*Contribution from the Istituto di Chimica Generale e Inorganica University of Modena, 41100 Modena, Italy.*

# Aromatic Molecular Complexes. XVI. Spectrophotometric Investigations on the $SbX_3$- and $BiX_3$-Pyrene Complexes in the Solid State and Organic Solvents

**G. Peyronel, I. M. Vezzosi, and S. Buffagni**

*Received June 16, 1970*

*The pyrene complexes of $SbX_3$ and $BiX_3$ ($X = Cl, Br$) have been comparatively studied with spectrophotometric methods. $SbCl_3$- and $SbBr_3$-pyrene solutions in dichloromethane, investigated by the Job method, give a 1:1complex. Its stability constant evaluated with the Benesi-Hildebrand method is thre times greater for the $SbBr_3$- than for the $SbCl_3$-complex. In the more polar acetonitrile the complex is so weak that no equilibrium constant could be calculated. The $BiCl_3$- and BiBr-pyrene solutions in acetonitrile form a complex with a $BiX_3$:Ar ratio different from 1:1. Electronic spectra of the solid 2:1 $SbX_3$ and $BiX_3$-pyrene complexes ($X = Cl, Br$) show a charge transfer band whose energy increases in the order $SbBr_3 < SbCl_3 < BiBr_3 < BiCl_3$ that is the order of increasing dipole moments of the halides. Other solid 2:1 complexes of $SbCl_3$ and $SbBr_3$ with anthracene, crysene, fluorene, fluoranthene, acenaphthene, methylene-phenanthrene were also prepared.*

## Introduction

Solid molecular complexes of $SbCl_3$, with benzene and naphthalene, were prepared for the first time by W. Smith,[1] W. Smith and G. W. Davis[2] and, with several other aromatic hydrocarbons, by B. Menschutkin.[3] A thermal analysis of some binary systems formed by aromatic hydrocarbons and $SbCl_3$ (or $SbBr_3$) was made by C. Shinomiya[4] who, from the order of « melting point elevation », affirmed that $SbCl_3$ is more strongly additive than $SbBr_3$. Viscosity measurements led N. K. Voskreienskaya[5] to conclude that $2SbCl_3 . C_6H_6$ exists in solution, and J. H. Melchiore[6] deduced from vapour tension and molecular weight measurements both complexes, 2:1 and 1:1 may be present in solution.

By using pure quadrupole resonance T. Okuda *et al.*[7] concluded that in $2SbCl_3 . C_6H_6$ one of the Sb–Cl bonds has a larger ionic character due to a charge transfer from the benzene ring to the chlorine atom through the Sb–Cl bond. The crystal structure of $2SbCl_3$-naphthalene[8] shows that each antimony atom has a distorted $sp^3d$ bipyramidal hybridisation, one empty axial position being utilized in bonding the Sb-atom to the $\pi$-system of the naphthalene, while the other axial position corresponds to a Sb–Cl bond, a little longer than the other two in equatorial position. These facts seem to indicate that the halogen atoms of the trihalides can play a role in the complexation.

In correlation with our previous studies on bismuth halide complexes with aromatic hydrocarbons[9] we have prepared the corresponding complexes of $SbCl_3$ and $SbBr_3$ in order to complete the series for the two metals with a view to start a comparative study of them. The pyrene complexes have been chosen for this first spectroscopic study, in the solid state and in solution, because of their higher stability and of the high symmetry of the pyrene molecule.

## Experimental Section

All the reagents employed were of the best commercial grade. The trihalides were recrystallized from dichloromethane; the aromatic hydrocarbons were purified by distillation or by chromatography on silica gel or neutral allumina and dried; acetonitrile was dried on $CaCl_2$, boiled with $P_2O_5$ until colourless, neutralized with melted $K_2CO_3$ and distilled collecting the fraction at 81°C; dichloromethane was dried on $CaCl_2$ and distilled collecting the fraction at 40°C. Because of the hygroscopicity of antimony trihalides all the manipulations were performed in a box dried with $P_2O_5$.

Solid complexes were prepared by cooling or by adding penthane to a saturated solution of the reagents in cyclohexane or dichloromethane for $SbCl_3$ and in benzene or ethylbenzene for $BiBr_3$. Most of the complexes are decomposed by humidity. Almost all complexes are yellow; those of $SbBr_3$ are of a more intense tonality. The trihalide was determined

---

(1) Watson Smith, *J. Chem. Soc. (London)*, *35*, 309 (1879).

