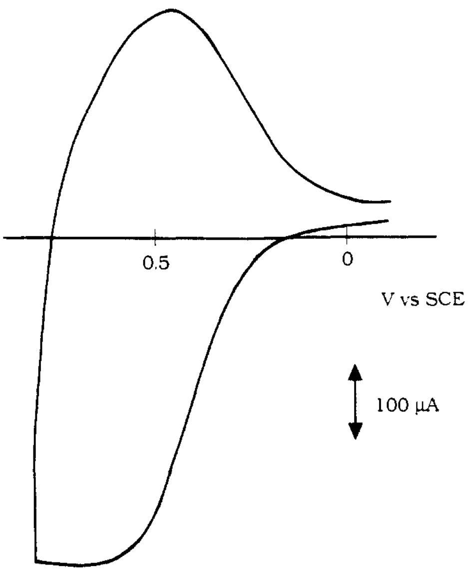

Figure 3. Cyclic voltammogram of an array of poly(*N*-methylpyrrole) microtubules (see Figure 2c). Tubule diameter was 1.0 μm. The substrate electrode was a 0.5-cm^2 Pt disk. The supporting electrolyte was 0.2 M Et_4NBF_4 in CH_3CN. The scan rate was 10 mV s^{-1}. Anodic currents are down and cathodic currents are up in this figure.

complished by dissolving the membrane in CH_2Cl_2 and collecting the tubules by filtration.[4c,6]

Figure 2a shows an electron micrograph of typical template-synthesized polypyrrole microtubules. Because the Nuclepore membrane used was 8 μm thick, these tubules are 8 μm long. This ability to produce tubules with monodisperse lengths is a unique and important feature of the template method. Furthermore, because Nuclepore membranes have monodisperse pore diameters,[4b] monodisperse tubule diameters are also obtained (Figure 2b). Finally, tubule diameter and length can be varied, at will, by varying the characteristics of the template membrane.[4b]

Figure 2c shows an electron micrograph of electrochemically synthesized poly(*N*-methylpyrrole) tubules. Note that while the template membrane has been dissolved away, the tubules are still arranged in an upright array. This is because electrochemically synthesized tubules are connected at their bases to a thin contiguous film of the heterocyclic polymer. This ability to produce an upright array of tubules, connected by a common base-layer film, is another unique, and perhaps useful, feature of the template method.

The polyheterocyclic tubules show redox reactions typical of the parent polymer[7] (Figure 3). Thus, like the parent polymer, these tubules can be reversibly switched between electronically insulating and electronically conductive states.[7] Furthermore, we have recently shown that template synthesis dramatically enhances the electronic conductivities of such polymers.[4a] The redox chemistry in Figure 3 also raises the interesting possibility of making tubule-based electroreleasing systems.[8] We are currently pursuing this possibility.

Finally, it is interesting to speculate on the mechanism responsible for tubule formation in the template process. The key to this process is the adsorption of the nascent polyheterocyclic chain to the pore wall. Heterocyclic polymers are synthesized via oxidation of the monomer and subsequent coupling of the radial cations obtained;[7] a cationic polymer is produced. The pore walls in Nuclepore membrane are anionic.[9] Thus, electrostatic attraction undoubtedly contributes to the adsorptive interaction between the pore wall and the nascent polyheterocyclic chain. We are using this hypothesis to identify other polymers and membranes which can be used for template syntheses of organic microtubules.

Acknowledgment. This work was supported by the Office of Naval Research and the Air Force Office of Scientific Research.

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Alkali Metal Recognition Induced Isomerization of Spiropyrans

Masahiko Inouye,* Masaru Ueno, and Teijiro Kitao

Department of Applied Chemistry, College of Engineering
University of Osaka Prefecture, Sakai, Osaka 591, Japan

Kikuo Tsuchiya

Special Compounds & Colorants Division
Dainippon Ink & Chemicals, Inc., Suita, Osaka 564, Japan

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A new class of host molecules whose optical properties are markedly perturbed by the presence of cations are of current interest.[1] These "recognition and signaling" molecules may stimulate the investigation of molecular sensors for biologically important alkali-metal ions. Thus, numerous fluoroionophores[2] and chromoionophores[3] have been synthesized.

