

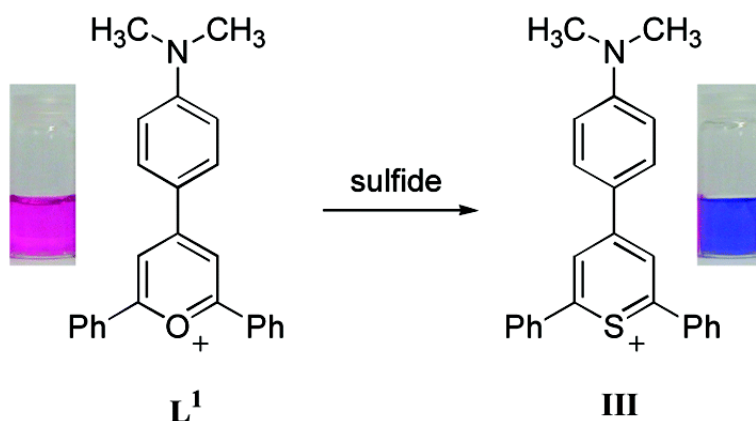
Communication

**A New Chromo-chemodosimeter Selective for Sulfide Anion**

Diego Jimnez, Ramn Martnez-Mez, Flix Sancenn, Jos V. Ros-Lis, A. Benito, and Juan Soto

*J. Am. Chem. Soc.*, **2003**, 125 (30), 9000-9001 • DOI: 10.1021/ja0347336 • Publication Date (Web): 08 July 2003

Downloaded from <http://pubs.acs.org> on March 29, 2009



**More About This Article**

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 8 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



## A New Chromo-chemodosimeter Selective for Sulfide Anion

Diego Jiménez, Ramón Martínez-Mañez,\* Félix Sancenón, José V. Ros-Lis, A. Benito, and Juan Soto

GDDS, Departamento de Química, Universidad Politécnica de Valencia, Camino de Vera s/n, E-46071 Valencia, Spain

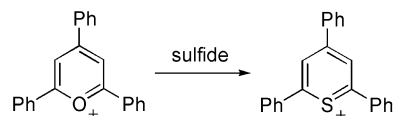
Received February 18, 2003; E-mail: rmaez@qim.upv.es

Sulfide is an inorganic anion used in a large number of applications by humans, for instance, conversion into sulfur and sulfuric acid, dyes and cosmetic manufacturing, production of wood pulp, etc.<sup>1</sup> As a consequence of this, the sulfide anion can be found in water not only due to industrial processes but also due to microbial reduction of sulfate by anaerobic bacteria or formed from the sulfur-containing amino acids in meat proteins. Although the disagreeable “rotten eggs” smell is well known, there are important reasons for developing a means to detect this anion, principally due to its high toxicity in human body. It can irritate mucous membranes and even cause unconsciousness and respiratory paralysis.<sup>1,2</sup> Therefore, the design of new and improved methods for detection and sensing of sulfide anion can be of interest.

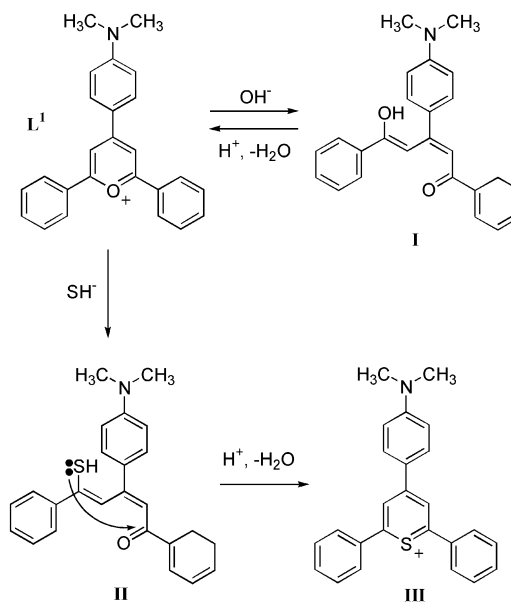
There has been recent attention in the development of a new generation of chromogenic-sensing molecules which have the advantage of showing easily observable color changes in the presence of target guests.<sup>3</sup> In this respect, anion detection by using chromogenic reagents is an area of emerging interest within the field of anion chemistry. There are not too many examples of chromogenic reagents for anion detection, and many of them are reported to work only in organic solvents. In this sense, the search for selective anion-sensing systems effective in aqueous environments is still a challenge.<sup>4</sup> The most common approach to colorimetric sensors is provided by linking a chromophore with a receptor unit by means of a covalent bond.<sup>5</sup> As an alternative to those chemosensors two main approaches have been reported. One is the use of competition assays between a dye bonded to a receptor and a certain anion.<sup>6</sup> When receptor and dye are carefully chosen, selective sensing even in water can be achieved. The other approach is related to the use of new molecular systems that undergo guest-induced chemical reactions coupled to suitable colorimetric events. Those molecules are usually called chemodosimeters or chromogenic reagents.<sup>7</sup> Such specific reactions have advantages such as the high selectivity usually reached and its accumulative effect. As a further advance in the field of chromogenic reagents, in this communication, we report a new design for the colorimetric and selective detection of the sulfide anion.

