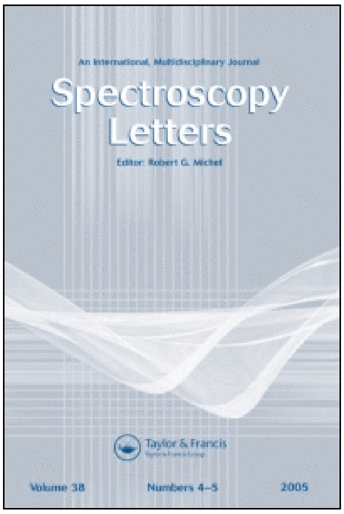

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Indirect Determination of Electronic Transition Frequencies of Coronene, Triphenylene and 1,2,5,6-Dibenzanthracene in the Vapor Phase

R. G. E. Morales[a]; G. Traverso[a]
[a] Departamento de Quimica, Universidad de Chile, Santiago, Chile

To cite this Article Morales, R. G. E. and Traverso, G.(1982) 'Indirect Determination of Electronic Transition Frequencies of Coronene, Triphenylene and 1,2,5,6-Dibenzanthracene in the Vapor Phase', Spectroscopy Letters, 15: 8, 623 — 629
To link to this Article: DOI: 10.1080/00387018208068018
URL: http://dx.doi.org/10.1080/00387018208068018

SPECTROSCOPY LETTERS, 15(8), 623-629 (1982)

INDIRECT DETERMINATION OF ELECTRONIC TRANSITION FREQUENCIES OF CORONENE, TRIPHENYLENE AND 1,2,5,6-DIBENZANTHRACENE IN THE VAPOR PHASE

Key words: Coronene, Triphenylene, 1,2,5,6 Dibenzanthracene, vapor spectra

Raul G. E. Morales and Gabriel Traverso
Departamento de Quimica
Universidad de Chile
Casilla 653 - Santiago, Chile

Frequencies of absorption band maxima for the first two electronic singlet transitions of coronene, triphenylene and 1,2,5,6-dibenzanthracene in vapor phase were calculated indirectly from solution spectral data. The calculations were based on two different models: the first one was a linear correlation between the solution absorption frequencies in nonpolar solvents and the solvent refractive indices. The accuracy of both methods was checked with anthracene and some of its derivatives: both methods gave a good agreement with the experimental values.

INTRODUCTION

In a broad study of excited state properties of several polycondensed hydrocarbons by solvatochromic spectral shifts[1,2], the vapor phase absorption frequencies were necessary. Due to the low vapor pressure of coronene, triphenylene and 1,2,5,6-dibenzanthracene, their vapor spectra could not be recorded. Two different semiempirical methods[3,4] were tested successfully in this work and were applied to get approximate frequency values for the frequencies of the first two electronic singlet transitions of these hydrocarbons.

MATERIALS AND METHODS

Coronene, triphenylene and 1,2,5,6-dibenzanthracene as well as anthracene as well as anthracene and its derivatives, were obtained from Aldrich Chemical Co., and they were purified by fractional sublimation. The spectroscopic grade solvents (Uvasol from Merck) were used without further purification. Measurements were made with a Cary 17 recording spectrophotometer. The instrumental calibration is known to be accurate to better than ± 1 Å over the spectral range of interest and the reproducibility of the measurements reported here is better than 0.5 Å.

Vapor spectra of a sample in a ten-centimeter cell were measured in a heated cell compartment with quartz windows in comparison with the absorption of air as a reference. The standard sample holder was replaced by a thermostated compartment, and the samples were equilibrated before measurement. Solution spectra had been obtained at room temperature.

One of the methods (method I) for predicting vapor transition frequencies was based on the solvent Stark effect model of Baur and Nicol[4,5,6]. They found that the frequency of an electronic transition in solution

(ν_s) can be expressed by:

$$\nu_s = \nu_v + A\,\frac{n^2-1}{2n^2+1} + B\,\frac{(2\varepsilon' + 1)(\varepsilon' - 1)}{\varepsilon'}$$

where ε' is the effective dielectric constant[6], n is the refractive index and A and B are molecular parameters dependent on the solute molecule in the ground and excited states. When the vapor frequency ν_v is unknow, it can be estimated from a set of ν_s values in different polar solvents by means of a least squares fitting[4,5].

The other method (method II) was based on the linerarity that holds between the solution frequencies and the refractive indices of the non-

TABLE 1

Frequencies of the 0'-0" absorption bands ($^1A-^1L_a$) of anthracene* and its derivatives** in solution at room temperature (cm^{-1}).

Solvent	A	DCA	DBA	DMA	DPA
n-pentane	26720	24994	24907	25214	25576
n-hexane	26685	24904	24891	25164	25536
n-heptane	26670	24931	24866	25135	25510
isoctane	26692	24966	24866	25154	25520
cyclohexane	26613	24891	24805	25091	25439
benzene	26399	24722	24637	24910	25291
dioxane	26469	24820	24722	24991	25355
chloroform	26406	24777	24698	24897	25253
diethylether	26649	24969	24888	25192	25513
dichloromethane	26445	24805	24716	24931	25294
ethanol	26624	24956	24873	25138	25504
isopropanol	26638	24975	24891	25151	25514
methanol	26652	25003	24913	25179	25553
acetone	26582	24941	24848	25097	25455
NNDFNA***	26403	24777	24667	24947	25304
acetonitrile	26592	24959	24873	25116	25442

---

* Ref.2.

** A : Anthracene; DCA : 9,10-dichloroanthracene; DBA : 9,10-dibromoanthracene; DMA : 9,10-dimethylanthracene; DPA :9,10-diphenylanthracene.

