar structure B.



The observation of a hypsochromic shift (negative solvatochromism) in the present system is hence indicative of a highly polar ground state, *i.e.*, approaching the configuration of the zwitterionic form IIa, and an excited state with decreased polarity. The branched linear plot with zero slope obtained in the less polar-solvent region ($E_T<40$) for the compound **1** and **2** may indicate and inbetween character in the ground state.

This doubly branched solvatochromic behavior of 5-chlorinated 1,3,3-spiro(2H-1-benzo-pyran-2,2′-indolines) (**1-3**) is quiet in coincidence with the recent our report[4] of the solvatokinetic behavior of those compounds **1-3**. Doubly branched solvatokinetics is certainly indicative of a structural change of the ring opened merocyanine, between polyene-like ionic structure IIa and the quinonoidal structure IIb in the ground state and hence alter the reaction mechanism for the spiroring formation.

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Macromolecular Modeling and NMR Distance Geometry Refinement: Conotoxin G1 in Solvent

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Conotoxin is a neurotoxin peptide of fish-hunting cone snails.[1] The structure of conotoxin-G1 is NH_3-Glu-Cys-Cys-Asn-Pro-Ala-Cys-Gly-Arg-His-Tyr-Ser-Cys-NH_2 with disulfide bridges of Cys2-Cys7 and Cys3-Cys13. In spite of the disulfide bridge, the molecule is rather flexible in solution.[1] To study the structure, Pardi *et al.*[2] reported 50 NOE distance geometries from 2-D NMR experiment. The 2-D NMR experiment has been a very useful method to study flexible molecular structures.[3] But, the NMR data can provide only a piece of information to analyze the overall structures. Nevertheless, the information is very useful to understand protein folding. To utilize such information, we have performed various simulations for conotoxin-G1 with new methodology, comparing the theoretical result with the NOE data.

To devise a realistic effective method to include solvent effects, we used water clusters that are pseudo-bound to charged residues with weak interaction potentials. The water cluster reduce direct interactions between charged residues, simulating solvent effects.[4] Therefore, the water-cluster method can be utilized to find the most statistically significant conformations of macromolecules in solution and to refine NMR distance geometries.

In our molecular dynamics simulation, we used Kollman's interaction potentials.[5] But, the dielectric constant for the coulombic interactions was chosen as $\varepsilon=1/[1-(r/r_c)^2]^3$, so that the long-range coulomb potential was smoothed near the cut-off region. Here, r, is the intersite distance, and r_c is the cut-off radius chosen as 8 Å. This method removes