The design is based on the use of 2,4,6-triphenylpyrylium derivatives<sup>8</sup> and on the well-known reactivity of the pyrylium cycle. Thus, it has been reported that pyrylium salts can be easily transformed into the parent thiopyrylium derivatives as is shown in Scheme 1.<sup>9</sup> Nevertheless, the conversion from pyrylium to thiopyrylium has never attracted attention as a potential colorimetric reaction because most of the triarylpyrylium derivatives are yellow as are also the thiopyrylium analogues. However, we envisioned that a similar reactive motif could be used with the family of 2,4,6-triaryl-pyrylium cations bearing an amine in the para position of the 4-aryl group (see Scheme 2, compound L<sup>1</sup>). In this case, the presence of the pyrylium–aniline backbone results in the appear-

**Scheme 1.** Transformation of Pyrylium to Thiopyrylium



**Scheme 2.** Reactivity of L<sup>1</sup> with Nucleophiles Such as OH<sup>-</sup> and SH<sup>-</sup>



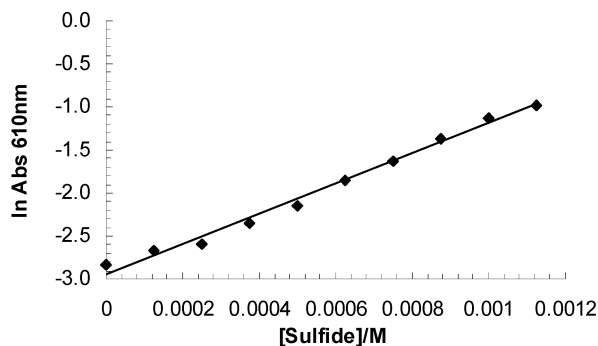
ance of a characteristic charge-transfer band due to the presence of the donor aniline group and the pyrylium acceptor moiety.

In fact, the presence of the amino group causes L<sup>1</sup> to be magenta ( $\lambda_{\text{max}} = 540 \text{ nm}$ ;  $\epsilon$  ca.  $3 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) in contrast to the 2,4,6-triphenylpyrylium cation which shows the lowest-energy absorption band at 405 nm.<sup>10</sup> We considered that by transforming the acceptor group in L<sup>1</sup> from pyrylium to thiopyrylium, the charge-transfer band would also change. This was confirmed by synthesizing<sup>11</sup> the derivative **III** that shows a red shift in the charge-transfer band ( $\lambda_{\text{max}} = 580 \text{ nm}$  for **III**) with respect to that of L<sup>1</sup>. Transformation of L<sup>1</sup> to the parent thiopyrylium **III** compound can take place even in mixtures containing a quite high percentage of water. Therefore, we envisioned that this color change associated with the reaction in Scheme 2 could potentially be applicable to the development of selective chromo-chemodosimeters for sulfide anion detection in aqueous environments.