(2) Watson Smith and G. W. Davis, *J. Chem. Soc. (London)*, *41*, 411 (1882).

(3) B. Menschutkin, *Iswiestja Petersberger Polytech.*, *13*, 263 (1910); *Zhur. Russ. Fiz. - Khim. Obschestva*, *43*, 395 (1911); *J. Russ. Phys. Chem. Soc.*, *43*, 1275 (1911).

(4) C. Shinomiya, *Bull. Chem. Soc. Japan*, *15*, (7), 259 (1940).

(5) N. K. Voskresenskaya and others, *Akad. Nauk. SSSR Tekh. Nauk. Inst. Mashinovedeniya, Soveshchanie Vyazkosti Zhidkostei ι Kolloid. Rastvorod 1*, 31 (1941).

(6) J. H. Melchiore, Ph D. Thesis, Purdue University, 1957.

(7) T. Okuda, A. Nakao, M. Shiroyama, and H. Negita, *Bull. Chem. Soc. Japan*, *41*, 61 (1968).

(8) R. Hulme and J. T. Szymansky, *Acta Cryst.*, *B25*, 753 (1969).

(9) G. Peyronel, S. Buffagni, and I. M. Vezzosi, *Gazz. Chim. It.*, *98*, 147 (1968); S. Buffagni I. M. Vezzosi, and G. Peyronel, *Gazz. Chim. It.*, *98*, 156 (1968); I M. Vezzosi, G. Peyronel, and S. Buffagni, *Gazz. Chim. It.*, *98*, 162 (1968).

**Table I.**

| Complex | SbCl$_3$ |  | Aromatic hydrocarbon |  | SbBr$_3$ |  | Aromatic hydrocarbon |  |
|---|---|---|---|---|---|---|---|---|
|  | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. |
| 2SbX$_3$ . Anthracene | 71.38 | 71.91 | 28.58 | 28.09 |  |  |  |  |
| . Crysene | 66.20 | 66.66 | 32.88 | 33.34 | 75.35 | 76.00 | 23.06 | 24.00 |
| . Pyrene | 68.77 | 69.29 | 31.35 | 30.77 | 78.53 | 78.15 | 22.20 | 21.85 |
| . Fluorene | 72.57 | 73.30 | 27.04 | 26.70 | 80.50 | 81.31 | 19.58 | 18.69 |
| . Fluorantene |  |  |  |  | 77.54 | 78.15 | 21.94 | 21.85 |
| . Acenaphtene |  |  |  |  | 81.89 | 82.61 | 16.30 | 17.39 |
| . Methylenephenanthrene | 69.75 | 70.57 | 30.15 | 29.43 | 78.39 | 79.13 | 20.95 | 20.87 |
| 9SbCl$_3$ . 5Fluoranthene . 1Cyclohexane | 65.43 | 65.40 | 31.91 | 31.80 |  |  |  |  |

by dissolving the complex in ethylbenzene, decomposing it with an aqueous solution of AgNO$_3$ and HNO$_3$ and titrating the excess of AgNO$_3$. By dissolving the complex in toluene, adding dilute HNO$_3$ for extracting SbX$_3$, and evaporating the toluene solution the solid aromatic hydrocarbon was determined by weighing. Results are given in Table I.

Electronic spectra were obtained with a Beckman DK 1A double beam recording spectrophotometer and, for more sensitive and accurate measurements, with an Hilgher Uvispek single beam spectrophotometer giving galvanometric reading.

## Results and Discussion

*SbCl$_3$ . pyrene complex in solution.* The solution of SbCl$_3$+pyrene (mol. ratio 912: 1) at moderate concentration in dichloromethane, in the range from 250 to 345 mμ, does not show (Figure 1), curve 4) any apparently significant shift of the positions of the intense bands of pyrene (curve 1) at 320 and 336 mμ. However, these maxima are, in the complex, lowered and their adjacent minima on the right side are raised. In the difference curve 5) this effect gives almost equal negative and positive areas corresponding to the maxima and the minima of the observed curves, respectively. We have also observed this broadening of the aromatic hydrocarbon bands with other metallic polyhalides.

