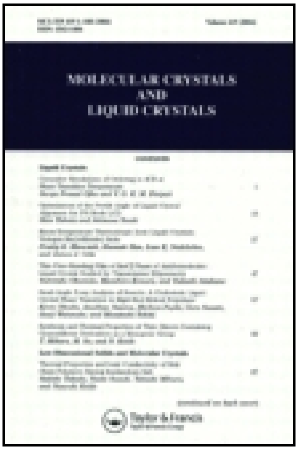

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A New Type of Photochromic Spirodihydroindolizines and Their Ability of Cation Binding

H. Dürr [a] & C. Kranz [a]

[a] Universität des Saarlandes, FB 11.2 Organische Chemie, 66041, Saarbrücken, Germany

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A NEW TYPE OF PHOTOCHROMIC SPIRODIHYDROINDOLIZINES AND THEIR ABILITY OF CATION BINDING

H. DÜRR* AND C. KRANZ
Universität des Saarlandes, FB 11.2 Organische Chemie,
66041 Saarbrücken, Germany

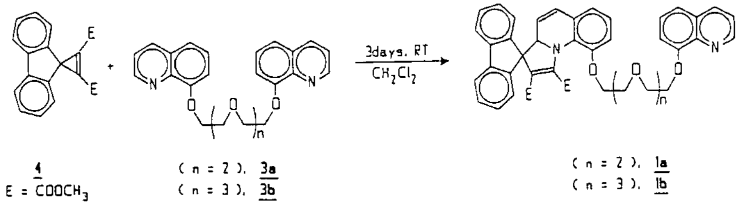
Abstract The photophysical properties of photochromic spirodihydroindolizines (DHI) with podand structures can be tuned by selective cation binding. Complexation of alkaline earth metal ions by the DHI provokes changes in the electronic states of the host molecules, which is evident in changes in the absorption spectra. Thus binding constants could be determined by uv spectroscopy. Two methods have been used to evaluate the titration data:. The double-reciprocal Benesi- Hildebrand plot and the direct fit of the observation equation by nonlinear least-squares analysis.

INTRODUCTION

Photochromism has received great interest in the last years and a recent review gives a good survey on the field[1]. We have used a new approach in our photochromic dihydroindolizines (DHI) to achieve fine tuning of physical properties[2]. Using the concept of podand or coronand structures supramolecular aggregates become possible. In this paper we present a new type of dihydroindolizine, able to selectively bind alkaline earth metal ions. The changes in the uv/visible spectra will be discussed as well as the determination of the binding constants using the uv titration method.

UV-SPECTRA

In order to provide DHI with sides for strong cation binding **1a** and **1b** have been synthesized by addition of the quinolines **3a** and **3b** to the spirocyclopropene **4** (Scheme 1). Their synthesis will be reported elsewhere. Addition of 0.1m solutions of $Ba(SCN)_2 \cdot 2H_2O$ and $SrCl_2 \cdot 6H_2O$ in methanol to 10^{-4}m solutions of **1a** and **1b** causes bathochromic shifts of the absorption maxima from 6 to 18nm (Figure 1), whereas addition of alkaline and alkaline earth metal ions to **3b** show a maximum shift of 2nm[3].



SCHEME 1 Synthesis of DHI **1a** and **1b**.

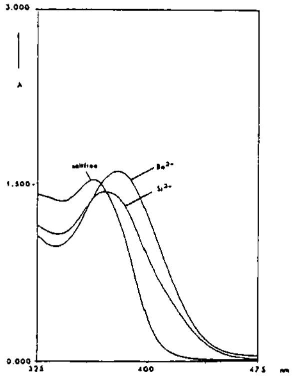


FIGURE 1 Absorption spectra of 10^{-4}m methanolic solution of **1b** saltfree and after addition of 0.1m Sr^{2+} and Ba^{2+}.

The effect of other alkaline and alkaline earth metal ions is rather weak (Figure 2).

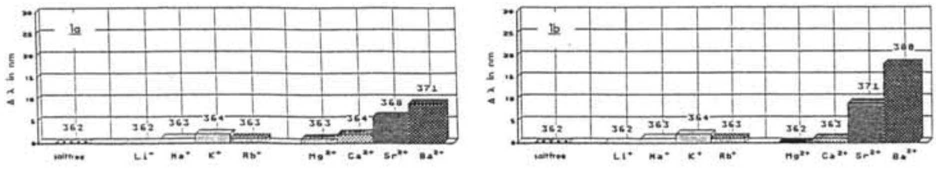


FIGURE 2 Changes in the absorption maxima of **1a** and **1b** by addition of alkaline and alkaline earth metal ions ([Lig] : [M^{n+}] = 1 : 1000).

