of Figure 3). Table 1 summarizes sensitivities and detection limits of compounds and elements observed. For alcohols, detection limit varies in the range of 26 pg/s to 7 pg/s upon increasing carbon number of compounds. In contrast, methyl chlorides gave around 5 ng/s of detection limit for chlorine and the values are not different significantly with the number of chlorines in the molecules. The sensitivity and detection limit of this system are comparable to those of FID for alcohols at this moment. Further, this system can be applied for selective monitoring of chlorine-containing molecules. Therefore with this system, it is possible to analyze unresolved peak which could not be separated completely in a typical GC column. Moreover, the MIP detector is sensitive for not only hydrogen or chlorine, but also most elements in principle, so this system has potential prospect for FID-inactive molecules, *e.g.*, CO, CO_2,….

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Unusual Solvatokinetic Behavior of 5-Chlorinated 1,3,3-Spiro(2H-1-Benzopyran-2,2'-Indoline) Derivatives

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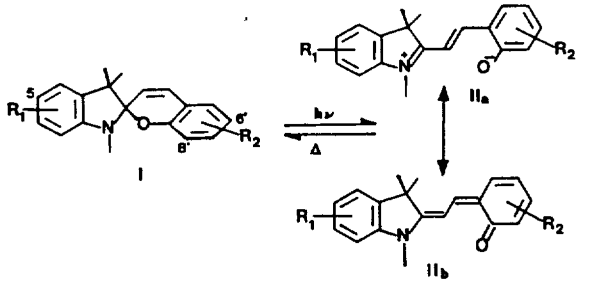
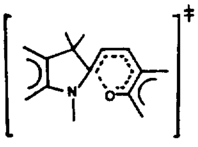
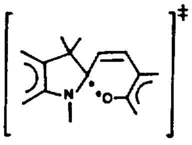
Thermo- and photochromic indolinobenzospiropyran dyes[1] have attracted considerable attention in the last few decades, with regard to various practical applications such as in recording, copying and displaying materials. Spiropyrans are known to be in equilibrium with their metastable colored forms. Absorption of ultraviolet light shifts the equilibrium towards the merocyanine colored form, II, while the reverse process to the colorless form, I, is induced by visible light, heat or spontaneously (Eq. 1). A number of studies[2-4] have reported important advances towards developing spiropyrans for the industrial purpose and understanding of the detailed photochemical processes and the backward spiro-ring formation processes

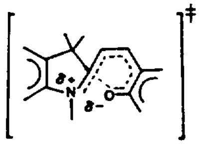


(1)

Three different mechanistic processes[5] *via* corresponding three transition states ($TS_{1,2\&3}$) have been suggested for the thermal ring closure reaction of the merocyanine open form of spiro-pyrans. TS_1 applies to a concerted electrocyclic process as suggested by Dürr and Ollis *et al.*, TS_2 represents the diradicaloid mechanism formed through homolytic cleavage of the C_2-O bond and is favored by Sueishi *et al.* Finally, TS_3 pertains to the ionic mechanism *via* a merocyanine type zwitterionic species, as suggested by Flannery *et al.*


TS_1


TS_2


TS_3

In recent years, we have reported the solvatokinetic studies[3,4] of the spiro-ring formation from the open-chain merocyanine form of 1,3,3-spiro(2H-1-benzopyran-2,2'-indolines). Excellent linear plots were obtained with negative slopes on plotting log (rate constant) versus the solvent parameter E_T. The large decrease in rate on increasing solvent polarity clearly supported the ionic transition state, TS_3. The diradicaloid TS_2 has been ruled out on the grounds that the colored solutions were unchanged on treatment with radical scavengers such as oxygen, hydrogen and hydroquinone. It is also apparent that the electrocyclic reaction is not expected to show a marked sensitivity to the medium polarity, in accordance with an isopolar, six-membered activated complex.[6]

The present communication reports unusual solvatokinetic behaviors of the 5-chlorinated spirobenzopyrans (**1**-**3**). The influence of substituents in the benzopyran ring on the closure reaction rate in various solvent systems is particular interest since it could yield mechanistic information on the nature of the spiro-ring formation process. Figure 1 shows the doublely branched linear plots for **1** and **2** on plotting log (rate constant) versus the solvent polarity parameter E_T, unlikely to the previous results.[3,4], in which no-branched lin-

