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SPIROPYRAN DERIVATIVES AS MULTIFUNCTIONAL ARTIFICIAL RECEPTORS FOR BIOLOGICALLY IMPORTANT SPECIES

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Abstract This paper deals with the syntheses and molecular recognition-induced coloration of two main types of the spiropyrans: (1) crowned spirobenzopyrans as alkali-metal cation receptors, and (2) spiropyridopyrans as nucleotide base receptors.

INTRODUCTION

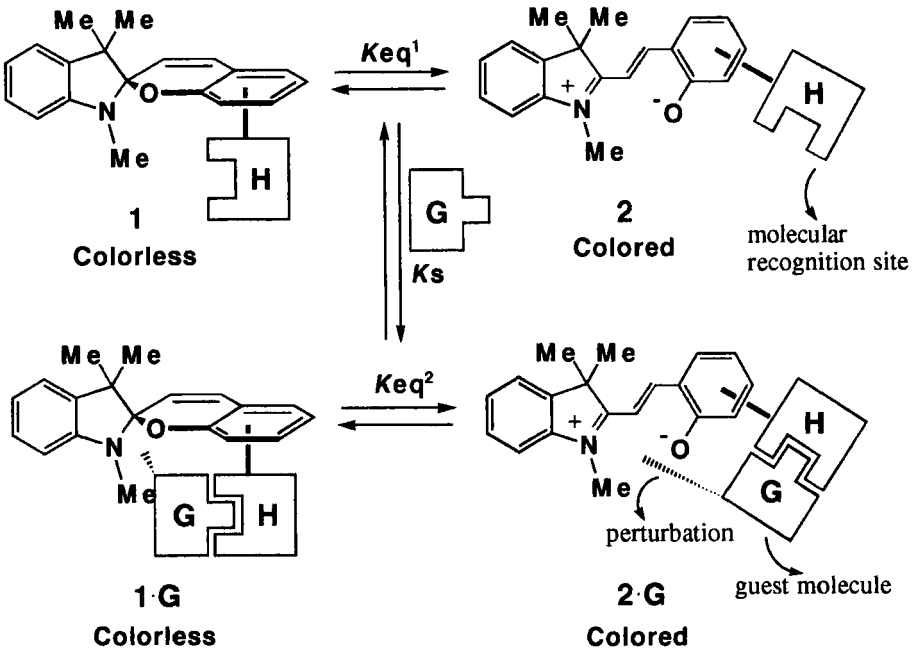
Artificial receptors whose optical properties are markedly perturbed by molecular recognition are of current interest and attracting much attention from the viewpoints of not only biomimetic chemistry but also molecular sensors.[1] Recently we developed a new class of spiropyran derivatives as multifunctional artificial receptors for biologically important species, namely, "recognition - structural change - signaling" receptors.[2] Our strategy utilized the fact that equilibrium between the colorless spiropyran **1** possessing a molecular recognition site and merocyanine **2** would be affected by molecular recognition, and that this change ($Keq^1 \neq Keq^2$) could be detected using a UV-vis spectrophotometer (Figure 1).

In this paper, we will discuss the syntheses and molecular recognition-induced coloration of two main types of the spiropyrans: that is, crowned spirobenzopyrans as alkali-metal cation receptors and spiropyridopyrans as nucleotide base receptors.

CROWNED SPIROBENZOPYRANS

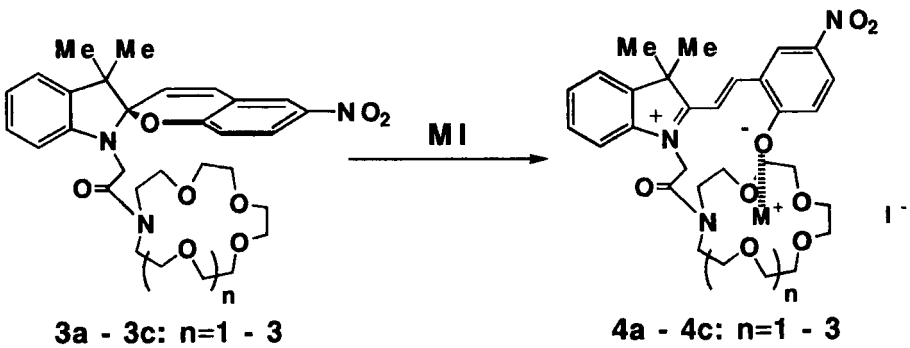
Crowned spirobenzopyrans **3** were prepared from crown-linked *exo*-methyleneindoline with 5-nitrosalicylaldehyde. Crowned spirobenzopyrans **3** thus prepared showed no absorption bands above 450 nm in nonhydroxylic solvents (CH_3CN, acetone, etc). When a 5-fold molar quantity of LiI was added to the CH_3CN solution solution of **3a** and **3b**, new absorption bands appeared (**3a**, λ_{max}=530 nm, ε=4700; **3b**, λ_{max}=530

FIGURE 1



nm, ε=10000). However, only negligible changes or no changes were observed upon addition of other alkali-metal iodides (Figure 2). The emerging absorption bands were shown to be due unambiguously to the merocyanine structures **4a** and **4b** on the basis of NMR experiments.

