Electronic Structure of a 1:2 Complex of Triphenyl-Pararosaniline and a Gallate Derivative

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Abstract

Triphenyl-pararosaniline (TPPR: Fig. 1) and a gallate derivative (PG: Fig. 2) are charge-control agents (CCA) of the positive and negative type, respectively. Furthermore, a 1:2 complex of TPPR and PG (colored deep blue) has been reported to be a powerful CCA due to the formation of a charge-transfer (CT) complex. The electronic structure of the present complex has been investigated in solution and in the solid state in order to clarify the charge-transfer mechanism. Quite contrary to our expectation, the blue color is found to arise from protonation of TPPR by means of PG, not due to a CT transition between TPPR and PG.

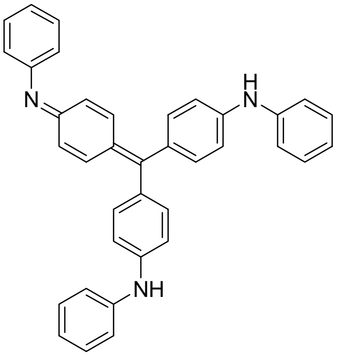


Figure 1. Triphenyl-pararosaniline (TPPR).

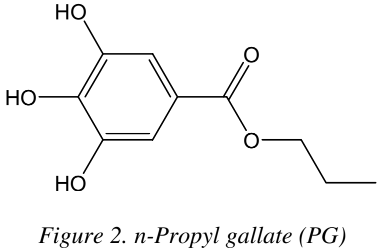


Figure 2. n-Propyl gallate (PG)

1. Introduction

Triphenyl-pararosaniline (TPPR: Fig. 1) is a leuco dye based on the triphenylmethane skeleton. TPPR is colored light brown in solution in MEK(methylethylketone) as well as in the solid state. However, the color changes drastically into deep blue in the presence of acidic compounds. On the other hand, *n*-propyl gallate (PG: Fig. 2) is an acid which has three hydroxides of the phenol type. Both TPPR and PG are also known as charge-control agents (CCA: used for toners) of the positive and negative type, respectively. Furthermore, the charge-control ability is greatly improved when a 1:2 charge-transfer (CT) complex (colored deep blue) is formed between TPPR and PG.[1] For this reason, an attempt has been made in the present investigation to clarify the electronic structure of the CT complex in order to clarify the charge-control mechanism.

2. Experimental

2-1. Sample Preparation

TPPR and PG were obtained from Morimura Chemical and Kanto Kagaku, respectively. An ethanol solution containing a 1:2 complex of TPPR and PG was prepared for measurements of solution spectra. On the other hand, a thin solid film was also prepared by spin coating technique, using a MEK solution of the 1:2 complex. The thickness is about 1000 Å.

2-2. Measurements

Absorption spectra in solution and in the solid state were measured on a UV-2400PC spectrophotometer (Shimadzu).

2-3. Molecular orbital (MO) Calculations

Geometry optimization was carried out by means of the AM1 Hamiltonian of MOPAC program package.[2] The INDO/S program used for spectroscopic calculations is part of the ZINDO program package.[3] Geometry optimization and subsequent spectroscopic calculations were made for the initial state of TPPR as well as mono-, di- and tri-protonated states.

1. Results and Discussion

3-1. Solution Spectra

Figure 3 shows the solution spectra in ethanol for TPPR and TPPR/PG (1:2). Surprising to say, the absorption maxima of both spectra occur exactly at the same wavelength (about 600 nm) and the color is deep blue. As stated in Introduction, TPPR is light brown both in MEK (abs. maximum: around 460 nm as shown later in Fig. 5) and in the solid state. Judging from the above results, we assumed that PG (an acid) turns TPPR vivid blue due to protonation while TPPR is also protonated due to ethanol which is slightly acidic. That is, TPPR is highly sensitive to protons. We further supposed that protonation takes place at the double bonded N atom which is the electron-richest part in the solid state (Fig. 1).

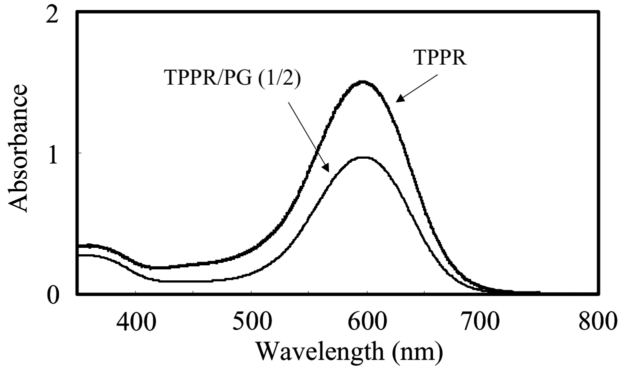


Figure 3. Absorption spectra in an ethanol solution.