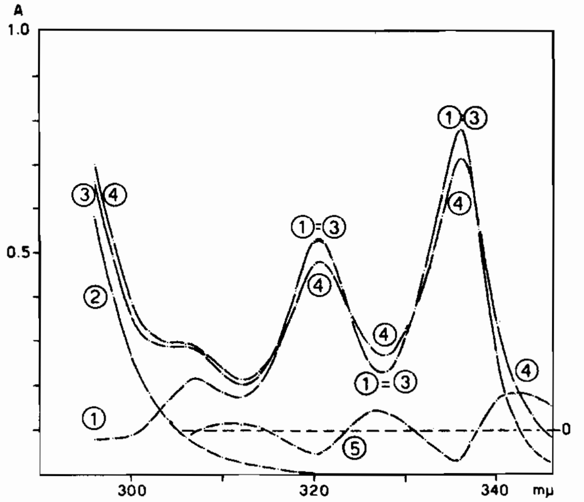

Figure 1. The broadening of pyrene bands at moderated SbCl$_3$ concentration. Electronic spectra in dichloromethane, 0.1 cm cell (conc. in mol/l) of: 1) Pyrene ($1.50\times10^{-4}$); 2) SbCl$_3$ ($1.37\times10^{-1}$); 3) Sum of the curves 1)+2); 4) Pyrene ($1.50\times10^{-4}$)+SbCl$_3$ ($1.37\times10^{-1}$); 5) Difference of the curves 4)—3)

A broadened absorption band without change of integrated intensity, with respect to that of the donor, was observed by K. M. C. Davis and M. F. Farmer[10] at about 275 mμ in the absorption spectra of tetracene with added carbon tetrachloride in n-heptane and was considered as being mainly due to contact effects in solution between the aromatic hydrocarbon and the halomethane. The broadening of the pyrene bands in SbCl$_3$ solutions may be attributed to such a contact charge-transfer effect, but another explanation might be that the vibronic states of the pyrene molecule are influenced by the interaction with the trihalide molecules in solution.

With a greater concentration of SbCl$_3$ (almost saturated solution) and pyrene (mol. ratio 4600: 1) in dichloromethane, the electronic spectrum from 310 to 390 mμ shows a greater depression and deformation of pyrene maxima at 320 and 336 mμ (Figure 2).

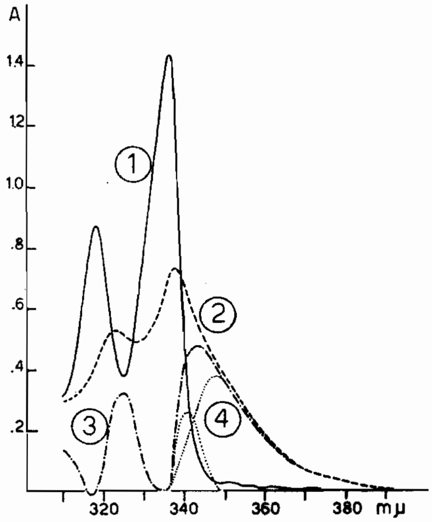

Figure 2. The charge transfer band of the 1: 1 SbCl$_3$-pyrene complex. Electronic spectra, in dichloromethane, 0.1 cm cell (conc. in mol./l) of: 1) Pyrene ($3.0\times10^{-4}$); 2) Pyrene ($3.0\times10^{-4}$)+SbCl$_3$ ($13.0\times10^{-1}$); 3) Difference curve obtained by substracting half of the absorbance of pyrene (curve 1) from that of the complex (curve 2); 4) Graphic decomposition of difference curve 3) to obtain the presumable C. T. band at 348 mμ.

---

(10) K. M. C. Davis and M. F. Farmer, *J. Chem. Soc. (B)*, *1968*, 859.

By substracting from the complex curve 2) half the absorption of the curve of pyrene 1), corresponding to the lowering of the 336 mμ maximum, the difference curve 3) was obtained. The maximum of this difference curve at about 342 mμ can be decomposed in two more symmetrical maxima 4), the greater of which, at about 348 mμ can be considered to be the true charge transfer band of the complex.

In order to investigate the effect of different solvents in this spectral region, the electronic spectra of isotonic solutions of pyrene in acetonitrile (A) benzene (B) and dichloromethane (D) were investigated from 345 to 390 mμ. Pyrene shows a bathochromic shift of its bands at about 350, 360 and 370 mμ in the sequence A<D<B which corresponds to the sequence of the refraction indexes $n_D$ (A = 1.33934, D = 1.4253, B = 1.50124), that is of the polarizabilities of the solvents, and is reversed with respect to their sequences of dipole moments (A = 3.37, D = 1.55, B = 0) and of dielectric constants (A = 37.5, D = 9.08, B = 2.3). This effect seems to indicate that the mentioned transitions of pyrene are correlated to some kind of polarizability of its molecule.

