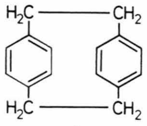
Photoluminescence of $[2_2]$Paracyclophane and *p*-Xylene in the Presence of Silver Ions

M. Zander
Laboratory of Rütgerswerke AG, Castrop-Rauxel

Z. Naturforsch. **39a**, 1009–1010 (1984);
received August 18, 1984

Phosphorescence spectra and phosphorescence lifetimes of $[2_2]$paracyclophane (**I**) and *p*-xylene have been measured in ethanol glass at 77 K in the presence of silver perchlorate at various concentrations. From the results it is concluded that the ground state complex formed with $AgClO_4$ is much more stable in the case of the cyclophane than with *p*-xylene. The results would indicate that under the conditions used $[2_2]$paracyclophane forms a 1:1 complex with $AgClO_4$ with the silver ion being located within the cyclophane cage. Fluorescence quenching measurements in fluid solution at room temperature using ethyl bromide and $AgClO_4$ as quenchers support this assumption.

The photoluminescence properties of many organic compounds with electron donor activity are significantly changed in the presence of silver ions (electron acceptor). Although complexation between *electronically excited* donor molecules and silver ions resulting in exciplex fluorescence has been reported [1], in most cases *ground state complexation* occurs. In rigid glasses at 77 K this results in changes of the vibronic structure of the donor phosphorescence spectrum [2, 3] and a decrease in phosphorescence lifetime by two to three orders of magnitude [2–4]. Since the phosphorescence lifetime of the uncomplexed donor molecules stays practically unchanged in the presence of silver ions, the bi-exponential phosphorescence decay curve contains the time constants of the unperturbed and the complexed donor molecules only. Therefore the silver ion concentration at which the phosphorescence time constant of the unperturbed donor molecules disappears can be taken as a rough relative measure for the strength of the donor/silver ion complex [3]. The present paper deals with the effect of silver ions on the photoluminescence of $[2_2]$paracyclophane (**I**) and *p*-xylene.



I

The phosphorescence of $5 \cdot 10^{-4}$ M ($[2_2]$paracyclophane) and $1 \cdot 10^{-3}$ M solutions (*p*-xylene), respectively, in ethanol at 77 K in the presence of $AgClO_4$ has been studied. The results obtained proved independent of the excitation wavelength.

While the phosphorescence lifetime of the uncomplexed $[2_2]$paracyclophane is 4.5 s at 77 K (for measurements at 1.3 K see [5]) it is 3.5 ms for the silver ion complexed molecule. At silver ion concentrations < 0.01 g atom $\cdot$ l^{-1} both time constants are observed in the phosphorescence decay curve. The phosphorescence lifetime of the unperturbed cyclophane is no longer observed at a silver ion concentration of approx. 0.01 g atom $\cdot$ l^{-1}, i.e. complexation is complete at this concentration. The corresponding figures for *p*-xylene are 8.8 s (phosphorescence lifetime of the unperturbed molecule), 3.2 ms (phosphorescence lifetime of the complexed xylene) and 1 g atom $\cdot$ l^{-1} (silver ion concentration necessary for complete complexation).

From the observation that the silver ion concentration necessary for complete complexation is lower by two orders of magnitude in the case of $[2_2]$paracyclophane compared to *p*-xylene it follows that the silver ion complex of the cyclophane is much stronger than that of *p*-xylene. This result cannot be explained by the different first ionization potentials of the compounds, these being 8.10 eV for $[2_2]$paracyclophane [6] and 8.44 eV for *p*-xylene [7], respectively. We found that the silver ion concentration necessary to eliminate the phosphorescence lifetime of the unperturbed molecules (10^{-3} M) is in the range from 0.75 to 1 g atom $\cdot$ l^{-1} for benzene, toluene, durene and hexamethylbenzene having first ionization potentials between 9.3 and 7.9 eV [7].

A possible explanation for the different stability of the silver ion complexes with xylene or the paracyclophane is that in the latter the silver ion is located within the cage of the cyclophane formed by the two parallel benzene units. Although this proposal cannot be proven on the basis of experimental data so far available, it is supported by the following findings: (i) *p*-xylene forms a 1:2 complex with $AgClO_4$($AgClO_4 \cdot 2\,C_8H_{10}$) which can be isolated [8]. (ii) The inter-ring separation in $[2_2]$paracyclophane is approx. 3 Å [9], while the ion radius of silver is 1.13 Å. (iii) A metal-organic compound

---

Reprint requests to Professor Dr. M. Zander, Rütgerswerke AG, D-4620 Castrop-Rauxel, FRG.