3-2. Absorption Spectra in the Solid State

Figure 4 shows the absorption spectrum of spin-coated TPPR/PG and the diffuse reflectance spectrum measured on powders. The absorption maximum appears in both spectra around 603 nm which is slightly displaced toward longer wavelengths as compared with those of solution spectra (Fig. 3). The present bathochromic displacement can be interpreted in terms of di-protonation as shown by the following experiments.

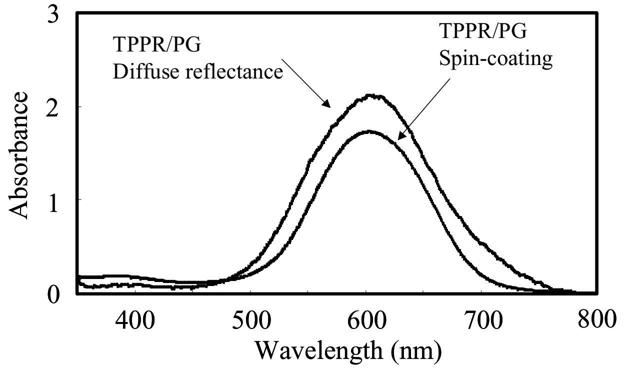


Figure 4. Absorption spectrum of TPPR/PG in the solid state.

3-3. Spectral Changes of TPPR Due to Protonation

Figure 5 shows the solution spectra of TPPR, mono-protonated and di-protonated TPPR with HCl. A broad absorption maximum appears in TPPR around 460 nm. Mono-protonation (TPPR/HCl=1/1) displaces the absorption band to about 600 nm. Di-protonation (TPPR/HCl=1/2) induces a further bathochoromic shift by about 10 nm. Addition of excess HCl brings about no further change in spectral shift.

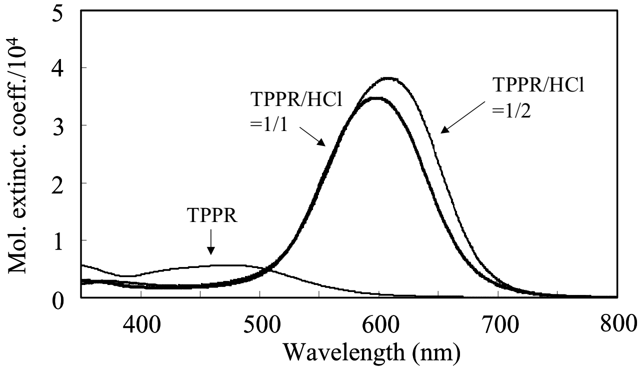


Figure 5. Solution spectrum of TPPR in MEK and its spectral change due to the addition of hydrochloric acid.

3-4. Color Generation Mechanism Due to Protonation

In order to generate a color in chemical compounds, there must exist an electron-conjugated system called "chromophore" together with "auxochromes" (*i,e.* electron donor and acceptor). That is, the chromophore should be sandwiched between electron donor and acceptor groups in order to construct a "push-pull" system. In the TPPR molecule shown in Fig. 1, we can definitely recognize an electron-conjugation system (*i.e.* bond alternation) as well as two electron donating groups based on the >NH group. However, an electron acceptor part is missing in TPPR. For this reason, TPPR is incapable of inducing an intense optical absorption in the visible region. However, protonation at the double-bonded N atom (-N=: the electron-richest part) creates newly an electron acceptor part (*i.e.* $\text{-N}^{+}\text{H=}$) and facilitates the electron transfer from the donor to the acceptor part as shown in Fig. 6. That is, the protonation forms an effective push-pull system, so that the electron can be transferred from the donor part (NH group) via an electron-conjugated system to the acceptor part (NH^{+} group) and *vice versa.* A deep blue color appears in this way. Further protonation occurs also at the NH site to displace the absorption maximum still toward longer wavelengths, as supported by MO calculations shown below.

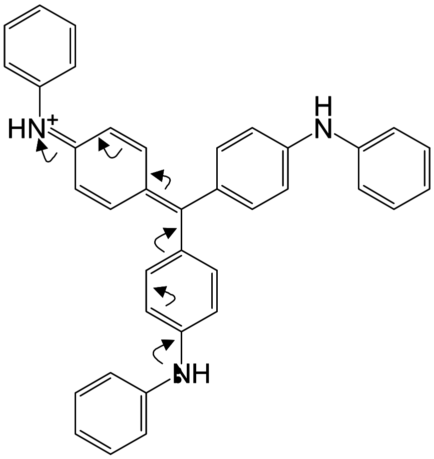


Figure 6. Protonation at the double-bonded N atom which is the electron-richest part.