The absorption of isotonic solutions of $SbCl_3$+ pyrene (ratio 59:1) in the same solvents decreases in the order: dichloromethane>benzene>acetonitrile. The lower absorption of the solution in the more polar acetonitrile may be due to the greater solvation of $SbCl_3$, which prevents the formation of the pyrene complex. Analogously, the absorption of the benzene solution may be reduced to an intermediate value because benzene with its π-electron system acts as a complexing agent of $SbCl_3$ in competition with pyrene. Dichloromethane is the least interacting solvent of the three with respect to the complex formation, notwithstanding its contact C. T. interaction with pyrene, which is distinct from a normal solvation effect,[10] and its solvating action toward the trihalides, because of its appreciable dipole moment.

The Job method was applied to the $SbCl_3$-pyrene solutions in dicloromethane, by substracting the absorption of the pyrene at the same concentration used in the sample. In the region of 350-380 mμ $SbCl_3$ is completely transparent. The Job curve (Figure 3A) clearly shows that the complex has a 1:1 composition and, from the parabolic shape of the curve, that it is appreciably dissociated at the concentration used.

By using a constant concentration of pyrene ($7.0\times10^{-3}$ mol./l) and much greater (from 20 to 200 times) concentrations of $SbCl_3$ in dichloromethane the Benesi-Hildebrand[11] method was applied; all the linear plots, exemplified in Figure 3B, have positive intercepts on the ordinate axis. From these plots the equilibrium constants K were calculated.

As has been shown by G. D. Johnson and R. E. Bowen,[12] the valid criterion for the existence of only a 1:1 complex is not only a linear B—H plot, but the constancy of the K value over a wide range of wavelengths. This condition is well fulfilled by the Figure 3C K-plot. This constancy and the symmetry of the Job curve to the central (1:1) position indicate that, at the concentration used, no other higher order complex should be significantly present.

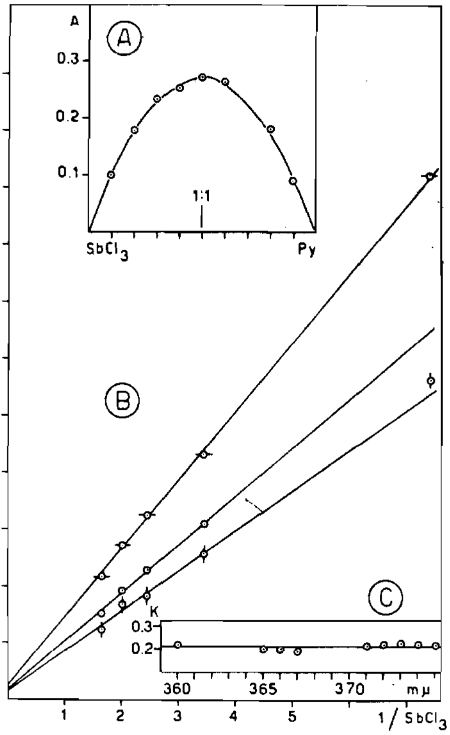

Figure 3. (A) The Job diagram of the 1:1 $SbCl_3$-pyrene complex in dichloromethane: total concentration $9.19\times10^{-2}$ mol/l; 0.1 cm cell; λ = 372 mμ; (B) The linear Benesi-Hildebrand plot of $10^4$[Pyrene]l/A versus 1/[$SbCl_3$] at wave-length: ϕ = 374 mμ, ⊙ = 367 mμ, -○- = 365 mμ. (C) K-values calculated from the Benesi-Hildebrand plots at different wave-lengths.

In the same spectral region some spectra have been recorded on $SbCl_3$-pyrene solutions in acetonitrile with a constant pyrene concentration of $7.0\times10^{-3}$ mol./l and $SbCl_3$ concentrations from 40 to 175 times greater. The Benesi-Hildebrand linear plots obtained from these curves, after substracting the absorption of pyrene, have negative intercepts on the ordinate axis. S. Carter *et al.*[13] have shown that negative intercepts are given by very weak complexes owing to a high solvation of the constituents, from which a large number of solvent molecules have to be extruded when the complex is formed. In that case the calculation of a K is impossible. The high value of the acetonitrile dipole moment explains this high solvation effect and the consequent destabilization of the complex.

