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The Solvent Effect on the Interaction between Perylene and Antimony Pentachloride

By Haruo KURODA, Takako SAKURAI and Hideo AKAMATU

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo

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The electronic spectrum of the mono-positive ions of perylene formed by the interaction of antimony pentachloride was examined in various solvents. The observed spectra may be classified into two types. The one is the spectrum observed when the solvent is of a high dielectric constant, a spectrum which almost coincides with the spectrum of perylene in sulfuric acid. The other is the spectrum observed for a solution in a solvent of a low dielectric constant, a spectrum consisting of broad absorption bands accompanied by an extra band at about 1200 mμ. The former type of spectrum may be attributed to the perylene ions in a free state stabilized by the solvation, and the latter to an associated state involving perylene and antimony pentachloride ions. It is suggested that, in the association of both kinds of ions, two or more perylene ions are in contact with each other, and that the interaction between them is responsible for the shift and broadening of the absorption bands of perylene ions, as well as for the appearance of the extra band.

Polycyclic aromatic hydrocarbons exhibit characteristic deep colors upon interaction with antimony pentachloride in a polar solvent. Aalbersberg, Hoijtink, Mackor and Weijland[1] have shown that this phenomenon is associated with the formation of positive ions of the hydrocarbons as a result of an electron transfer from the hydrocarbons to antimony pentachloride, which is known as a strong electron acceptor. The interaction between perylene and antimony pentachloride is a typical example of such electron transfer. In effect, as antimony pentachloride is added to a nitrobenzene solution of perylene, the absorption bands of the neutral perylene molecule are replaced with new absorption bands which coincide well with the spectrum of perylene in sulfuric acid. Apparently this change in the spectrum indicates the formation of perylene ions, since the spectrum of a sulfuric acid solution of perylene is known to be due to the mono-positive ions of perylene.[2-4] The electron transfer from perylene to antimony pentachloride also occurs in other solvents. We have noticed, however, that the absorption bands are shifted more or less depending on the solvent. This shift is quite remarkable in some cases, too large for the ordinary solvent effect, so that it seems questionable to regard the perylene ions formed by the interaction of antimony pentachloride as always in a free state

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[1] W. Ij. Aalbersberg, G. J. Hoijtink, E. L. Mackor and W. P. Weijland, *J. Chem. Soc.*, **1959**, 3055.

[2] G. J. Hoijtink and W. P. Weijland, *Rec. trav. chim.*, **76**, 836 (1957).

[3] Y. Yokozawa and I. Miyashita, *J. Chem. Phys.*, **25**, 796 (1956).

[4] S. I. Weissman, E. de Boer and J. J. Conradi, ibid., **26**, 963 (1956).

in any kind of solvent. The present investigation was undertaken in order to elucidate the effect of solvents on the interaction between perylene and antimony pentachloride.

Experimental

Perylene obtained from the K & K Laboratory was purified by alumina column chromatography, and then by sublimation in vacuo. The following solvents were used: (1) *n*-heptane, (2) cyclohexane, (3) carbon tetrachloride, (4) benzene, (5) toluene, (6) carbon disulfide, (7) trichloroethylene, (8) chloroform, (9) α-chloronaphthalene, (10) bromobenzene, (11) chlorobenzene, (12) tetrachloroethane, (13) *cis*-dichloroethylene, (14) *o*-dichlorobenzene, (15) nitrobenzene, and (16) acetonitrile. A solution of perylene, about 10^{-5} mol./l., was prepared with each solvent after it had been well dried by using calcium chloride. Antimony pentachloride was added to the solutions until the absorption spectrum of the neutral perylene molecule was replaced almost completely with the spectrum of the perylene ion. This was usually made with an excess amount of antimony pentachloride. The solutions were not very stable since antimony pentachloride decomposes slowly in most solvents. Therefore, the spectrum was observed immediately after the preparation of each solution. The absorption spectrum in the visible and near-infrared region was measured by means of a Hitachi EPS-2U recording spectrophotometer.