We report herein the preliminary results obtained for spiropyrans[4] bearing a monoaza-crown ring (**1**) as a recognition site,[5] of which isomerization to the colored merocyanines (**2**) is induced by recognition of alkali-metal cations (Scheme I). This new type of chromoionophore is conceptually different from the crown ether dyes so far synthesized, because in the latter cases, the absorption bands of chromophores are merely shifted by the complexation of cations.

The new spiropyrans **1** were prepared in three steps from *N*-chloroacetyl monoaza-crown ethers **7**[6] in 28-32% overall yields (Scheme II).

The spiropyrans **1** thus prepared showed no absorption bands above 450 nm in nonhydroxylic solvents (CH_3CN, acetone, etc.). However, addition of alkali-metal iodides to these solutions gave rise to changes in their absorption spectra. When a 5-fold molar

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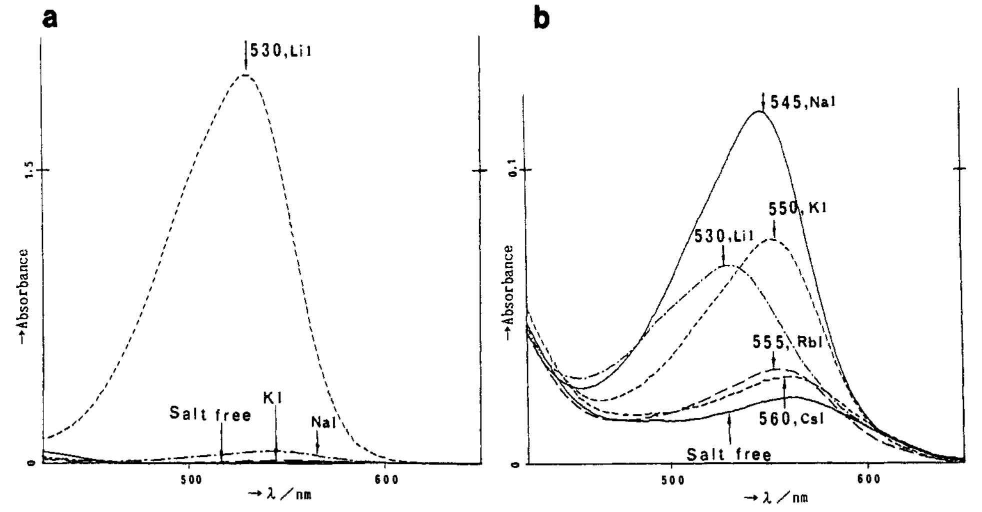
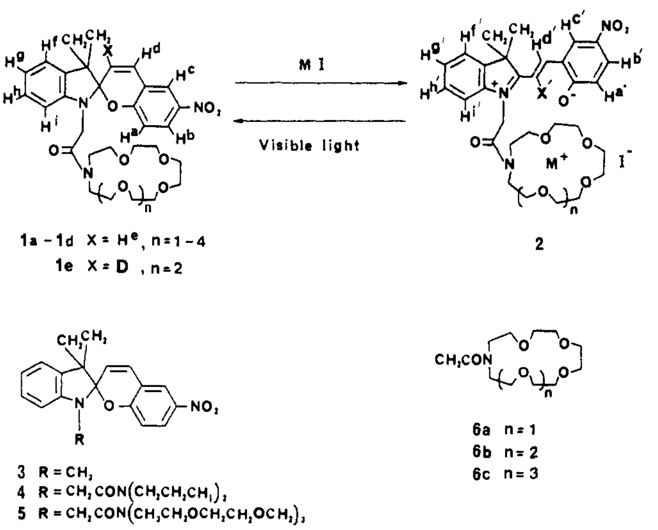


Figure 1. The electronic absorption spectra of the acetonitrile solutions of (a) **1b** and (b) **1c** in the presence or absence of alkali-metal iodides.[8] The spectrum of **1a** was similar to that of **1b**. In part a, the spectra with RbI and CsI were omitted for clarity.

