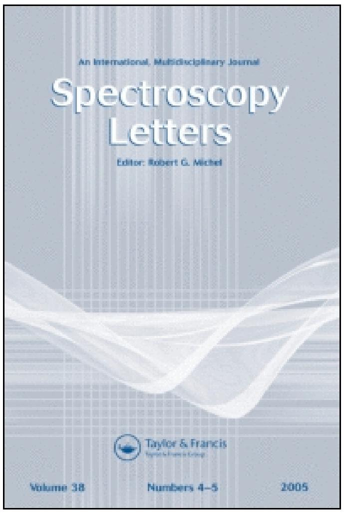

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AGGREGATION BEHAVIOR OF AZOANTHRACENE COMPOUNDS IN SOLUTION

Key Words: Azoanthracene compounds, Aggregation,
UV-Vis absorption spectroscopy

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ABSTRACT

Aggregation of azoanthracene compounds 10-(4'-carboxylphenylazo)-9-anthranol and 10-(2'-carboxylphenylazo)-9-anthranol in solution was investigated by UV-vis spectroscopy. It was determined that the forming of a hydrogen bond, either intermolecular or intramolecular, can affect the wavelength of π-π* transition absorption. Using this principle the aggregation state of azoanthracene compounds was characterized.

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INTRODUCTION

The 21st century might become a photonics century, in a similar way to the 20th century being called an electronic one. Information will be transferred by a new kind of media— light. During this new era, the development of a whole new family of photoresponsive materials will most likely be required. Azo compounds are one of the choices that can meet this need for its potential use in nonlinear optical materials [1-4] , as a molecular switching device, or for use as a high-density information storage media[5]. Azo compounds are a primary candidate for these materials due to their conjugated π-electron system or its *cis-trans* reversible photoisomerization ability.

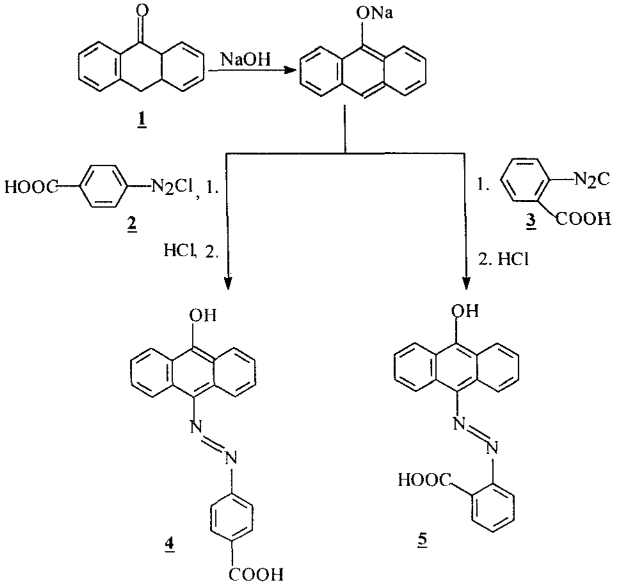
To fabricate Langmuir-Blodgget (LB) film by using azo compounds is one of the methods used to realize their utility. Unfortunately, the *cis-trans* photoisomerization of azo compounds was seriously hampered in typical LB films, in which the azo molecules were densely packed together. This problem can be solved using a few methods. One of them is to increase the free volume among the azo molecules in LB film, such as in the formation of a polyion system[6], or by the UV-pretreatment method [7]. Another alternative is to introduce a large spacing group within the azo molecules. As an example of this method, azonaphthalene has been used in our laboratory [8]. Azoanthracene compounds contain a larger spacing group, and so we synthesized 10-(4'-carboxylphenylazo)-9-Anthranol (4) and 10-(2'-carboxylphenylazo)-9-anthranol (5) (Scheme 1). 4 and 5 were synthesized, using a more feasible measure, because an unstable compound — anthranol was used in the reported methods[9]. Anthranol can isomerize to anthraquinone or anthrone within 24 hours. In our method, this unstable compound was generated and used *in situ*.

As a prerequisite of further research, the aggregation behavior of 4 and 5 in solution was investigated by using UV-vis spectroscopy. The details of this are shown in the following.

EXPERIMENTAL SECTION

Materials and Instruments

9-Anthrone, *o*-aminobenzoic acid and *p*-aminobenzoic acid were commercially obtained (A.R.) and used without further purification. All solvents were also



Scheme 1. Synthesis of the 10-(4'-carboxylphenylazo)-9-Anthranol (4) and 10-(2'-carboxylphenylazo)-9-anthranol (5)

commercially obtained (A.R.), dried and distilled before use. UV-vis spectra were record on a Shimadzu UV-3100 UV-VIS-NIR recording spectrophotometer. The analytical data of the compounds will be included in a further paper [10].