Results and Discussion

The absorption spectra observed in the presence of an excess amount of antimony pentachloride can be classified into two types. The one type of the spectra, which we shall call "type A," has a weak band at about 740 mμ and a strong and sharp band in the 540—560 mμ region. An example of the type A spectrum is given in Fig. 1. This coincides very well with the spectrum of perylene in sulfuric acid (Fig. 2), except for the small red-shift of the strong band. The other type of spectrum, "type B", is shown in Fig. 3; this is observed for a trichloroethylene solution. A spectrum of this type is observed when the solvent is of a low dielectric constant. In this case, the absorption bands are appreciably broadened and, at the same time, the strong band of perylene ions at about 550 mμ is considerably blue-shifted. Interestingly, a broad absorption band appears at about 1200 mμ in the spectra of type B, a band which can never be found in the spectra of type A. The origin of this band will be discussed later. The observed wavelengths of the absorption bands are summarized in Table I.

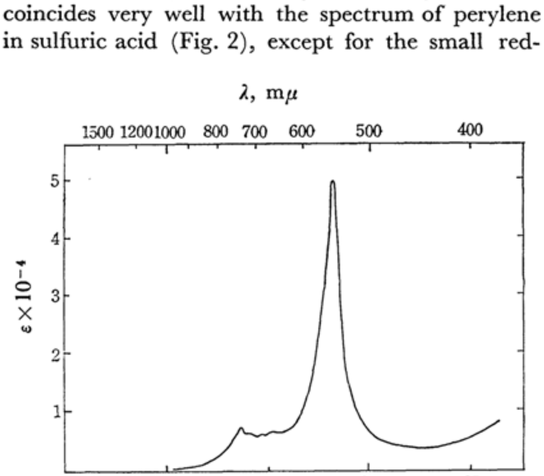

Fig. 1. Absorption spectrum of perylene-SbCl$_5$ in chlorobenzene.

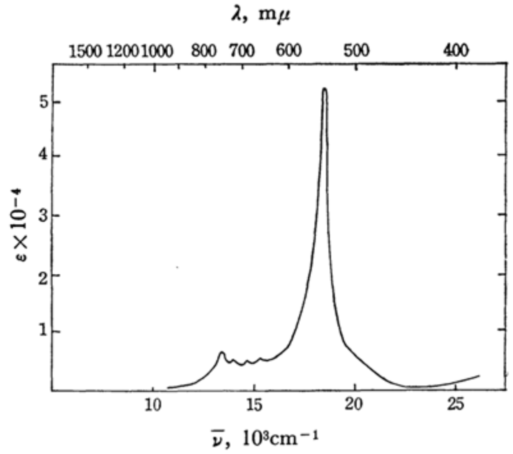

Fig. 2. Absorption spectrum of a sulfuric acid solution of perylene.

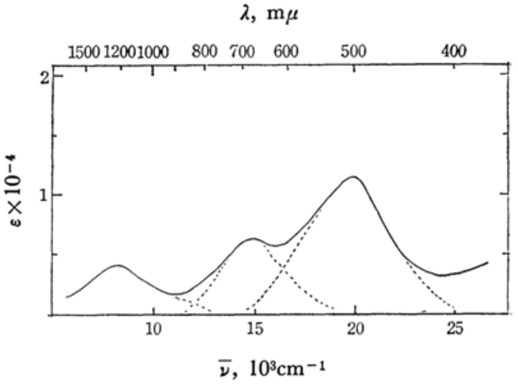

Fig. 3. Absorption spectrum of perylene-SbCl$_5$ in trichloroethylene.

Accoring to Bayliss' theory on the solvent effect,[5] the frequency difference in an absorption band between the gaseous state and the solution is approximately expressed by the following equation:

$$\Delta\nu = b(n^2 - 1)/(2n^2 + 1) \qquad (1)$$

where n is the refractive index of the solvent for the sodium-D line, and b is a constant dependent

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5) N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950).