*$SbBr_3$-pyrene complex in solution.* Electronic spectra of $SbBr_3$ and pyrene in acetonitrile and dichloromethane show a much greater absorbance for the dichloromethane solutions. Because of the much higher absorbance of $SbBr_3$ in the region from 310 to 370 mμ it was not possible to identify the charge transfer band of the $SbBr_3$-pyrene complex as was done for the $SbCl_3$ complex.

---

(11) H. A. Benesi and J. H Hildebrand, *J. Am. Chem. Soc.*, *71*, 2703 (1949).

(12) G. D. Johnson and R. E. Bowen, *J. Am. Chem. Soc.*, *87*, 1655 (1965).

(13) S. Carter, J. N. Murrell and E. J. Rosch, *J. Chem. Soc.*, *1965*, 2048; S. Carter, *J. Chem. Soc. (A)*, *1968*, 404.

The Job diagram clearly showed the formation of the 1:1 complex in dichloromethane solutions, with an apparently smaller dissociation than the corresponding $SbCl_3$ complex formed at comparable concentrations of reagents in the same solvent. Linear Benesi-Hildebrand plots, all with positive intercepts on the ordinate axis, were obtained, and from them the equilibrium constants K were deduced. Their consistency over the wave-length range considered, and the symmetrical shape of the Job diagram enable us to conclude that at the concentration used, higher order complexes are practically absent in these $SbBr_3$-pyrene solutions as well.

*Stability of $SbX_3$-pyrene complexes in solution.* The equilibrium constants K obtained by the Benesi-Hildebrand method are generally underestimated[13] by an amount which depends on the solvation of the donor and acceptor molecules. Therefore the $K_{B-H}$ values obtained for the two 1:1 complexes, cannot be considered as true K values.

Tribromide complex has a $K_{B-H}$ constant (0.65 $l/mol^{-1}$) three times greater than that (0.22 $l/mole^{-1}$) of trichloride complex, so that tribromide could be considered as a better acceptor for pyrene than trichloride. But the dipole moments of these trihalides in the vapour state are[14] very different: $SbCl_3 = 3.9$ D and $SbBr_3 = 2.8$ D.

The inversion of the values of the stability constants of the complexes with respect to the order of dipole moments of the trihalides could be due to the fact that in the polar dichloromethane the more polar $SbCl_3$ molecules are more strongly solvated than the $SbBr_3$ molecules, so that the equilibrium constant for the $SbCl_3$-pyrene 1:1 complex is much lower than for the $SbBr_3$-pyrene complex. In fact, in the still more polar acetonitrile $SbCl_3$ gives a so weak complex that its constant K cannot be evaluated by the Benesi-Hildebrand method.

But this inversion could also be explained by admitting that in solution an electron transfer may take place from the $\pi$ system of the pyrene to the d orbitals of a halogen atom of antimony trihalide, even if through the Sb–X bond as it seems to occur in the 2:1 complexes of benzene[7] and of naphthalene.[8] It has been shown[15] for the C. T. complexes of oxalyl bromide and chloride and of bromine and chlorine with dioxane, that the bromine atom is a better acceptor than chlorine atom. If this were also true for $SbX_3$ molecules in solution, the better acceptor properties of tribromide, together perhaps with the smaller solvation due to its lower dipole moment, could account for the greater stability of its complex.

*$BiCl_3$- and $BiBr_3$-pyrene complexes in solution.* It is more difficult to investigate the electronic spectra of the $BiX_3$ complexes in solution because of the intense absorption, especially of $BiBr_3$, and of the reduced solubility in organic solvents of bismuth halides. The spectrum of pyrene is very little affected by the two Bi halides in dichloromethane from 260 and 350 mμ, as indicated by the good agreement of the observed spectra with those obtained by adding the spectra of both components of the solution.

In the range from 355 and 390 mμ for $BiCl_3$ and from 380 to 410 mμ for $BiBr_3$-pyrene solutions in acetonitrile the difference curves 4) show, at about 360 mμ for the $BiCl_3$- and 380-390 mμ for the $BiBr_3$-complex (Figures 4, A-B)), a maximum which may correspond to a charge transfer band.