Scheme I



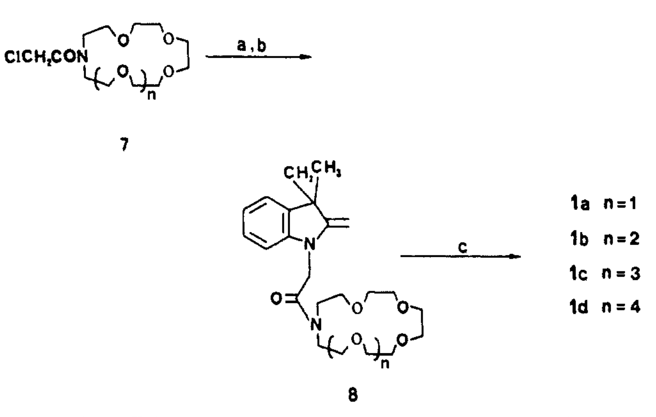
1a - 1d X = H^e, n = 1-4
1e X = D , n = 2

2

3 R = CH_3
4 R = $CH_2CON(CH_2CH_2CH_3)_2$
5 R = $CH_2CON(CH_2CH_2OCH_2CH_2OCH_3)_2$

6a n = 1
6b n = 2
6c n = 3

Scheme II[a]



7

8

1a n=1
1b n=2
1c n=3
1d n=4

[a] (a) 2,3,3-Trimethylindolenine, NaI, CH_3CN, reflux, 12 h; (b) NaOH or KOH, H_2O, room temperature, 10 min; (c) 5-nitrosalicylaldehyde, EtOH, reflux, 5-6 h.

quantity of LiI was added to the acetonitrile solutions of **1a** and **1b**, new absorption bands appeared (**1a**, λ_{max} = 530 nm, ϵ = 4700; **1b**, λ_{max} = 530 nm, ϵ = 10000). However, only negligible changes or no changes were observed upon addition of NaI, KI, RbI, and CsI (Figure 1a). While **1c** revealed a small but significant selective absorption with NaI, cation-induced hypsochromic band shifts of Li^+, Na^+, K^+, Rb^+, and Cs^+, which decreased in that order, were explained satisfactorily by the electrostatic interactions between the complexed cations and the *p*-nitrophenolate dipole of the merocyanine (Figure 1b).[1a] Unfortunately, **1d** showed no changes in its absorption spectrum in the presence of any alkali-metal iodides.

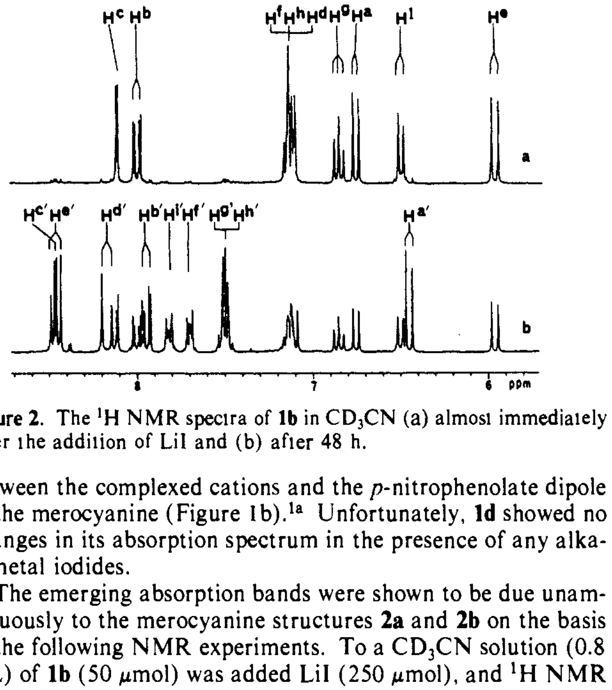


Figure 2. The ^1H NMR spectra of **1b** in CD_3CN (a) almost immediately after the addition of LiI and (b) after 48 h.

The emerging absorption bands were shown to be due unambiguously to the merocyanine structures **2a** and **2b** on the basis of the following NMR experiments. To a CD_3CN solution (0.8 mL) of **1b** (50 μmol) was added LiI (250 μmol), and ^1H NMR spectra were measured as a function of time in the dark. Almost immediately after the addition of LiI, the signals of only **1b** were detected. With the elapse of time, however, new resonances began to appear, and after 48 h, equilibrium was reached (Figure 2). The new resonances were unambiguously assigned as those of a merocyanine (**2b**) on the basis of chemical shifts, coupling constants, and ^1H-^1H COSY. The determination of olefinic protons of **2b** ($H^{d'}$ and $H^{e'}$: J = 15.3 Hz) was made by comparison of its NMR spectrum with that of **2e**.[7]

Subsequently, NOE experiments were carried out in order to determine the conformation of **2b**. Irradiation of geminal dimethyl protons resulted in significant changes in the intensities of $H^{d'}$ (+16.7%) and $H^{c'}$ (−4.6%), but only a negligible change was observed for $H^{e'}$. Furthermore, irradiation of $H^{c'}$ resulted in a +23.0% NOE for $H^{d'}$. These results suggest that the conformation of **2b** is that depicted in Scheme I and that neither the 3*H*-indolium nor *p*-nitrophenolate units rotate around the olefinic double bond.