TABLE I. ABSORPTION BANDS OF PERYLENE-$SbCl_5$ IN VARIOUS SOLVENTS

Solvent	Wavelengths of absorption bands (mμ)			Type of spectrum
	I	II	III	
(1) *n*-Heptane	504 (b)	700 (b)	1200 (b)	B
(2) Cyclohexane	512 (b)	710 (b)	1250 (b)	B
(3) Carbon tetrachloride	521 (b)	700 (b)	1250 (b)	B
(4) Benzene	510 (b)	710 (b)	1200 (b)	B
(5) Toluene	517 (b)	710 (b)	1200 (b)	B
(6) Carbon disulfide	508 (b)	650 (b)	1550 (b) (shoulder at 1200)	B*
(7) Trichloroethylene	502 (b)	680 (b)	1250	B
(8) Chloroform	545 (s)	742 (s)		A
(9) α-Chloronaphthalene	558 (s)	755 (s)		A
(10) Bromobenzene	562 (s)	748 (s)		A
(11) Chlorobenzene	559 (s)	745 (s)		A
(12) Tetrachloroethane	547 (s)	745 (s)		A
(13) *cis*-Dichloroethylene	546 (s)	740 (s)		A
(14) *o*-Dichlorobenzene	560 (s)	745 (s)		A
(15) Nitrobenzene	556 (s)	740 (s)		A
(16) Acetonitrile	538 (s)	735 (s)		A
(17) Sulfuric acid**	540 (s)	735 (s)		A

b=broad. s=sharp

* This spectrum is appreciably different from other spectra of type B.

** The spectrum of perylene ion in sulfuric acid.

on the oscillator strength of the transition. In the more refined theories given by McRae⁶⁾ and Ooshika,⁷⁾ it is shown that the solvent shift depends not only on the refractive index, but also on the dielectric constant and other properties of the solvent. However, the Bayliss' relation would be approximately satisfied in the case of an absorption band of a non-polar molecule in a non-polar solvent. This relation can be extended even to the absorption band of a non-polar molecule in a polar solvent, but not to the band of a polar molecule.

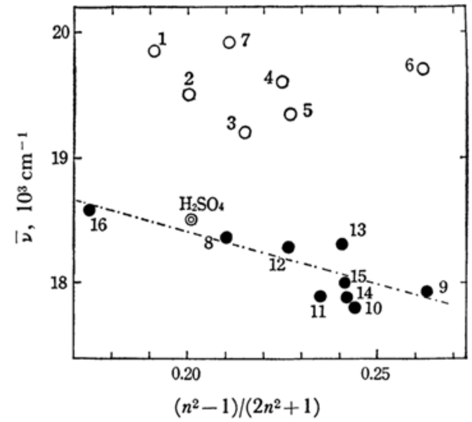

Fig. 4. Solvent shift of a strong absorption band of perylene ion at about 540 mμ. The number of each point indicates the solvent (see Table I).

In Fig. 4, the wave number of the strong band in the 500—560 mμ region is plotted against the value of $(n^2-1)/(2n^2+1)$. The points for the spectra of type A are shown by solid circles, and those for the spectra of type B, by open circles. The solid circles fall on a straight line, as is to be expected from Bayliss' relation. Clearly the solvent shift in the spectra of type A is one that can be understood without the consideration of any specific interaction of perylene ions with solvent molecules or with antimony pentachloride ions. In other words, we can assign the spectra of type A to monopositive ions of perylene in a relatively free state.

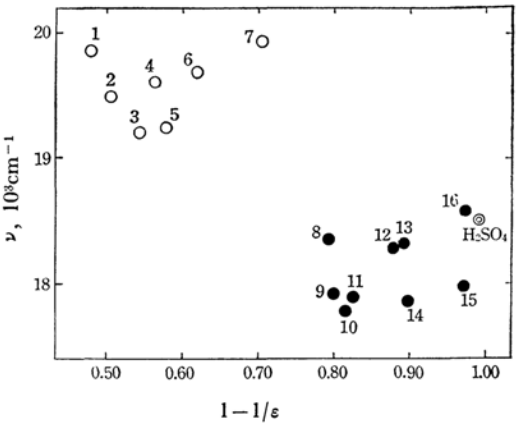

Fig. 5. Relation between the wave number of an absorption band of perylene ion and the dielectric constant of solvent.