*** NNDMFA : N,N-dimethylformamide.

plar solvents[3,4]. The vapor frequency could be obtained by extrapolation of $_s$ to n = 1, by means of the following empirical expression:

$$\nu_s = a \cdot n + (\nu_v - a) \qquad /2/$$

where a is a constant of the system. Again $_v$ was obtained by a least squares procedure.

TABLE 2.

Frequencies of absorption band maxima in vapor phase calculated from Nicol and Baur model (ν_v^I) and linear relationship of refraction index in nonpolar solvents (ν_v^{II}), and experimental values extrapolated to room temperature ($\nu_{v,exp.}$).

Compound	band	ν_v^I, (cm^{-1})	ν_v^{II}, (cm^{-1})	$\nu_{v,exp.}$, (cm^{-1})
Anthracene	$^1A-^1L_a$	28097 ± 283	27589 ± 47	27643
9,10-Dichloro-anthracene	$^1A-^1L_a$	26069 ± 158	25634 ± 34	25836
9,10-Dibromo-anthracene	$^1A-^1L_a$	26111 ± 143	25644 ± 28	25736
9,10-Dimethyl-anthracene	$^1A-^1L_a$	26483 ± 219	25977 ± 47	25962
9,10-Diphenyl-anthracene	$^1A-^1L_a$	26895 ± 227	25317 ± 33	26202

RESULTS AND DISCUSSION

The solution frequencies (0 - 0 band of the $^1A-^1L_a$ transition) of anthracene[2] and several of its derivatives are shown in Table 1. At room temperature the vapor pressures were too low to record the spectra of these compounds. However, they were recorded at several temperatures between 80 and 260°C. The vapor frequencies at room temperature were obtained by extrapolation (ν_v. exp. values in Table 2). The vapor frequencies ν_v^I and ν_v^I were also calculated by methods I and II and they are shown in Table 2.

in Table 1. At room temperature the vapor pressures were too low

A good agreement between experimental and calculated frequencies was found: the experimental results usually occur between the two calculated results, i.e.,

The solution frequencies of the absorption maxima of coronene[2], triphenylene and 1,2,5,6-dibenzanthracene[2] are shown in Table 3. The calculated vapor frequencies are given in Table 4 for the $^1A-^1L_a$ and $^1A-^1B_b$ transitions.

TABLE 3.

Frequencies of absorption band maxima in solution of coronene, triphenylene and 1,2;5,6-dibenzanthracene.

	Coronene*		Triphenylene		1,2;5,6-dibenzanthracene*	
Solvent	$^1A\rightarrow{}^1L_b$	$^1A\rightarrow{}^1L_a$	$^1A\rightarrow{}^1L_b$	$^1A\rightarrow{}^1L_a$	$^1A\rightarrow{}^1L_b$	$^1A\rightarrow{}^1L_a$
n-pentane	23881	28381	29918	35214	25452	28781
n-hexane	23875	28341	29904	35168	25356	28740
n-heptane	23864	28329	29885	35112	25426	28715
isooctane	23892	28365	29906	35168	25442	28744
cyclohexane	23858	28289	29877	35075	25410	28662
benzene	23812	28110	29797	34886	25307	28421
dioxane	23858	28217	29864	35014	25371	28551
chloroform	23827	28145	29789	34922	25313	28490
diethylether	23892	28349	29900	35193	25429	28727
dichloromethane	23846	28129	29837	34983	25332	28612
ethanol	23886	28317	29972	35205	25410	28694
isopropanol	23898	28337	29909	35187	25465	28707
methanol	23898	28349	29936	35251	25439	28744
acetone	23881	28293	29918	-	25407	28686
NNDMFA	23852	28173	29855	34833	25336	28495
acetronitrile					25419	29711

- Ref.2.

TABLE 4.

Frequencies of absorption band maxima in vapor phase calculated from Nicol and Baur model (ν_I) and a linear relationship on refraction index of nonpolar solvents (ν_{II}).

Compound	band	ν_I, (cm^{-1})	ν_{II}, (cm^{-1})
Coronene	$^1A-^1L_b$	24161 ± 52	24067 ± 10
	$^1A-^1L_a$	29459 ± 196	29089 ± 28
Triphenylene	$^1A-^1L_b$	30455 ± 103	30222 ± 10
	$^1A-^1L_a$	36794 ± 199	36036 ± 28
1,2;5,6-Dibenzanthracene	$^1A-^1L_b$	25962 ± 151	25736 ± 32
	$^1A-^1L_a$	30163 ± 172	29731 ± 37

Again method I gave slightly higher values than method II, but the differences were not significant.

The complexity of the solvent interaction and the lack of a comprehensive theory that gives an accurate and general interpretation of spectral solvent shifts do not allow a simple explanation for the fact that method I gave generally higher values than method II.

However, methods I and II can be used to give upper and lower limits for the experimental value.

ACKNOWLEDGMENTS

We are grateful for the financial support from the Servicio de Desarrollo Cientifico, Artistico y de Cooperacion Internacional de la Universidad de Chile.

REFERENCES

1. R. G. E. Morales, Ph"D. Dissertation, Universidad de Chile, (1981).
2. R. G. E. Morales, J. Phys. Chem. (June, 1982) (in press).
3. W. West and A. L. Geddes, J. Phys. Chem., 68, 837 (1964).
4. M. E. Baur and M. Nicol, J. Chem. Phys., 44, 3337 (1966).
5. M. Nicol, J. Swain, Y. Shum, R. Merin and R. Chen. J. Chem. Phys., 48, 3587 (1968).
6. G. A. Gerhold and E. Miller, J. Phys. Chem., 72, 2737 (1968).