10-(4'-Carboxylphenylazo)-9-Anthranol (4)

10 g of pulverized 9-anthrone 1(5.15 mmol) was added into a solution of 5.0 g of NaOH and 50 mL of water under nitrogen. The mixture was boiled gently for 30 minutes, then filtered; the filtrate was cooled to 0~5°C for use. The diazonium solution of 0.9 g of *p*-aminobenzoic acid (5.10 mmol) was added into the above anthranol salt solution and the temperature was maintained at 0~5°C. After stirring for 4 hours, the solution is then acidifed with 1:1 HCl until pH = 1. Heat the mixture at 60~70°C for 10 minutes, then collect the deep red solid under suction. The crude product was

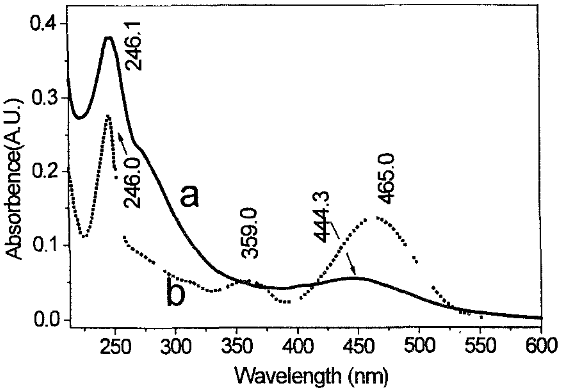


FIG.1 UV-vis absorption spectra of 4(a) and 5(b) in ethanol solution (1.0×10^{-4}M).

recrystallized 2 times from acetic acid. From this procedure, 0.8 g of brown powder 4 was obtained. Yield was 46%.

10-(2'-Carboxylphenylazo)-9-anthranol (5)

The procedure is similar to that of 4. The product was recrystallized from chlorobenzene 2 times. Yield was 58%.

RESULTS AND DISCUSSION

The UV-vis of 4 and 5 in ethanol was shown in Fig.1(c= 1.0×10^{-4}M). The absorption centered at about 450~460 nm ($\lambda\pi$-π^*) was attributed to the π-π^* transition of –N=N- group. The absorption of the anthracene ring appeared in the range of 200~300 nm. The $\lambda\pi$-π^* of 4 and 5 was used to monitor their aggregation behavior in solution.

It was found that the $\lambda\pi$-π^* of 4 and 5 varied in some degree if different solvent was used, or the concentration of 4 or 5 was changed. The detail is shown in Fig. 2.

The $\lambda\pi$-π^* of 4 in ethanol, tetrahydrofuran, chloroform, and cyclohexane were 445.5, 438.2, 433.0 and 432.4 nm, respectively. The corresponding $\lambda\pi$-π^* of 5 were 453.8, 435.6, 442.4 and 432.4 nm, respectively. The wavelength of $\lambda\pi$-π^* in ethanol was

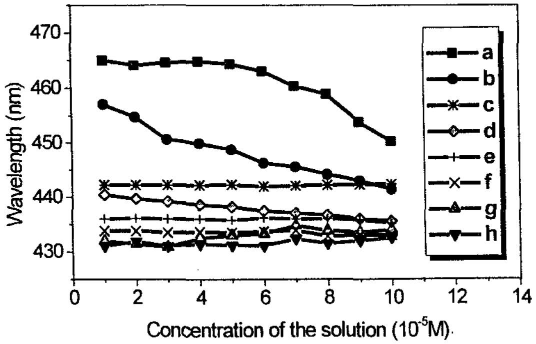


FIG. 2 Variation of λπ-π* absorption of 4 and 5 if its concentration was changed in different solvent(**a**: 5 in ethanol; **b**: 4 in ethanol; **c**: 5 in $CHCl_3$; **d**: 4 in THF; e: 5 in THF; **f**: 4 in $CHCl_3$; **g**: 5 in cyclohexane; **h**: 4 in cyclohexane)

longer than that in any other solvents. Another phenomenon deserving attention was that the λπ-π* of 4 or 5 varied *differently* if the concentration of 4 or 5 was reduced in *different* solvent. A simple explanation for this is that the polarity of the exited state of 4 and 5 is stronger than that of their ground state,

therefore, the exited state could be stabilized further than the ground state did due to the efficient solvation by ethanol. As a result, the energy gap between the exited and ground state was decreased and the λπ-π* move bathochromically. In the other solvents, such as, the tetrahydrofuran, chloroform or cyclohexane, no efficient solvation can be formed, so the λπ-π* move hypsochromically, relatively.

Another observation to be explained was why the λπ-π* varied *differently* if the concentration of 4 or 5 was reduced in *different* solvent. The solvation of 4 or 5 is weak when non-protonic solvents were used, so the interaction among 4 or 5 molecules play an important role in this system. Therefore, the λπ-π* would not change drastically when the concentration of 4 or 5 was reduced since the aggregation state of 4 or 5 would not change greatly (the variation of λπ-π* is less than 3 nm). However, it is not the same in ethanol. The exited state of 4 or 5 would be solvated more effectively and gain extra stabilizing energy when the concentration of 4 or 5 was reduced, as a result, the λπ-π* shows an obvious red shift (larger than 10 nm).