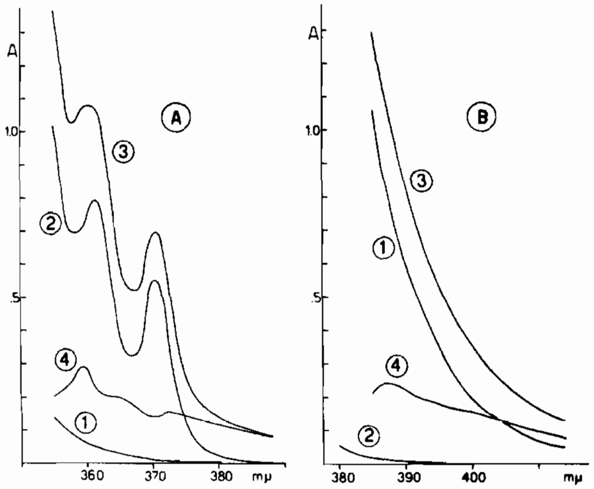

Figure 4. $BiX_3$—pyrene complexes in acetonitrile. Electronic spectra of solutions, in 0.1 cm cell, conc. in mol/l, of: A, 1) $BiCl_3$ ($3.7 \times 10^{-1}$); 2) Pyrene ($2.8 \times 10^{-2}$); 3) $BiCl_3$ ($3.7 \times 10^{-1}$)+pyrene ($2.8 \times 10^{-2}$); 4) Sum of the curves 1+2; 5) Difference curve 3-4. B, 1) $BiBr_3$ ($1.6 \times 10^{-1}$); 2) Pyrene ($5.6 \times 10^{-2}$); 3) $BiBr_3$ ($1.6 \times 10^{-1}$)+pyrene ($5.6 \times 10^{-2}$); 4) Sum of curves 1+2; 5) Difference of curves 3-4.

A Benesi-Hildebrand analysis of the $BiBr_3$-pyrene system in acetonitrile solution did not give consistent values within the explored wave-lengths, and this fact excludes the presence of a single 1:1 complex in solution.

The Job diagram obtained from the $BiCl_3$-pyrene solutions in acetonitrile at $\lambda = 373$ shows a well defined maximum at a pyrene ratio of 0.4. It seems more likely that this ratio corresponds to the existence of both 1:1 and 2:1 complexes in equilibrium rather than to a $3BiCl_3 \cdot 2$Pyrene complex, too complicated to be admitted as existing in solution. The observed rather large maxima in the difference curves of the solutions could, in this case, correspond to the sum of the spectra of the two complexes.

*Spectra of the solid $2SbX_3$- and $2BiX_3$-pyrene complexes.* The spectra of the four 2:1 solid complexes of pyrene with antimony and bismuth trichlorides and tribromides have been recorded in nujol mulls between silica slides (Figure 5). The 2:1 bismuth tribromide-pyrene complex contained about 2.5% dichloromethane, which does not interfere with the spectrum of pyrene.

Antimony trichloride and tribromide and bismuth tribromide complexes show rather broad but distinct charge transfer bands at about 400, 420 and 390 mμ respectively, which interfere more or less with the four small contiguous bands of pyrene. By decomposing the maximum of the bismuth tribromide complex the pyrene spectrum is obtained without any de-

---

(14) J. W. Smith, « Electric Dipole Moments », Butterworths, 1955 p. 86.

(15) L. J. Andrews and R. M. Keefer, « Molecular complex in organic chemistry », Holden-Day Inc , S. Francisco, 1964, p. 53.

formation. The bismuth trichloride complex shows pyrene bands more deformed than in the other complexes. A charge transfer band probably exists at about 350-360 mμ which is responsible for this deformation.