FIGURE 2

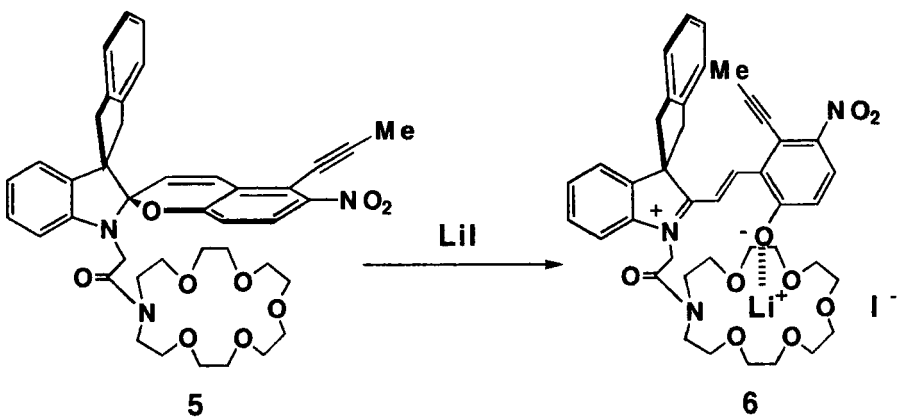


ADVANCED CROWNED SPIROBENZOPYRANS

We prepared an advanced artificial receptor in which recognition induced a structural change in the molecule accompanying coloration that results in a proximity of two remote sites in the molecules. Our strategy utilizes the fact that isomerization of the spirobenzopyrans possessing a monoaza-crown ring as a recognition site to the open colored merocyanines is induced by recognition of alkali-metal cations. We expected that the isomerization of a rationally designed new spirobenzopyran (**5**) possessing a monoaza-crown ether, propynyl, and indane groups might have propynyl-Me groups approach the π-electrons of the indane-benzene ring, and any change in the microscopic environment of the Me groups could be easily detected by NMR (Figure 3).

In the ^{1}H NMR spectrum, the propynyl-Me protons of **5** appeared at 2.19 ppm, a normal position. After LiI was added to the solution, initially, only the downfield shifts and broadening of the signals in the aza-crown ring were observed, which indicated that the lithium cations were bound to the macrocycle. With the elapse of time, however, new resonances began to appear. The new resonances were assigned as those of a merocyanine (**6**), and noteworthy is that the Me protons of **6** were largely shifted upfield by 0.90 ppm, reflecting that the Me groups of **6** were placed on the center of the indane-benzene ring, as expected.

FIGURE 3



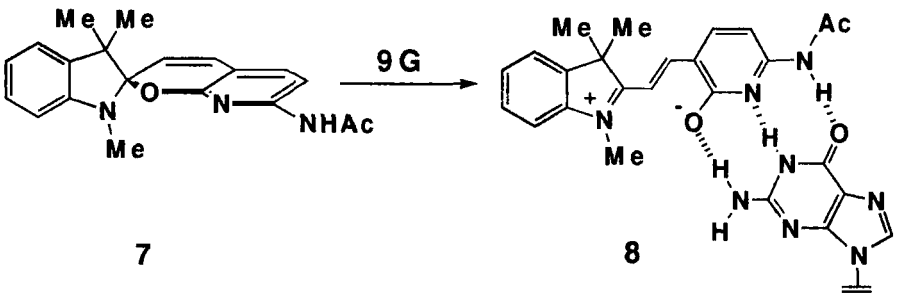
5 **6**

SPIROPYRIDOPYRANS

The design of the spiropyridopyran **7** was based on the triple hydrogen bond complementarity between the acetamidopyridone anion unit of the open merocyanine form **8** and guanine. We might expect that equilibrium between the colorless spiropyridopyran and the colored merocyanine would be affected by recognition of guanine and that this change could be detected. The spiropyridopyran **7** thus prepared showed only weak absorption bands above 350 nm in nonhydroxylic solvents, indicating that **7** exists mainly as the closed spiropyran form. In CH_2Cl_2, however,

addition of 2',3',5'-tris-*O*-(*tert*-butyldimethylsilyl)guanosine (**9G**, 10 equiv) to **7** produced changes in the absorption spectra, and strong absorption bands appeared. On the other hand, only negligible changes were observed upon addition of other nucleoside derivatives (Figure 4). The increasing absorption bands were attributed to the increasing proportion of the merocyanine form to that of the spiropyran form by recognition of **9G**.

FIGURE 4



CONCLUSION

We have developed a new class of spiropyrans, crowned spirobenzopyrans as alkali-metal cation receptors and spiropyridopyrans as nucleotide base receptors, which were conceptually new artificial receptors, namely,"recognition - structural change - signaling" receptors.

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