

# Photochemistry of *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminocyclohexane and its Co(II) complex in chloroform

Horst Kunkely, Arnd Vogler\*

Institut für Anorganische Chemie, Universität Regensburg, D-93040 Regensburg, Germany

Received 29 September 2000; accepted 3 October 2000

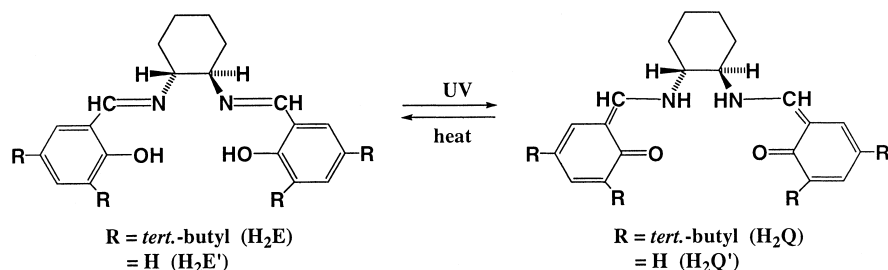
## Abstract

*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminocyclohexane ( $H_2E$ ) is photochromic. In  $CHCl_3$  it undergoes a phototautomerization ( $\phi = 3 \times 10^{-4}$  at  $\lambda_{irr} = 333$  nm) to its keto isomer  $H_2Q$  which is thermally reconverted to the original enol form. The enol is not luminescent but the keto isomer shows a green fluorescence at  $\lambda_{max} = 506$  nm with  $\phi = 10^{-2}$  at  $\lambda_{exc} = 410$  nm. Accordingly, the photoreversible system does not only display a conventional photochromism but also a luminescence photochromism. The complex  $Co^{II}(E)$  in  $CHCl_3$  is also light sensitive. It is irreversibly photooxidized to  $Co(E)^+$  with  $\phi = 5 \times 10^{-3}$  at  $\lambda_{irr} = 436$  nm. The electron is not removed from the metal but from the ligand. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Photochromism; Luminescence photochromism; Photooxidation; Salen-type Schiff base; Cobalt(II)

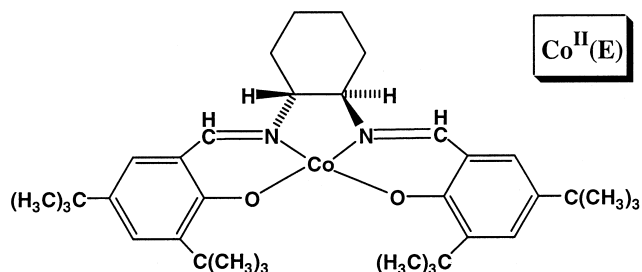
## 1. Introduction

Photochromism has recently attracted much interest owing to potential applications in photonic devices [1,2]. *N*-salicylideneanilines constitute an important family of photochromic compounds [1,3,4]. This photochromism has been also observed for the derivative *N,N'*-bis(salicylidene)-1,2-diaminocyclohexane  $H_2E'$  [5].



The photoconversion of the phenol (or enol) form  $H_2E'$  to the quinoid (or keto) isomer  $H_2Q'$  proceeds as a tautomerization which involves a proton shift from oxygen to nitrogen. This photoisomerization is associated with a colour change of the chloroform solution from colourless to yellow. The deprotonated forms of such compounds including  $[E]^{2-}$  and  $[E']^{2-}$  are important ligands in coordination chemistry [6,7].  $Co(II)$

complexes of these ligands have been used as oxygen carriers [8] and catalysts in organic chemistry [9]. While their electronic absorption spectra have been studied in some detail [6,10–12] other optical properties are largely unknown. Some related  $Ni(II)$  complexes have been recently shown to display non-linear optical properties [13]. In the present work we explored the photoreactivity of  $Co^{II}(E)$  [14].



\* Corresponding author. Fax: +49-941-943-4488.  
E-mail address: arnd.vogler@chemie.uni-regensburg.de (A. Vogler).

For comparison we examined also the photochemistry of  $H_2E$  which was expected to be similar to that of  $H_2E'$  [5]. Nevertheless, electronic and steric influences by  $R = tert\text{-butyl}$  might modify the photochemical behaviour.