0340-4811 / 84 / 1000-1009 $ 01.30/0. – Please order a reprint rather than making your own copy.

of $[2_2]$paracyclophane (η^{12}-$[2_2]$paracyclophane-chromium(0)) is known [10] where the chromium(0) is located within the cage of the cyclophane molecule.

By silver complexation the phosphorescence spectrum of *p*-xylene looses its vibronic structure and the centre of gravity of the spectrum is shifted to longer wavelengths by approx. 1200 cm^{-1}, and a similar shift is found for e.g. toluene. On the other hand, the unstructured broad phosphorescence band of $[2_2]$paracyclophane is shifted by silver complexation by approx. 390 cm^{-1} to longer wavelengths. In the latter case the long wavelength shift due to silver complexation is possibly partly compensated by removing the trans-annullar interaction between the π-electron systems which is assumed on the basis of quantum mechanical calculations [11] for both the ground state and the excited states. Cancellation of the trans-annullar interaction again may be more effective if the silver ion stays inside the cyclophane cage.

We have also studied fluorescence quenching of $[2_2]$paracyclophane and *p*-xylene in fluid solution (ethanol) at room temperature using ethyl bromide and $AgClO_4$ as fluorescence quenchers. From Stern-Volmer plots (fluorescence intensity measurements) it follows that the ratio of the bimolecular rate constant $k_q^{AgClO_4}$ of fluorescence quenching by $AgClO_4$ to the rate constant $k_q^{C_2H_5Br}$ amounts to approx. 8 for *p*-xylene and approx. 29 for $[2_2]$paracyclophane. On the other hand, identical half-value concentrations of fluorescence quenching by ethyl bromide (0.2 M) were obtained for the cyclophane and *p*-xylene. These results again are in accordance with the assumption that silver ion complexation is stronger in the case of $[2_2]$paracyclophane compared to *p*-xylene and, on the other hand, the mechanism of external spin-orbit coupling perturbation is similar in both molecules.

Experimental

$[2_2]$paracyclophane was a highly purified sample kindly provided by Professor H. Hopf, Department of Organic Chemistry of the Technical University of Braunschweig. UV- and luminescence spectra of all compounds studied were identical to those reported in the literature.

Fluorescence- and phosphorescence measurements were done on an Aminco-Keirs spectrophosphorimeter and a Perkin-Elmer PE 44 E spectrofluorimeter using an oscillograph Tektronix 5403 for the phosphorescence lifetime measurements.

I wish to thank Professor H. Hopf, Braunschweig, for kindly providing me with a sample of $[2_2]$paracyclophane and Mr. K. Bullik for valuable experimental assistance.

[1] H. Dreeskamp, A. Läufer, and M. Zander, Z. Naturforsch. **38a**, 698 (1983).

[2] G. D. Boutilier and J. D. Winefordner, Anal. Chem. **51**, 1391 (1979).

[3] M. Zander, Z. Naturforsch. **37a**, 1348 (1982).

[4] M. Zander, Z. Naturforsch. **33a**, 998 (1978).

[5] G. Melzer, D. Schweitzer, K. H. Hauser, J. P. Colpa, and M. W. Haenel, Chem. Phys. **39**, 229 (1979).

[6] B. Kovac, M. Allan, E. Heilbronner, and J. P. Maier, J. Electr. Spectr. **19**, 167 (1980).

[7] Taken from: J. B. Birks, Photophysics of Aromatic Molecules, Wiley-Intersci., New York 1970.

[8] P. Avimur and J. Eliezer, Anal. Chem. **42**, 1317 (1970).

[9] K. Lonsdale, H. J. Milledge, and K. V. K. Rao, Proc. Roy. Soc. London **A 255**, 82 (1960).

[10] C. Elschenbroich, R. Möckel, and U. Zenneck, Angew. Chem. Int. Ed. **17**, 531 (1978).

[11] J. H. Hillier, L. Glass, and S. A. Rice, J. Chem. Phys. **45**, 3015 (1966).

Verantwortlich für den Inhalt: A. KLEMM
Satz und Druck: Konrad Triltsch, Würzburg