Polarizability Change in the Excited Electronic States of Nonpolar Aromatic Hydrocarbons

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A method for investigating the polarizability change in the excited electronic states of nonpolar aromatic hydrocarbons from spectral solvent shifts has been developed. Comparisons with electrochromic measurements of anthracene, coronene, and 1,2;5,6-dibenzanthracene in the first and the second electronic band are made.

Introduction

The effect of dispersion interactions on electronic absorption bands in solution have been measured and analyzed in order to determine the polarizability change involved in an electronic transition.[1-3]

Generally, condensed aromatic hydrocarbons have been selected as model systems in order to obtain insight into dispersive or inductive forces, but, unfortunately, the results have been interpreted in many different ways because of the approximations involved in the different theories of spectral solvent shift.[1,4]

In order to standardize the discussion of the solvatochromic results, this work presents an analysis of the magnitudes of the polarizability change in excited states based on electrochromic and solvatochromic data for anthracene, coronene, and 1,2;5,6-dibenzanthracene.

Method

Many reviews have treated the theoretical aspects of dispersion forces on the solvent shift effect.[1-7] Amos and Burrows some time ago[1] have discussed the application of London equation (eq 1) to molecular systems in different solvatochromic models. From London dispersion theory[8] the interaction energy between two particles, i.e., a solute molecule (u) and a solvent molecule (v), is given by

$$E = C\frac{\alpha_i^{u}\alpha^{v}}{r^6} \tag{1}$$

where α_i^{u} and α^{v} are the polarizabilities in the ith and the ground state, respectively, C is a constant for the system, and r represent the interaction radii.

Albeit the interpretation of C is not easy when eq 1 is extended to molecules, the dispersion part of the solvent shift of any particular solute molecule in a number of nonpolar solvents can be represented quite well by the semiempirical relation

$$\Delta\nu_{ij} = \theta(\alpha_i^{u} - \alpha_j^{u})\phi(n^2) \tag{2}$$

where

$$\phi(n^2) = \frac{n^2 - 1}{n^2 + 2} = \frac{4\pi N_0 d}{3M}\alpha^{v}$$

and $\phi(n^2)$ represents the solvent property, and $\Delta\nu_{ij} = \nu_{ij}$(gas) $- \nu_{ij}$ (solution), where ν_{ij} represents the energy differences in cm^{-1} between the ith and jth states of the solute.

If $(\alpha_i^{u} - \alpha_j^{u})$ is obtained from eq 2, θ must be obtained independently. Several studies have been made at this point and they show that C (eq 1), in general, can be considered the same for both ground and excited states.[1,7] Therefore our parameter θ is assumed to be independent of the involved electronic transition and so the following equation is obtained:

$$\Delta\alpha_{ij} = \frac{m_{ij}}{m_{kl}}\Delta\alpha_{kl} \tag{3}$$

where

$$\Delta\alpha_{ij} = (\alpha_i^{u} - \alpha_j^{u}) \qquad m_{ij} = \theta\Delta\alpha_{ij}$$

and m_{ij} is the slope corresponding to the linear relationship between $\Delta\nu_{ij}$ and $\phi(n^2)$.

Experimental Section

The absorption spectra were obtained with a Cary 17 recording spectrophotometer operated at room temperature (about 20 °C). The instrumental calibration is known to be accurate to better than ±2 Å and the reproducibility of the measurements reported was better than ±0.5 Å.

The chromophores anthracene, coronene, and 1,2;5,6-dibenzanthracene were obtained from Aldrich Chemical Co. and they were fractionally sublimed.

Vapor spectra of anthracene were obtained by heating the cell compartment and using a 10-cm cell with quartz windows compared to air as reference. The transition energies in the vapor-phase of coronene and 1,2;5,6-dibenzanthracene were determined from indirect measurements.[9] The solvents, spectroscopic grade, Uvasol Merck, were used without further purification.

Results and Discussion

The frequencies (cm^{-1}) of the electronic transitions in solution and in the vapor phase of anthracene, coronene, and 1,2;5,6-dibenzanthracene are presented in Table I.