## 2. Experimental

### 2.1. Materials

All solvents used were of spectrograde quality, dried and saturated with argon.  $N,N'$ -bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminocyclohexane and  $N,N'$ -bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminocyclohexanecobalt(II) were commercially available from Aldrich and used as received.

### 2.2. Instrumentation

Absorption spectra were measured with a Hewlett Packard 8452A diode array or an Uvikon 860 absorption spectrometer. The light source used was an Osram HBO 200 W/2 or a Hanovia Xe/Hg 977 B-1 (1 kW) lamp. Additional cutoff filters Schott WG 305 and WG 345 were applied to avoid short-wavelength photolysis of chloroform. Monochromatic light was obtained using Schott PIL/IL interference filters or a Schoeffel GM 250/1 high-intensity monochromator. In all cases the light beam was focused on a thermostated photolysis cell by a quartz lens. Emission spectra were obtained on a Hitachi 850 spectrofluorimeter equipped with a Hamamatsu 928 photomultiplier for measurements up to 900 nm. The luminescence spectra were corrected for monochromator and photomultiplier efficiency variations. Absolute emission quantum yields were determined by comparison of the integrated emission intensity with that of Rhodamine B [15] under identical conditions such as exciting wavelength, optical density, and apparatus parameters.

### 2.3. Photolyses

The photolyses were carried out in solutions of  $CHCl_3$  in 1 cm spectrophotometer cells at room temperature. Progress of the photolyses was monitored by UV–Visible spectrophotometry. For quantum yield determinations the complex concentrations were such as to have essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproduct. Absorbed light intensities were determined by a Polytec pyroelectric radiometer which was calibrated by actinometry and equipped with a RkP-345 detector.

## 3. Results

The electronic spectrum of  $H_2E$  in  $CHCl_3$  (Fig. 1) shows absorptions at  $\lambda_{max} = 429$  sh ( $\epsilon = 130 \text{ dm}^3 \text{ M}^{-1} \text{ cm}^{-1}$ ), 332 (9800), 270 sh (19900) and 263 (23100) nm.  $H_2E$  in  $CHCl_3$

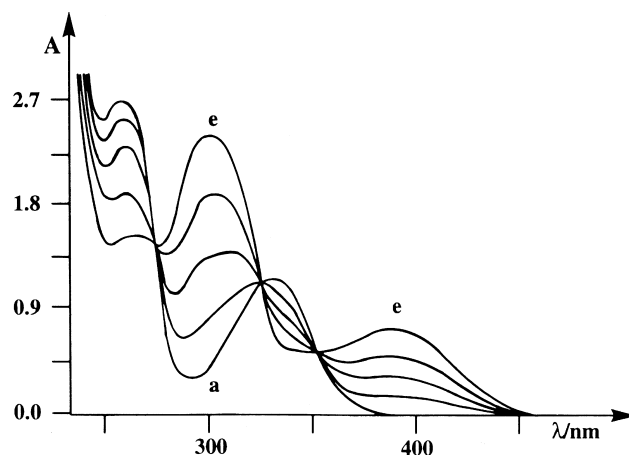


Fig. 1. Spectral changes during the photolysis of  $7.29 \times 10^{-5} \text{ M}$   $N,N'$ -bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminocyclohexane in  $CHCl_3$  at room temperature at 0 (a), 10 (b), 20 (c), 40 (d) and 80 (e) min irradiation times with  $\lambda_{irr} > 290$  nm (HBO 200 W/2 lamp), 1-cm cell.

is not luminescent but light sensitive. Upon irradiation with  $\lambda > 290$  nm the colourless solution turns yellow. As indicated by the concomitant spectral changes (Fig. 1) the yellow colouration is caused by a new absorption at  $\lambda_{max} = 389$  nm. This wavelength is used to monitor the photolysis by measuring the increase of absorption. The photoproduct is formed with  $\phi = 3 \times 10^{-4}$  at  $\lambda_{irr} = 333$  nm. The photoproduct displays a green RT luminescence at 506 nm (Fig. 2) with an emission quantum yield of  $\phi = 10^{-2}$  at  $\lambda_{exc} = 410$  nm. This luminescence is hardly affected by oxygen. Upon standing in the dark  $H_2E$  is slowly regenerated. The spectral variations of the photolysis (Fig. 1) are simply reversed.