UV-TITRATION

The shifts in the uv-spectra of **1a** and **1b** by addition of Sr^{2+} and Ba^{2+} can be used to determine the binding constant Ks with Ks = $[DHI\text{-}M^{2+}]/[DHI]\cdot[M^{2+}]$. The concentration ranges of DHI and cation have been chosen based on a preliminary estimate of the binding constant in order to cover a complexation degree of 20-80% during titration. The changes in the absorption spectra of **1b** by addition of Ba^{2+} can be seen in Figure 3. Successive addition of Ba^{2+} leads to a bathochromic shift of 14nm. The difference spectra Ao-A with Ao = absorption spectra of the free ligand and A absorption spectra after addition of different amounts of Ba^{2+} show the effect more clearly (Figure 3).

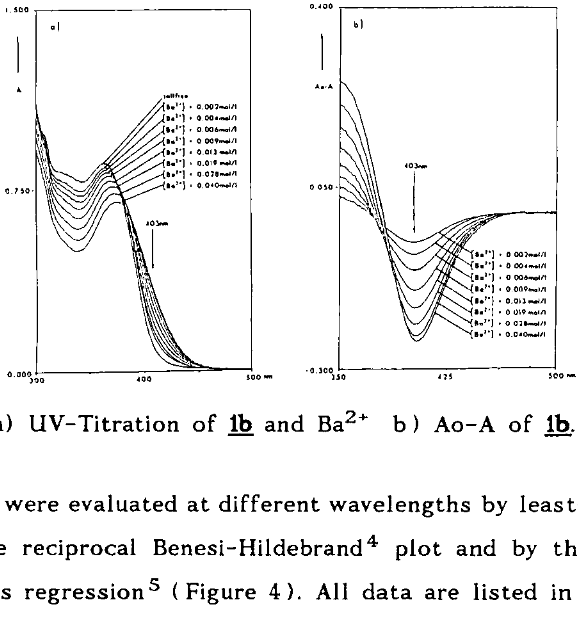


FIGURE 3 a) UV-Titration of **1b** and Ba^{2+} b) Ao-A of **1b**.

The binding constants were evaluated at different wavelengths by least-squares analysis of the double reciprocal Benesi-Hildebrand[4] plot and by the better nonlinear least-squares regression[5] (Figure 4). All data are listed in Table I.

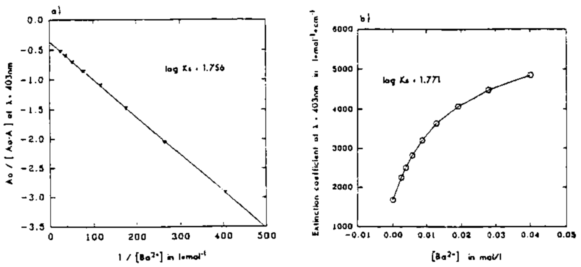


FIGURE 4 a) Linear least-squares analysis and b) Nonlinear least-squares analysis of the uv-titration of **1b** with Ba^{2+}.

TABLE I Log Ks of **1a** and **1b** with Sr^{2+} and Ba^{2+}

		Sr^{2+}	Ba^{2+}
1a	Benesi-Hildebrand	1.00∓0.10	0.90∓0.10
1a	Nonlinear curve fitting	0.78∓0.08	1.00∓0.05
1b	Benesi-Hildebrand	1.57∓0.06	1.75∓0.02
1b	Nonlinear curve fitting	1.51∓0.03	1.77∓0.02

DISCUSSION

The complexation behavior of **1a** and **1b** with Sr^{2+} and Ba^{2+} can be followed by absorption changes in the uv spectra. Evaluation of the titration data by least-squares analysis are in good agreement with evaluation by nonlinear least-squares regression. The complex stabilities of **1b** are 3 to 5 times higher than complex stabilities of **1a** due to the increased number of binding sites of **1b**. Solely **1b** shows selectivity for Ba^{2+}. In comparison with complex stability of **3b** with alkaline and alkaline earth metal ions[3] the stability constants of **1a** and **1b** are rather weak. Reasons could be the reduced flexibility of the podand in the DHI and the loss of one nitrogen atom for binding in the second quinoline unit of **1a** and **1b**.

CONCLUSIONS

It has been shown that metal ions even though complex stability is weak, influence the absorption spectra of **1a** and **1b**.

REFERENCES

1. H. Dürr and H. Bouas-Laurent, *Photochromism. Molecules and Systems*, Elsevier Amsterdam (1990).
2. H. Dürr, A. Thome, C. Kranz, H. Kilburg, S. Bossmann and B. Braun, K.-P. Janzen, E. Blasius, *J. Phys. Org. Chem.*, *5*, 689 (1992).
3. B. Tümmler, G. Maass, E. Weber, W. Wehner, F. Vögtle, *J. Am. Chem. Soc.*, *99*, 4683 (1977).
4. K. A. Connors, *Binding Constants* (Wiley & Sons, New York, 1987).
5. C. S. Wilcox, in *Frontiers in Supramolecular Organic Chemistry and Photochemistry* ,edited by H. J. Schneider and H. Dürr (VCH, Weinheim, 1991), pp. 123-143.