The pyrylium–thiopyrylium transformation takes place in two steps. It is known that pyrylium ring can undergo nucleophilic addition to the C1 carbon. For instance, OH<sup>-</sup> attack results in the formation of **I**. In a similar manner, reaction with hydrogen sulfide results in the formation of **II**. When acid is added to basic solutions



**Figure 1.** Color changes on solution of  $L^1$  (see text,  $[L^1] = 5 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ) in water:acetonitrile, 1:1 v/v, in the presence of certain anions at pH 9 and further addition of 30  $\mu\text{L}$  of  $\text{H}_2\text{SO}_4$  (30%). From left to right; no anion, fluoride, chloride, bromide, iodide, acetate, benzoate, sulfide, phosphate, sulfate, nitrate, and cyanide.



**Figure 2.** Logarithm of the absorbance at 610 nm versus sulfide concentration in water:acetonitrile, 1:1 v/v, at pH 9 (TRIS 0.01 M).  $[L^1] = 2.5 \times 10^{-5}$  mol  $\text{dm}^{-3}$  after addition of 30  $\mu\text{L}$  of  $\text{H}_2\text{SO}_4$  (30%).

of **I**, cyclization occurs, and  $L^1$  is obtained. In contrast acid addition to **II** results in the formation of the thiopyrylium cation **III**. These processes are depicted in Scheme 2.

In a typical experiment solutions of  $L^1$  ( $[L^1] = 5 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ) in water:acetonitrile (1:1 v/v) buffered at pH 9 (TRIS 0.01 mol  $\text{dm}^{-3}$ ) were mixed with 30 equiv of different anions such as fluoride, chloride, bromide, iodide, acetate, benzoate, sulfide, phosphate, sulfate, nitrate, and cyanide. After 2 min of reaction, 30  $\mu\text{L}$  of  $\text{H}_2\text{SO}_4$  (30%) was added to induce cyclization (see Scheme 2). As it can be seen in Figure 1, only the sulfide anion gave a color change from magenta to blue.

The blue band increased with the concentration of sulfide anion. Figure 2 shows a plot of the logarithm of the absorbance versus sulfide anion concentration following the method described above. Preliminary competitive assays revealed that the anions ATP, oxalate, and sulfate (which previously have been reported to give interactions with the **I**- $L^1$  system) were interfering species in the determination of sulfide following the method outlined above (see Supporting Information). Among other species tested it was found that cyanide also produced ring opening. In a similar manner the presence of primary aliphatic amines transformed the pyrylium ring into a pyridinium one.<sup>12</sup> When present, all those species induced a less effective transformation from magenta to blue in solutions containing the sulfide anion. However, the combination of ring opening and cyclization to give thiopyrylium (blue color) from pyrylium (magenta) was only observed in the presence of sulfide, making the reaction and color change highly specific and suggesting that even in the presence of some interfering species the chromogenic reaction could be used for the qualitative determination of the sulfide anion in water.

In summary, a new colorimetric probe for sulfide anion determination in aqueous environments has been developed. The design concept is based on the use of a pyrylium–thiopyrylium transformation. The molecule  $L^1$  shows a charge-transfer band due to the presence of the aniline–pyrylium backbone that selectively changes in color in the presence of sulfide anion when transformation to aniline–thiopyrylium is achieved. The simplicity of the analysis and low cost of the starting materials suggests that this new method may find application in a variety of different environments where easy and rapid determination of sulfide anion might be required.

**Acknowledgment.** We thank the DGICYT (MAT2000-1387-C02-02 and REN2002-04237-C02-01) for support. J.V.R.L. thanks the Ministerio de Educación, Cultura y Deporte for a Doctoral Fellowship, and F.S.G. thanks the Ministerio de Ciencia y Tecnología for a Doctoral Fellowship.