The electronic spectrum of Co(E) in  $CHCl_3$  (Fig. 3) shows absorptions at  $\lambda_{max} = 574$  sh (1300), 492 sh (3540), 434

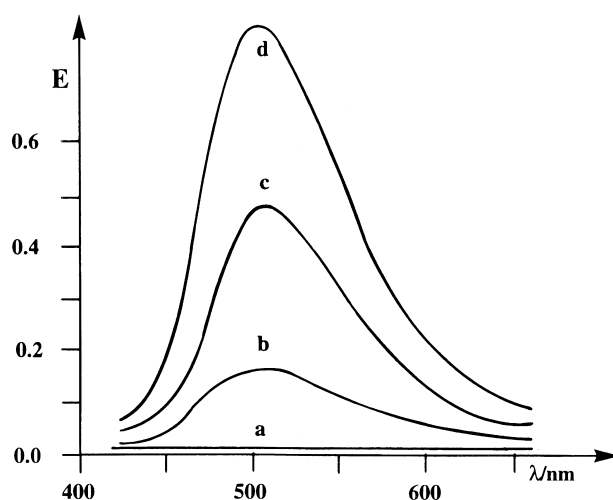


Fig. 2. Changes of the emission spectrum during the photolysis of  $7.29 \times 10^{-5} \text{ M}$   $N,N'$ -bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminocyclohexane in  $CHCl_3$  at room temperature with  $\lambda_{irr} = 333$  nm (Xe/Hg 977 B-1 lamp) at 0 (a), 3 (b), 10 (c) and 20 (d) min irradiation times, 1-cm cell, emission excitation at  $\lambda_{exc} = 410$  nm, intensity in arbitrary units.

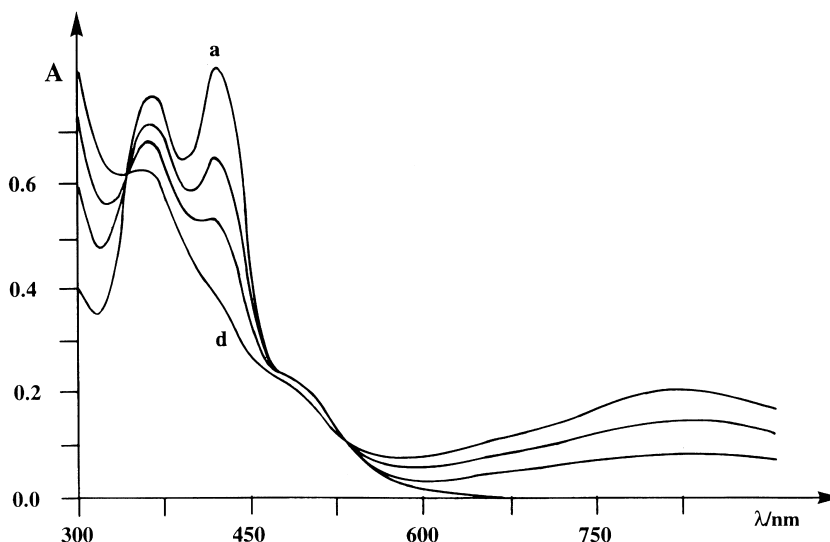


Fig. 3. Spectral changes during the photolysis of  $6.13 \times 10^{-5}$  M *N,N*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminocyclohexanecobalt(II) in  $\text{CHCl}_3$  at room temperature at 0 (a), 2 (b), 4 (c) and 8 (d) min irradiation times with  $\lambda_{\text{irr}} > 320$  nm (HBO 200 W/2 lamp), 1-cm cell.