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6) E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

7) Y. Ooshika, *J. Phys. Soc. Japan*, **9**, 594 (1954).

On the other hand, in Fig. 4, the points for the spectra of type B deviate markedly from the regularity found for the spectra of type A. Apparently the shift of the peak is too large for a usual solvent shift. Hardly any simple relation can be found between the shift and the refractive index of the solvent in this case. These facts, as well as the broadness of the absorption band, suggest the presence of some specific interaction between a perylene ion and its surroundings in a case that exhibits a spectrum of type B.*

It should be noticed that the solvents which give spectra of type B are of a wide variety with respect to the electronic states. It is hard to expect that carbon tetrachloride, *n*-heptane and benzene will exhibit the same specific interaction with perylene ions. Therefore, we can exclude the possibility that the spectrum of type B is caused by a strong interaction between perylene ions and solvent molecules.

In a solution, perylene ions are stabilized by the solvation. The solvation energy which is associated with an electrostatic interaction of the electronic charge on a molecular ion with solvent molecules can be approximately expressed as follows:9)

$$\varDelta E \simeq \sum_i (q_i/2r)(1 - 1/\varepsilon) \tag{2}$$

where q_i is the charge on the ith atom in the molecular ion; r is the effective interaction radius for the atomic centers, and ε is the dielectric constant of the solvent. Thus $\varDelta E$ can be regarded as being proportional to $(1-1/\varepsilon)$. The wave number of the strong absorption band is plotted against $(1-1/\varepsilon)$ in Fig. 5. It can be seen that the spectra of type A and those of type B appear in different regions, the boundary between which is at the $(1-1/\varepsilon)$ value of about 0.75. The results described above suggest that, in a solvent with a high dielectric constant, a perylene ion is in a relatively free state as it is fully stabilized by the solvation, whereas in a solvent with a low dielectric constant the solvation energy is not large enough to free a perylene ion from an antimony pentachloride ion; this results in keeping them in an associated state involving the two kinds of ions. One may expect the presence of an equilibrium between the free ion state and the associated state when the dielectric constant of the solvent is a value intermediate between the two regions. In effect, such an equilibrium can be demonstrated by the spectra observed in the case of a mixed solvent consisting of benzene and chlorobenzene. The chlorobenzene solution gives a typical spectrum of type A, while the benzene solution gives a spectrum of type B. The spectra observed for the mixed solvent are shown in Fig. 6. The equilibrium of the two states appears when the volume ratio of chlorobenzene to benzene is 0.6—1.0. As we have already mentioned, the spectra of type B have an extra absorption band at about 1200 mμ which can not be found in the spectra of type A. Seemingly, this absorption band is due to the associated state, and it might be a charge-transfer band.

It is known that a solid complex can be obtained from the interaction between perylene and antimony pentachloride. Unfortunately, the crystal structure of this solid complex has not yet been determined. One could suppose, however, that the positive ions of perylene and the negative ions of antimony pentachloride are arranged alternately in the crystal. The minute crystals of the solid complex are formed when a chloroform solution of antimony pentachloride is sprayed onto the surface of a thin flake of perylene crystal. The difference between the absorption spectra of the crystal before and after the formation of a complex on its surface

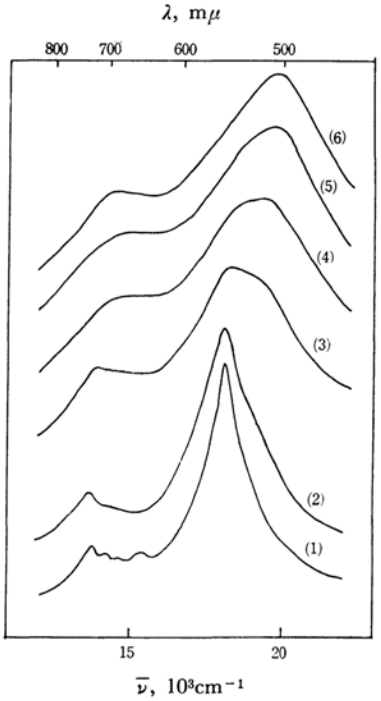

Fig. 6. Absorption spectrum of perylene-SbCl$_5$ in a mixed solvent, benzene-chlorobenzene. The volume ratio of chlorobenzene to benzene is: (1) 2.0, (2) 1.0, (3) 0.9, (4) 0.75, (5) 0.65 and (6) 0.5.