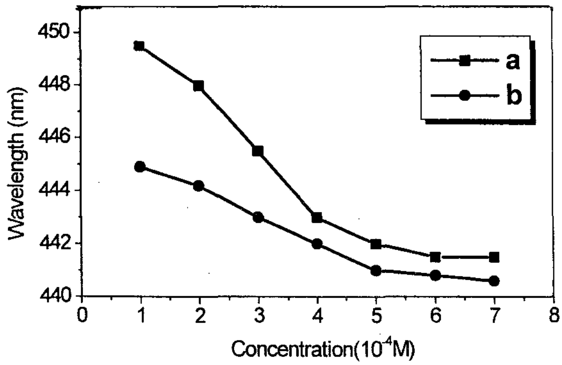


FIG. 3 Variation of λπ-π* absorption of 4 and 5 in mixed solvent of Cyclohexane / ethanol (c/e=3:1 v/v, **a**: 4; **b**: 5)

It appears that the ethanol can affect greatly the aggregation of 4 and 5 in solution. In order to prove this point of view, the UV-vis spectra of 4 and 5 in a mixed solvent — cyclohexane-ethanol were also investigated (Fig. 3).

The variation of λπ-π* of 4 or 5 would be identical to that shown in Fig.2 c~h if the ethanol couldn't affect the aggregation of 4 and 5 by a higher degree than the cyclohexane does since the c/e=3:1(v/v) and the cyclohexane is the majority in the solution. But the results show that the λπ-π* varied identically to what it did in ethanol(Fig. 2 a~b). This result offered evidence to the above hypothesis. However, the presence of the cyclohexane in the solvent can not be ignored completely, for the red shift of λπ-π*(less than 8 nm) was smaller than that in ethanol (larger than 12 nm) if the concentration of 4 or 5 was reduced.

It will be interesting to investigate the variation of λπ-π* if the cyclohexane:ethanol ratio (c/e, v/v) of the above mixed solvent was changed. The results were shown in Fig.4. It was not surprising to observe a blue shift for λπ-π* of both 4 and 5, for the weakening of the solvation when the concentration of ethanol was decreased. The λπ-π* of 5 changed drastically at the beginning of the dilution, but the λπ-π* of 4 did not. In order to explain this, the following mechanism (scheme 2) was suggested.[11]

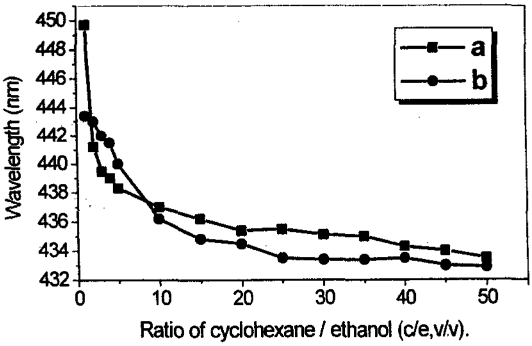
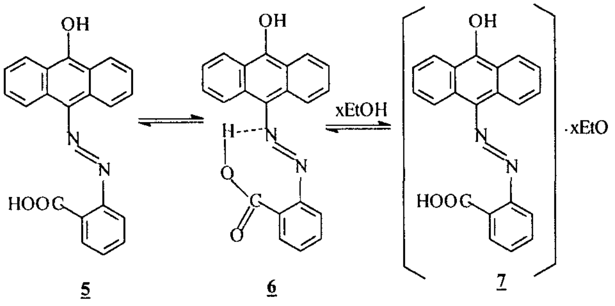


FIG. 4 Variation of $\lambda\pi$-π^* absorption of 4 and 5 in mixed solvent of Cyclohexane / ethanol (c/e was changed. a: 5; b: 4)



Scheme 2. Intramolecular hydrogen form (6) and the ethanol solvated form (7) of compound 5.

4 can not form an intramolecular hydrogen bond and can be solvated well by ethanol. The $\lambda\pi$-π^* of 4 would decrease accordingly if the c/e was reduced and the relation between these two kinds of change should be almost linear. Intramolecular hydrogen bond form 6 cannot be solvated by ethanol as well as 4. The concentration of 7(solvated form) can be expressed by the following equation (C_7, C_6 and C_{EtOH} are the concentration of 7, 6 and ethanol, respectively; k is a constant).

$$C_7=kC_6^xC_{EtOH}^y$$

Although no definite values for x and y are available, it is safe to say that the relation between C_6 and C_{EtOH} is reciprocal. This means that 6 will abruptly became dominant in the mixed solvent as soon as the concentration of ethanol in solution is reduced to a critical value. As a result, the $\lambda\pi$-π^* of 5 will show a sharp blue shift. The experimental result shown in Fig. 4 was consistent with this mechanism.

CONCLUSION

The aggregation behavior of two azoanthracene compounds in four different solvents was investigated by UV-vis spectra and found that the forming of a hydrogen bond could affect the transition absorption $\lambda\pi$-π^* by a considerable degree. An intramolecular hydrogen bond could also affect the $\lambda\pi$-π^* greatly. The $\lambda\pi$-π^* of azoanthracene compounds, which could form an intramolecular hydrogen bond, has shown a sharp blue shift if the ethanol concentration in the solution is reduced.

Further study on the derivatives of azoanthracene compounds is under investigation.

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