**Supporting Information Available:** NMR, mass, and visible spectra data for compounds **II** and **III**, competition assays and pH effect on the ability of the sensor (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) *Hydrogen Sulfide*; Geneva, World Health Organization, 1981 (Environmental Health Criteria, No. 19).
- (2) (a) Gosselin, R. E.; Smith, R. P.; Hodge, H. C. *Hydrogen Sulfide*. In *Clinical Toxicology of Commercial Products*, 5th ed.; Williams and Wilkins: Baltimore, MD, 1984; pp III-198–III-202. (b) Patwardhan, S. A.; Abhyankar, S. M. *Toxic and Hazardous Gases. IV. Colourage* **1988**, 35, 15–18.
- (3) (a) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, 40, 486–516. (b) Gale, P. A. *Coord. Chem. Rev.* **2001**, 213, 79–128. (c) Amendola, V.; Fabbrizzi, L.; Mangano, C.; Pallavicini, P.; Poggi, A.; Taglietti, A. *Coord. Chem. Rev.* **2001**, 219–221, 821–837. (d) Wiskur, S. L.; Ait-Haddou, H.; Lavigne, J. J.; Anslyn, E. V. *Acc. Chem. Res.* **2001**, 34, 963–972.
- (4) (a) Amendola, V.; Bastianello, E.; Fabbrizzi, L.; Mangano, C.; Pallavicini, P.; Perotti, A.; Manotti-Lanfredi, A.; Ugozzoli, F. *Angew. Chem., Int. Ed.* **2000**, 39, 2917–2920. (b) Hayashita, T.; Honodera, T.; Kato, R.; Nishizawa, S.; Teramae, N. *Chem. Commun.* **2000**, 755–756. (c) Han, M. S.; Kim, D. H. *Angew. Chem., Int. Ed.* **2002**, 41, 3809–3811.
- (5) (a) Black, C. B.; Andrioletti, B.; Try, A. C.; Ruiperez, C.; Sessler, J. L. *J. Am. Chem. Soc.* **1999**, 121, 10438–10439. (b) Miyajii, H.; Sato, W.; Sessler, J. L. *Angew. Chem., Int. Ed.* **2000**, 39, 1777–1780. (c) Lee, D. H.; Lee, H. Y.; Lee, K. H.; Hong, J.-I. *Chem. Commun.* **2001**, 1188–1189. (d) Piatek, P.; Jurczak, J. *Chem. Commun.* **2002**, 2450–2451.
- (6) (a) Metzger, A.; Anslyn, E. V. *Angew. Chem., Int. Ed.* **1998**, 37, 649–652. (b) Niikura, K.; Metzger, A.; Anslyn, E. V. *J. Am. Chem. Soc.* **1998**, 120, 8533–8534. (c) Lavigne, J. J.; Anslyn, E. V. *Angew. Chem., Int. Ed.* **1999**, 38, 3666–3669. (d) Wiskur, S. L.; Anslyn, E. V. *J. Am. Chem. Soc.* **2001**, 123, 10109–10110. (e) Ait-Haddou, H.; Wiskur, S. L.; Lynch, V. M.; Anslyn, E. V. *J. Am. Chem. Soc.* **2001**, 123, 11296–11297.
- (7) (a) Mohr, G. J. *Chem. Commun.* **2002**, 2646–2647. (b) Dujols, V.; Ford, F.; Czarnik, A. W. *J. Am. Chem. Soc.* **1997**, 119, 7386–7387. (c) Sancenón, F.; Descalzo, A. B.; Martínez-Máñez, R.; Miranda, M. A.; Soto, J. *Angew. Chem., Int. Ed.* **2001**, 40, 2640–2643. (d) Ros-Lis, J. V.; Martínez-Máñez, R.; Soto, J. *Chem. Commun.* **2002**, 2248–2249. (e) Sancenón, F.; Martínez-Máñez, R.; Miranda, M. A.; Seguí, M. J.; Soto, J. *Angew. Chem., Int. Ed.* **2003**, 42, 647–650.
- (8) The synthesis of  $L^1$  is straightforward by reaction of 2,6-diphenylpyrylium perchlorate with *N,N*-dimethylaniline in DMF at 150 °C. Subsequent addition to the reaction crude of diethyl ether afforded the desired compound in 53% yield as a red-magenta solid.
- (9) Staunton, J. *Compr. Org. Chem.* **1979**, 4, 607–627.
- (10) Miranda, M. A.; García, H. *Chem. Rev.* **1994**, 94, 1063–1089.
- (11) Compound **III** was prepared by following the experimental procedure described in *J. Org. Chem.* **2002**, 67, 2065–2074.
- (12) In fact under certain circumstances  $L^1$  might be used as chromogenic reagent for the determination of moderate amounts of cyanide and primary aliphatic amines (the color change from magenta to yellow is observed in the presence of ca. 100 equiv) in water:acetonitrile mixtures.

JA0347336