Although it may be difficult to determine all the factors contributing to the coloration of the spiropyrans (i.e., isomerization

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[7] Spiropyran **1e** was prepared from the corresponding deuterated precursor in EtOD according to the procedure described for **1a-d**.

[8] The absorption spectra were measured for 0.2 mM acetonitrile solutions of **2a** and **2b** in the presence or absence of alkali-metal iodides (1.0 mM) after the solutions had been allowed to stand in the dark for 12 h.

to the merocyanines), it is anticipated that recognition of alkali-metal cations in the neighborhood of the spiropyran unit is essential. Indeed, the absorption spectra of **3**[9] and **4**[10] were not at all affected by the alkali-metal iodides, and **5**,[10] the corresponding acyclic analogue of **1a**, showed much less Li^+ selectivity than **1a**. Furthermore, little change in the spectrum of **3** occurred even in the presence of 1 equiv of *N*-acetylmonoaza-18-crown-6 (**6b**) and the alkali-metal iodides.[11] These results substantiate the interpretation previously described.

In conclusion, the present work demonstrates that recognition of lithium cations causes a spiropyran to isomerize to a merocyanine, of which structural details have been obtained for the first time.[12] This result illustrates the concept of a new type of artificial receptor in which guest recognition induces a change in the molecular structure, which in turn causes development of a spectral signal.

Supplementary Material Available: Preparations and physical and spectral data for **1**, **4**, **5**, and **8** (5 pages). Ordering information is given on any current masthead page.

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[10] Spiropyrans **4** and **5** were prepared from the corresponding chloroacetamides by a manner similar to that described for **1**.

[11] On the basis of picrate extractions, it was found that alkali-metal cation complexing abilities of model compounds **6** decreased in the order $Na^+ > Li^+ > K^+$ for **6b** and $K^+ > Li^+ > Na^+$ for **6c**. CPK molecular models showed, however, that the radius of the cavity of spiropyrans **1** was smaller than that of the corresponding model compounds **6**.

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Application of Tetrakis(trifluoroacetato)dirhodium(II) to Determination of Chirality: The First Structural Characterization of an Axial Bisolefin Complex of a Dimetal Core

F. Albert Cotton* and Larry R. Falvello

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University
College Station, Texas 77843

Michael Gerards and Günther Snatzke*

Fakultät für Chemie, Lehrstuhl für Strukturchemie
Ruhr-Universität Bochum, 4630 Bochum, Germany

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It was recognized several years ago[1] that $M_2(O_2CR)_4$ molecules could serve as chromophores capable of manifesting the chirality of organic molecules with donor functionalities as readily observable CD effects in the visible region of the spectrum. For this purpose $Mo_2(O_2CCH_3)_4$ was first employed.[1,2] Other studies have provided a great deal of information about the assignment of the spectrum[3] and the response of the Mo_2^{4+} chromophore to chiral surroundings.[4] Nevertheless, $Mo_2(O_2CCH_3)_4$ and related Mo_2^{4+} species are not entirely satisfactory because of their low acceptor strength in the axial position, so that they form optically active complexes only by ligand-exchange reactions with bidentate ligands such as carboxylic acids, diols, aminoles, and others. The search for a more effective compound then turned to the $Rh_2(O_2CR)_4$ molecules, which are stable, easily prepared and handled,[5] and which also have well-understood electronic spectra.[6]