A linear correlation between $\Delta\nu$ and $\phi(n^2)$ is shown in Figure 1 and 2 where the slopes have been determined by

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(6) A. Amos and B. Burrows, *Adv. Quantum Chem.*, **7**, 289 (1973).
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(9) Two models were used in order to obtain the frequencies of the absorption band maxima in the vapor phase of coronene and 1,2;5,6-dibenzanthracene: the Nicol and Baur model (solvent Stark effect) and a linear correlation between the frequencies of nonpolar solvents in solution and their refractive indexes. These results have been obtained from ref 17 and will be submitted for publication to *Spectrosc. Lett.*

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TABLE I: Frequencies of Absorption Band Maxima (cm^{-1}) and $\phi(n^2)$

solvent	anthracene[a]		1,2;5,6-dibenzanthracene		coronene		$\phi(n^2)$
	^1L_a-^1A	^1B_b-^1A	^1L_b-^1A	^1L_a-^1A	^1L_b-^1A	^1L_a-^1A	
vapor	27 643	42 497	25 736	29 731	24 067	29 089	
n-pentane	26 720	39 873	25 452	28 781	23 881	28 381	0.219 54
n-hexane	26 685	39 787	25 356	28 740	23 875	28 341	0.227 44
n-heptane	26 670	39 738	25 426	28 715	23 864	28 329	0.234 40
cyclohexane	26 613	39 580	25 410	28 662	23 858	28 289	0.254 91
benzene	26 399		25 307	28 421	23 812	28 110	0.293 07
dioxane	26 469	39 459	25 371	28 551	23 858	28 217	0.253 22
chloroform	26 406	39 222	25 313	28 490	23 827	28 145	0.265 06
ethyl ether	26 649	39 825	25 429	28 727	23 892	28 349	0.214 90
dichloromethane	25 445	39 339	25 332	28 612	23 846	28 129	0.253 64
ethanol	26 624	39 815	25 410	28 694	23 886	28 317	0.220 37
2-propanol	26 638	39 807	25 465	28 707	23 898	28 337	0.230 11
methanol	26 652	39 919	25 439	28 744	23 898	28 349	0.202 04
acetone	26 582		25 407	28 686	23 881	28 293	0.218 49
N,*N*-dimethylformamide	26 403		25 336	28 495	23 852	28 173	0.257 38
acetonitrile	26 592	39 841	25 419	28 711			0.210 50

[a] 0′-0″ transition.

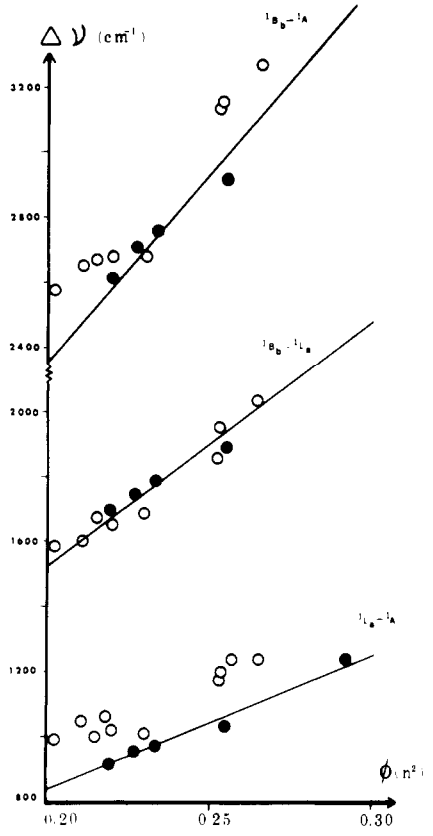

Figure 1. Solvatochromic effect of anthracene: (O) polar solvents; (●) nonpolar solvents. The ^1B_b-^1L_a electronic transition is calculated from the ^1B_b-^1A and ^1L_a-^1A electronic bands.