sh (12400), 420 (13700), 374 (12000), 363 (12300), 308 sh (6900), 270 sh (33100) and 251 (42500) nm. Co(E) in  $\text{CHCl}_3$  is not luminescent but light sensitive. Upon irradiation with  $\lambda > 320$  nm the orange solution turns green. The concomitant spectral changes (Fig. 3) are dominated by a new long-wavelength band at  $\lambda_{\text{max}}=820$  nm ( $\epsilon \sim 3000$ ). The photoproduct is persistent in  $\text{CHCl}_3$  for about 2 h as indicated by the invariance of the absorption spectrum. The photolysis is monitored by measuring the increase of the absorption at  $\lambda_{\text{max}}=820$  nm. The photoproduct is formed with  $\phi = 5 \times 10^{-3}$  at  $\lambda_{\text{irr}} = 436$  nm. The spectral variations which accompany the photolysis are duplicated when solutions of Co(E) in  $\text{CHCl}_3$  are treated with  $\text{AgBF}_4$ . In this case Co(E) is oxidized by  $\text{Ag}^+$  to  $\text{Co(E)}^+$  [14]. Upon addition of  $\text{Na}_2\text{S}_2\text{O}_4$  as reductant the oxidation of Co(E) to  $\text{Co(E)}^+$  can be reversed. The original spectrum, of Co(E) is partially regenerated.

#### 4. Discussion

The free ligand  $\text{H}_2\text{E}$  dissolved in  $\text{CHCl}_3$  undergoes a photochemical enol  $\rightarrow$  keto tautomerization to  $\text{H}_2\text{Q}$  in analogy to  $\text{H}_2\text{E}'$  [5]. This conclusion is based on the observation that the spectral changes which accompany the photolysis are very similar in both cases. This assumption is also in accord with the general behaviour of *N*-salicylideneanilines which are photoconverted from colourless or pale yellow enol forms to deep yellow or orange keto tautomers.  $\text{H}_2\text{E}$  as well as  $\text{H}_2\text{E}'$  [5] and other *N*-salicylideneanilines [1–4] are photochromic since they are thermally regenerated from their phototautomers, e.g.  $\text{H}_2\text{Q}$  and  $\text{H}_2\text{Q}'$ . While  $\text{H}_2\text{E}$  is photoreactive and not luminescent,  $\text{H}_2\text{Q}$  displays a distinct green fluorescence. Accordingly,  $\text{H}_2\text{E}$  does not only show an ordinary photochromism due to a colour change, but also a

“luminescence photochromism” which is present when both forms of a photoreversible system have different luminescence colours. This expression is derived from the definition of luminescence thermochromism [16–18]. Luminescence photochromism has been previously termed photochromic fluorescence [19].

While Co(E) is not light sensitive in most solvents it is irreversibly photooxidized to  $\text{Co(E)}^+$  in  $\text{CHCl}_3$ . Generally, neutral Co(II) complexes of bidentate or quadridentate Schiff base ligands with *N*-salicylidene moieties are oxidized to the cationic Co(III) complexes provided the solvent is protic or coordinating [9,14,20]. In non-coordinating solvents these Co(II) and the corresponding Ni(II) complexes undergo an oxidation of the Schiff base ligand to a radical while the metal preserves its oxidation state [14]. Usually, this oxidation is followed by a C–C coupling of the ligand radicals leading to polymeric Co(II) and Ni(II) complexes. However, if bulky substituents such as the *tert*-butyl group of  $\text{E}^{2-}$  prevent this coupling the ligand radical complexes are persistent in solution at least for some time. The intense absorption of  $\text{Co(E)}^+$  at  $\lambda_{\text{max}}=820$  nm is a strong indication for the presence of  $\text{Co}^{\text{II}}(\text{E}^{\bullet})^+$  which can be generated thermally by oxidation of Co(E) with  $\text{AgBF}_4$  [14] or by photooxidation in  $\text{CHCl}_3$ . Co(III) complexes with Schiff base ligands including  $\text{Co}^{\text{III}}(\text{E}')\text{X}$  do not show an intense band near 800 nm [6,20].

The absorption spectrum of Co(II) complexes with *N*-salicylidene Schiff base ligands shows ligand field (LF) bands of rather low intensities ( $\epsilon \sim 100$ ) in the near IR spectral region [6,10–12,21]. Bands of much higher intensities which appear below 600 nm (Fig. 3) are certainly of the intraligand (IL)  $\pi\pi^*$  (<400 nm) [13] and CT type. Since Co(II) is reducing metal-to-ligand charge transfer (MLCT) transitions should exist at relatively low energies.