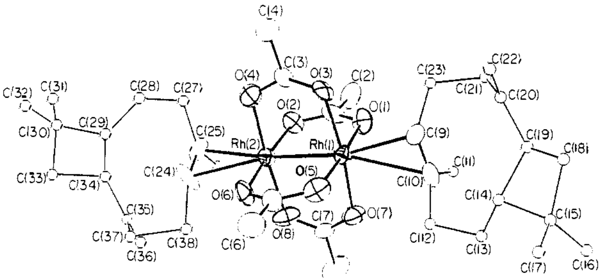

Figure 1. Molecular structure and atom-naming scheme for $Rh_2(CF_3COO)_4((-)$-*trans*-caryophyllene$)_2$, with atoms of the core represented by their 50% probability ellipsoids. Selected distances (in Å) and angles (in degrees): Rh(1)–Rh(2), 2.461 (1); $\langle$Rh–O$\rangle_{av}$, 2.052 [4]; Rh(1)–C(9), 2.46 (1); Rh(1)–C(10), 2.63 (1); Rh(2)–C(24), 2.46 (1); Rh(2)–C(25), 2.62 (1); $\langle$Rh–Rh–O$\rangle_{av}$, 87.2 [3]; Rh(2)–Rh(1)–C(9), 165.2 (3); Rh(2)–Rh(1)–C(10), 163.1 (3); Rh(1)–Rh(2)–C(24), 162.5 (3); Rh(1)–Rh(2)–C(25), 166.4 (3).

Recently it was shown[7] that $Rh_2(O_2CCF_3)_4$ is broadly useful because of its (already well-established[5]) ability to bond many types of axial ligands. From spectral observations it even appeared capable of binding unfunctionalized olefins,[7–9] presumably by direct attachment of C=C bonds at one or both of the axial positions. There has never before been structural evidence for the binding of *any* olefin to *any* $M_2(O_2CR)_4$ species.[10] Moreover, in order to make the most intelligent interpretation of the induced CD effects for $Rh_2(O_2CCF_3)_4$/olefin systems, it is necessary to know the spatial relationship of the olefin molecule or molecules to the $Rh_2(O_2CCF_3)_4$ molecule. For these two reasons we have determined for the first time the structure of a $M_2(O_2CR)_4(\text{olefin})_n$-type compound, namely, $Rh_2(O_2CCF_3)_4((-)$*trans*-caryophyllene$)_2$.

The molecular structure is shown in Figure 1. The compound crystallizes in chiral space group $P2_12_12_1$ (No. 19), and the structure determination proceeded normally.[11] The caryophyllene molecules are bound through the endo double bonds and the binding appears to be strong though unsymmetrical. The Rh–C distances are longer to the more hindered carbon atoms (ca. 2.63 Å). The shorter Rh–C distances (both 2.46 (1) Å) are indicative of genuine bonding. The strength of the axial interaction is evidenced indirectly by the length of the Rh–Rh bond, 2.461 (1) Å, which is one of the longest known among all $Rh_2(O_2CR)_4L_2$ molecules.[12]

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[10] Axial interaction of benzene molecules with the metal dπ orbitals of $Cr_2(O_2CCPh_3)_4$ has previously been reported: Cotton, F. A.; Feng, X.; Kibala, P. A.; Matusz, M. *J. Am. Chem. Soc.* **1988**, *110*, 2807.

[11] (a) Single crystals were obtained from hexane solutions of dirhodium tetraperfluoroacetate and excess of (−)-*trans*-caryophyllene by slow evaporation under argon. $Rh_2F_{12}O_8C_{38}H_{48}$, fw 1066.6, crystallizes in the orthorhombic system, space group $P2_12_12_1$, with $a = 8.652$ (1), $b = 16.523$ (3), $c = 31.240$ (7) Å; $V = 4466$ (1) Å^3; $Z = 4$. The structure was solved by direct methods and refined (full matrix least squares) to residuals of $R = 0.0456$, $R_w = 0.0579$, quality of fit = 1.093, with 3069 observations ($F_o^2 > 3\sigma(F_o^2)$) and 541 variables. The absolute configuration was established at the 99% confidence level[11b] and is in agreement with the previously established configuration of (−)-*trans*-caryophyllene.[11c] (b) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502. Program HamSig by L. M. Daniels. (c) Barton, D. H. R.; Nickon, A. *J. Chem. Soc.* **1954**, 4665. (d) Full details of the crystal structure analysis will be reported elsewhere.

[12] The great majority have Rh–Rh distances between 2.37 and 2.45 Å. Only for $Rh_2(O_2CCF_3)_4L_2$ with L = $P(OPh)_3$ and $P(Ph)_3$ have distances of 2.47 and 2.49 Å been found. Cf. ref. 5a, p 314.

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