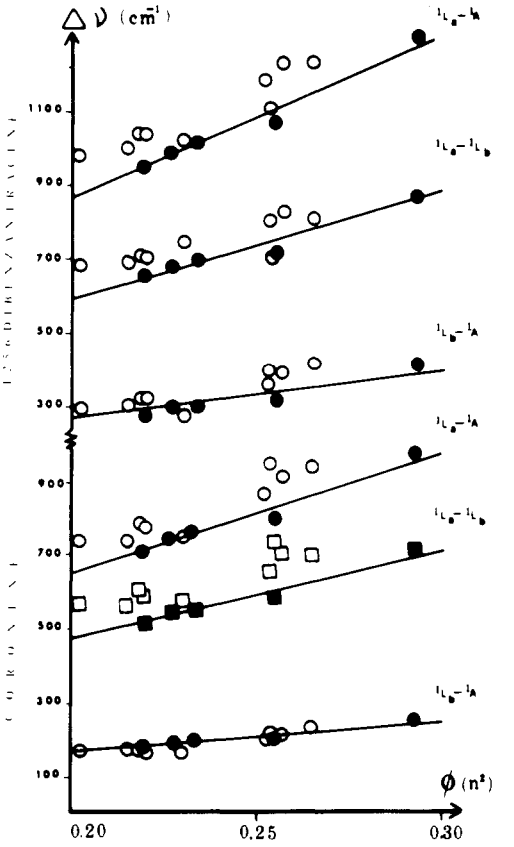

Figure 2. Solvatochromic effect of coronene and 1,2;5,6-dibenzanthracene: (O) polar solvents; (●) nonpolar solvents. The ^1L_a-^1L_b electronic transition is calculated from the ^1L_a-^1A and ^1L_b-^1A electronic bands.

considering only the nonpolar solvents and the origin.

If we assumed that the red shift of electronic absorption spectra in solution with respect to its position in the vapor phase for these nonpolar aromatic hydrocarbons is determined by dispersion interaction and inductive forces, then the plots in Figures 1 and 2 can be separated into two contributions. Thus the energy difference between the experimental values for each polar solvent and the straight line could be considered as a measure of the solvent Stark effect between the electronic states. An interesting case is observed between both ^1B_b and ^1L_a states of anthracene, where this electronic transition has been calculated from the difference between the ^1B_b-^1A and ^1L_a-^1A electronic bands (Figure 1). Here, the polar and nonpolar solvents show similar effects, therefore it can be considered that the solvent Stark effect between these states is surprisingly smaller than the dispersion interactions. The ^1L_b-^1A electronic band of coronene shows the same effect.

The van der Waals forces have been utilized in different spectral solvent shift theories with the purpose of determining polarizabilities in the excited states.[5,7,10,11] However, the two great approximations involved in these theories, the interaction radii and the London *C* constant, do not permit obtaining results with the required accuracy.

Nevertheless, when eq 3 is used to estimate the polarizability change produced in different excited states, a

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TABLE II: Polarizability Change in Different Electronic Transistions

compd	transition	$10^{-3}m$,[a] cm^{-1}	$\Delta\alpha$, Å^3	$\Delta\alpha$,[b] Å^3
anthracene	^1L_a-^1A	4.17 ± 0.07	36 ± 3[c]	1.2
	^1B_b-^1A	11.8 ± 0.2	(102 ± 8)[d]	3.2
	^1B_b-^1L_a	7.62 ± 0.11	(66 ± 6)	
coronene	^1L_b-^1A	0.82 ± 0.02	(8 ± 1)	0.4
	^1L_a-^1A	3.25 ± 0.07	33 ± 4[c]	1.5
	^1L_a-^1L_b	2.40 ± 0.05	(24 ± 3)	
1,2;5,6-dibenzanthracene	^1L_b-^1A	1.34 ± 0.07	(15 ± 2)	0.7
	^1L_a-^1A	4.34 ± 0.09	47 ± 5[c]	2.0
	^1L_a-^1L_b	3.00 ± 0.05	(32 ± 4)	

[a] See eq 3. [b] Suppan. Reference 9. [c] Electrochromic data, ref 12 and 13. [d] Values in parentheses are interpolated by using eq 3.

relative value can be obtained without having to know the aforementioned parameters.

Several workers have observed changes in the excited-state polarizability of nonpolar molecules from electrochromic measurements.[12-16] But normally the reported values are confined to one electronic absorption band and therefore it is not possible to observe a more general picture about these changes. Based on the high remarks (accuracy mainly) attained by electrochromic measurements, we used these data to estimate the polarizability change from our solvatochromic data.

Table II shows the slope obtained from Figures 1 and 2 for each electronic transition and their respective polarizability change.

A comparison with other experimental or theoretical data is desirable. Our values are higher than the results obtained by the solvent-shift method of Suppan,[2,7] which for anthracene, coronene, and 1,2;5,6-dibenzanthracene gives a much smaller $\Delta\alpha$ because of the parameter dependence on the solvent cavity radius thus introducing a large uncertainty.[17]

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