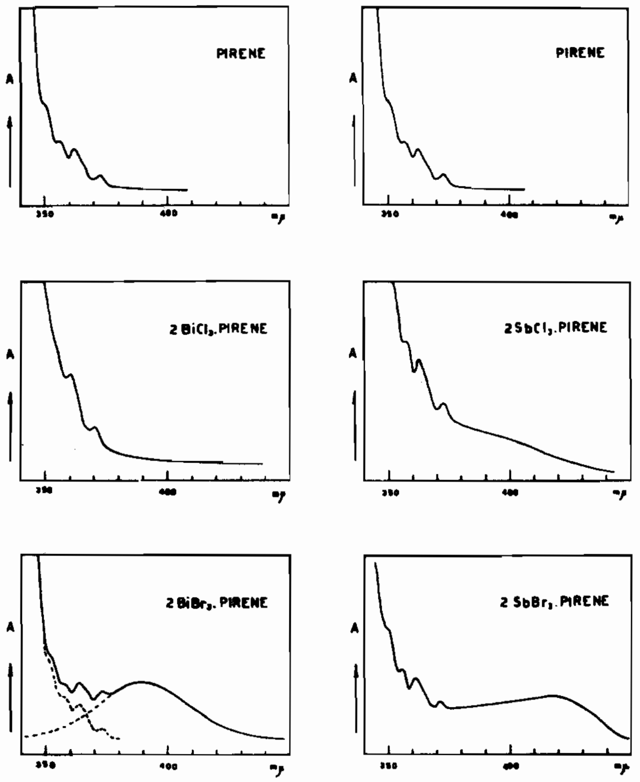

Figure 5. Electronic spectra in nujol mulls of pyrene and those of 2:1 $BiX_3$— and $SbX_3$-pyrene solid complexes, showing charge transfer bands.

These charge transfer bands can be correlated to the dipole moments of the four trihalides. Those of bismuth trihalides, not given in the literature, may be reasonably obtained by extrapolation of the dipole moment values of the other trihalides of the V group, measured in the vapour state[14] (Figure 6A). By plotting the charge transfer band frequencies of the solid complexes against the dipole moments of their trihalides, a straight line (Figure 6B) is obtained, indicating that the transition energy of the charge transfer is roughly proportional to the halide dipole moment.

This could mean that with a greater dipole moment of the halide less energy is required to create, in the ground state, a dative structure ($D^+$–$A^-$) in resonance with the no bond structure (D ... A); this results in a larger splitting of the ground state and excited states, leading in turn to a blue shift of the C. T. band. This interpretation has been given by H. W. Offen *et al.*[16] for the C. T. blue shift in polar solvents.

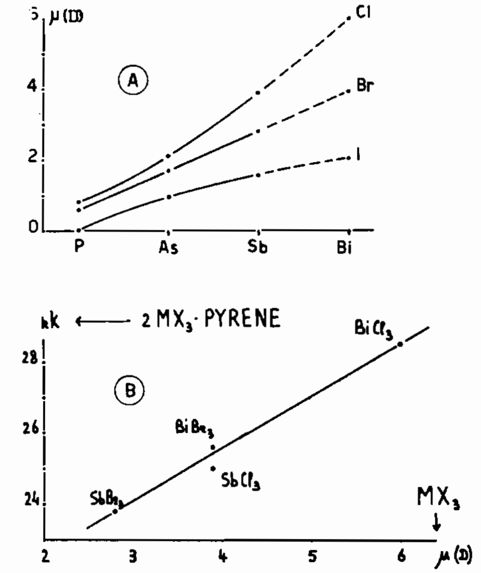

Figure 6. A) Extrapolation of dipole moments of $BiX_3$ from the dipole moments of $PX_3$, $AsX_3$, $SbX_3$; B) The linear plot of C. T. band energy (in kK) of the $SbX_3$— and $BiX_3$— pyrene solid complexes against the dipole moments of the corresponding Sb and Bi halides.

The IR spectra of the solid complexes in nujol mulls compared with those of pyrene show some differences for the C–H stretching and deformations bands. The C–H deformations at 962 and 746 cm$^{-1}$ are enlarged to the intervals 962-972 and 742-722. Beside the pyrene CH stretching at 3051 cm$^{-1}$ a new broad CH band appears in all four complexes between 3150 and 3180 cm$^{-1}$ which may be due to the higher double bond character of some C–C bonds. This is agreement with a structure like that found[8] for the $2SbCl_3$-naphthalene complex, in which the two $SbCl_3$ molecules are bonded to the naphthalene molecule on two opposite sites. The C–C bonds corresponding to these two sites have shorter distances, that is a higher double bond character, than in the free molecule, correspondingly to a delocalization of π electrons on these sites bonded to an antimony atom.

*Acknowledgment.* This work has been supported by a financial aid of the Consiglio Nazionale delle Ricerche of Italy.

---

(16) H. W. Offen and M. S. F. A. Abidi, *J. Chem. Phys.*, *44*, 4642 (1966).