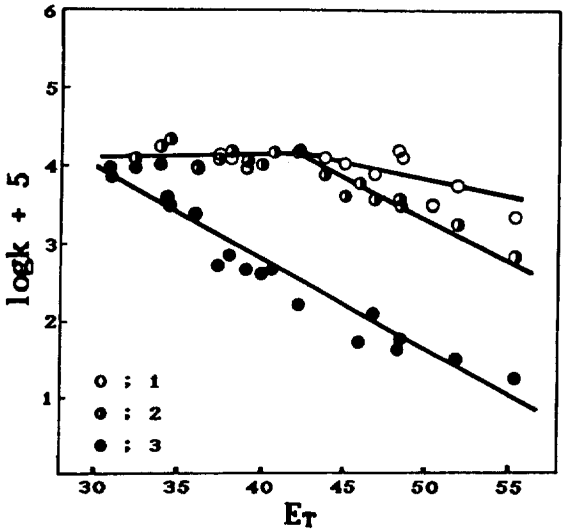


Figure 1. Plots of log k_{obs} versus E_T value for the ring closure reaction of the open form of 6'-substituted 5-Chloro-8'-nitro-1,3,3-trimethyl-indolinobenzospiropyrans [**1**; (6'-CH_3), **2**: (6'-H) and **3**; (6'-Br)] in various solvents.

ear plots were obtained. No branched linear plot is however obtained for the compound **3**.

In the highly polar-solvent region (E_T>40), good linear plots with negative slopes have been obtained as we observed[3,4]. The rate of the ring closure from the open-chain merocyanine form depends markedly on the substitutents in the present series **1**-**3**. The sensitivity of rate on medium polarity is highetest (slope=0.37) for the compound **3**, whereas it is lowest (slope=0.064) for the compound **1**. This finds an explanation that electron withdrawing groups (6'-Br and 8'-NO_2) will stabilize the dipolar structure **IIa** in the ground state. This provides further support for the dipolar structure of the merocyanines formed on ring opening of the spiropyrans in polar solvent media. Surprisingly, branched linear plots with zero slopes were obtained in the less polar-solvent region (E_T<40) for the compounds **1** and **2**, which have no electrowithdrawing substituent in the 6'-position. There are little sensitivities to both media and substituents.

This unusual observation of doubly branched solvatokinetics in the present system is hence indicative of a structural change of the ring opened merocyanine, between polyene-like structure **IIa** and the quinonoidal structures **IIb** in the ground state and hence alter the reaction mechanism for the spiro-ring formation. This is in coincedence with the recent report[7] of the solvatochromic merocyanine dye, 4-[2-(1-methyl-4-pyridino)ethyl]phenolate which exhibits both bathochromic (E_T<40) and hypsochromic shift (E_T>40) of long wavelength $\pi \rightarrow \pi^*$ absorption band as the solvent polarity increases.

Dual mechanistic processes are thus suggested to be operating in the spiro-ring formations. Namely the ionic process *via* TS_3 in polar solvent media and the concerted electrocyclic process *via* TS_1 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. Further investigations for the doubly branched solvatokinetics and solvatochromism of the 5-substituted indolinobenzo-spiropyran derivatives and their open-chain merocyanines are currently underway.

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Synthesis of Sterically Hindered Strapped Porphyrins

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Heme proteins which contain iron porphyrins as prosthetic group are responsible for oxygen transport and storage, electron transport, oxygen reduction and hydrocarbon oxidation.[1,2] An ideal chemical model for these enzymes should satisfy a few structural characteristics such as similar active site geometry, protective structural feature and similar domain. The design and synthesis of model compounds for heme proteins become increasingly important in the investigation of various enzymatic processes. In these regards, many systems have been designed and synthesized since 1960.[2] Also there are various means by which a tetraphenylporphyrin ring can be constructed.[3-5] The common procedure is to react pyrrole with an appropriate benzaldehyde.