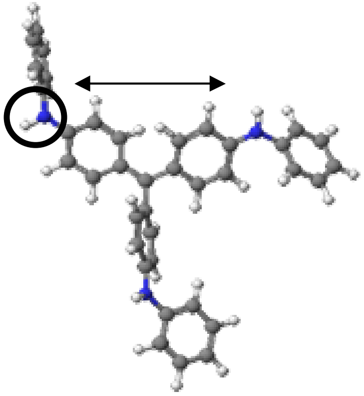
3-5. MO Calculations for the Initial, Mono-Protonated, Di-Protonated and Tri-Protonated States

Table 1 details the heat of formation and absorption maxima calculated for the initial (Fig. 1), mono-protonated (Fig. 7(a)), di-protonated (Fig. 7(b)) and tri-protonated (Fig. 7(c)) states.

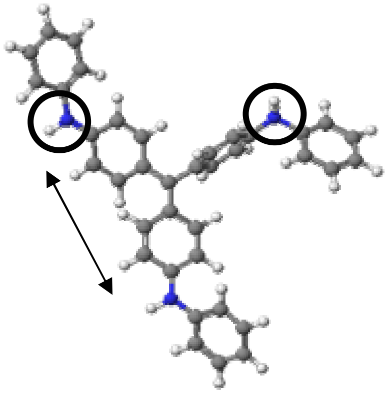
Table 1. Results of MO Calculations

	Heat of formation (kcal/mole)	Absorption maxma (nm)	Figure
Initial state	219.8	374.6	Fig. 1
Mono-protonation (-N^+H=)	341.8	**473.0**	Fig. 7(a)
Di-protonation (-N^+H= & -N^+H_2-)	537.5	**529.0**	Fig. 7(b)
Tri-protonation (-N^+H=, -N^+H_2- & -N^+H_2-)	**778.5**	453.7	Fig. 7(c)

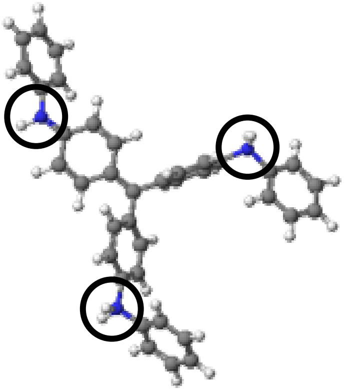
Mono-protonation at the double-bonded N atom (-N=: the electron-richest part) induces a large bathochromic shift by about 100 nm (374.6 → 473.0 nm), although the heat of formation is increased as compared with that of the initial state (219.8 → 471.0 kcal/mole). It is also apparent from Fig. 7(a) that the two phenyl groups of the triphenyl methane system is co-planar to facilitate the electron transfer from the donor to the acceptor. Di-protonation (-N^+H= & -N^+H_2-) makes the relatively planar system more perfect, leading to the further bathochromic shift. However, this induces an increase in heat of formation considerably (537.5 kcal/mole). The above mono- and di-protonations are qualitatively in good agreement with experiment. Tri-protonation disturbs greatly the planarity of the triphenylmethane system to cause a hypsochromic shift to occur (453.7 nm). At the same time, the heat of formation becomes extremely high (778.5 kcal/mole). Therefore, tri-protonation is unlikely to occur in practice.



(a) Mono-protonation



(b) Di-protonation



(c) Tri-protonation

Figure 7. Optimized geometry of protonated TPPR.

Conclusion

The electronic structure of a 1:2 complex of TPPR with PG has been studied from the standpoint of color generation mechanism. The following conclusions can be drawn from the present investigation.

1. TPPR and PG do not form a CT complex. The deep blue color reported previously is due to protonation of TPPR by means of PG (1:2 complex).
2. The charge-control ability of the 1:2 complex is presumably attributed to the property of protonated TPPR.
3. The coloration of TPPR arises from protonation at the double-bonded N atom (*i.e.* -N=), leading to the formation of a powerful push-pull system.

References

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Biography

Yasuo Imura received his Bachelor of Education from Yokohama National University in 2004. He is currently in the graduate course of engineering at Yokohama National University. His research interest includes electronic characterization of organic pigments together with their electronic applications.