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* The possibility of the formation of a covalent complex between perylene and antimony pentachloride can not be excluded, but it is not likely that the spectrum of type B is associated with the covalent complex, as it is quite different from the spectrum known for the proton complex.8) The spectrum of type B is also different from the spectrum of a colloidal suspension of the solid complex reported by Blomgren and Kommandeur.10)

8) W. Ij. Aalbergsberg, G. J. Hoijtink, E. L. Mackor and W. P. Weijland, *J. Chem. Soc.*, **1959**, 3049.

9) N. S. Hush and J. Blackledge, *J. Chem. Phys.*, **23**, 514 (1955).

10) G. F. Blomgren and J. Kommandeur, ibid., **35**, 1636 (1961).

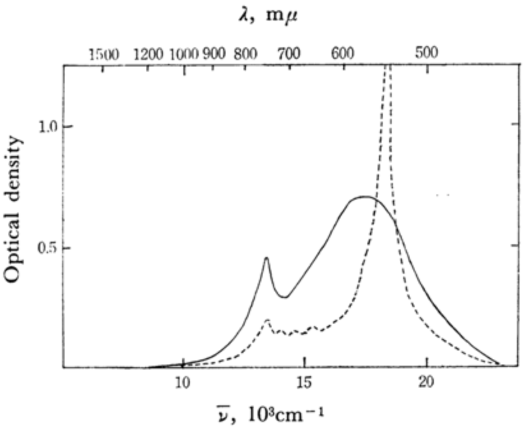

Fig. 7. Absorption spectrum of perylene-$SbCl_5$ solid complex. The broken line is the spectrum of perylene ion in sulfuric acid.

can be taken as the spectrum of the solid complex. The spectrum obtained in this way is shown in Fig. 7. The absorption spectrum of the solid complex has also been observed by Blomgren and Kommandeur⁽¹⁰⁾ by using the KBr-pellet method; their spectrum is similar to the spectrum we show in Fig. 7.

The spectrum of the solid complex seems to correspond to the spectrum of type A rather than to that of type B, because: (i) the red-shift of the absorption peak from its position in a spectrum of type A is of the order that can be expected for the solid state, (ii) the band at 760 mμ is relatively sharp, while it is very broad in the spectra of type B, and (iii) the band at 1200 mμ is absent, or very weak. If we assume that the appearance of the spectrum of type B is due to the charge-transfer interaction between a perylene ion and an antimony pentachloride ion, the same type of spectrum could be expected for the solid complex. This is not the case, however, and the charge-transfer band due to the interaction between perylene and antimony pentachloride can not be observed for the solid complex. This leads to the conclusion that the spectrum of type B is caused by some specific interaction of perylene ions which does not take place in the free state nor in the crystal. Probably the large blue-shift and the marked broadening of the absorption bands in the spectrum of type B are due to the effect of interaction between perylene ions; the new band at 1200 mμ could be a charge-transfer band also caused by the interaction between perylene ions, not by the interaction between a perylene ion and an antimony pentachloride ion. This interpretation is possible if we suppose that the associated state formed in the solvents with low dielectric constants does not correspond to the pair of a perylene ion and an antimony pentachloride ion, but to an aggregate of two or more pairs, in which the arrangement of ions is quite different from that in the crystal, and in which perylene ions are in direct contact with each other. Thus the situation that gives the spectrum of type B seems similar to the dimer of radical ions as that has been presented by Hauser and Murrell⁽¹¹⁾ in the case of Wurster's blue perchlorate. Further evidence for the interaction between perylene ions might be obtained from a study of the electron spin resonance absorption.

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11) K. H. Hausser and J. N. Murrell, ibid., **27**, 500 (1957).