In most solvents Co(E) is not light sensitive. Higher excited states are apparently deactivated to non-reactive LF states. Photosubstitutions which would be indicative of reactive LF states are certainly prevented by the quadridentate ligand  $E^{2-}$ . The photooxidation of E in Co(E) must then start from IL or MLCT states at higher energies. In analogy to the photochemical ligand oxidation of various 1,2-dithiolene complexes in halocarbon solvents [22] it is suggested that the photooxidation of Co(E) in  $CHCl_3$  is induced by charge-transfer-to-solvent (CTTS) excitation. Such reactive CTTS states can apparently be populated by a facile internal conversion from higher intramolecular excited states.

### Acknowledgements

Support of this research by the Fonds der Chemischen Industrie is gratefully acknowledged.

### References

- [1] H. Dürr, H. Bouas-Laurent (Eds.), *Photochromism: Molecules and Systems*. Studies in Organic Chemistry, Vol. 40, Elsevier, Amsterdam, 1990.
- [2] M. Irie (Ed.), *Photochromism: Memories and Switches*, A Special Thematic Issue of Chemical Reviews, Vol. 100, No. 5, 2000, pp. 1685–1890.
- [3] E. Hadjoudis, M. Vittorakis, I. Moustakali-Mavidis, *Tetrahedron* 43 (1987) 1345.
- [4] E. Hadjoudis, *Mol. Eng.* 5 (1995) 301.
- [5] J. Zjao, B. Zhao, J. Liu, A. Ren, J. Feng, *Chem. Lett.* (2000) 385.
- [6] S. Yamada, *Coord. Chem. Rev.* 1 (1966) 415.
- [7] M. Calligaris, G. Nardin, L. Randaccio, *Coord. Chem. Rev.* 7 (1972) 385.
- [8] E.C. Niederhoffer, J.H. Timmons, A.E. Martell, *Chem. Rev.* 84 (1984) 137.
- [9] A. Nishikawa, H. Yamato, T. Abe, K. Maruyama, T. Matsuura, *Tetrahedron Lett.* 29 (1988) 6309 and references cited therein.
- [10] A. Nishikawa, S. Yamada, *Bull. Chem. Soc. Jpn.* 37 (1964) 8.
- [11] L. Sacconi, M. Ciampolini, G.P. Speroni, *J. Am. Chem. Soc.* 87 (1965) 3102.
- [12] M.A. Hitchman, *Inorg. Chem.* 16 (1977) 1985.
- [13] S.D. Di Bella, I. Fragala, I. Ledoux, M.A. Diaz-Garcia, T.J. Marks, *J. Am. Chem. Soc.* 119 (1997) 9550.
- [14] W.-H. Leung, E.Y.Y. Chan, E.K.F. Chow, I.D. Williams, S.-M. Peng, *J. Chem. Soc., Dalton Trans.* (1996) 1229.
- [15] J.N. Demas, G.A. Crosby, *J. Phys. Chem.* 75 (1971) 991.
- [16] H.D. Hardt, H.-J. Stoll, *Z. Anorg. Allg. Chem.* 480 (1981) 193/199, and references cited therein.
- [17] P.C. Ford, A. Vogler, *Acc. Chem. Res.* 26 (1993) 220.
- [18] P.C. Ford, E. Cariati, J. Bourassa, *Chem. Rev.* 99 (1999) 3625.
- [19] K. Kownacki, A. Mordzinski, R. Wilbrandt, A. Grabowska, *Chem. Phys. Lett.* 227 (1994) 270.
- [20] A. Nishinaga, T. Kondo, T. Matsuura, *Chem. Lett.* (1985) 905.
- [21] C. Daul, C.W. Schäpfer, A. von Zelewsky, *Struct. Bonding* 36 (1979) 129.
- [22] A. Vogler, H. Kunkely, *Inorg. Chem.* 21 (1982) 1172 and references cited therein.