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Effects of Alkyl Substituents on the Excited States of Naphthalene: Semiempirical Study

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The effects of the successive addition of alkyl substituents (methyl and reduced rings) on the excited states of naphthalene are reported. The calculated electronic states of all the reduced derivatives with two, three, and four substituents are compared with the excited states of their methylated analogues. The excited states of several reduced derivatives with seven and eight substituents are also studied. The AM1 method was used to optimize the geometry of 57 naphthalene derivatives, and excited states were calculated with the ZINDO/S (INDO/S) method. ZINDO/S calculations on naphthalene gave excited states in better agreement with experimental results than with results of other semiempirical (CNDO/S and CNDOL) and ab initio (CIS, TD-HF, and TD-DFT) methods. Successive alkyl substitutions are accompanied by bathochromic displacements of the UV−visible bands, since the occupied orbitals are raised in energy more than the unoccupied orbitals. However, not all available substituent positions in naphthalene alter its orbital energy distribution in the same way when they are occupied by alkyl substituents. Distortion from planarity of the naphthalene skeleton of some reduced derivatives is the cause of “anomalous” bathochromic displacements of the absorption bands.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are aromatic compounds containing only carbon and hydrogen atoms in a series of interconnected rings. The alkyl-, amino-, halogen-, and nitro-substituted derivatives, along with the mono- and poly-N, -S, and -O heteroatomic analogues of PAHs, constitute a much larger and diverse class of molecules, the polycyclic aromatic compounds (PACs).[1] These materials are found in nature, e.g., in petroleum, and are generated by human activity, e.g., by combustion. Interest in PACs can be traced back to Michael Faraday’s isolation of benzene in 1825 and has continued to the present by virtue of the central role of the concept of aromaticity in the development of modern chemistry. The high incidence of scrotal cancer in chimney sweeps in England was noted more than 200 years ago and is now known to be due to the highly carcinogenic properties of some PAHs. To avoid the health hazards and to improve the efficiency of refining processes, it is imperative to have methods that can identify and determine the amount of PACs in various materials.

The petroleum industry is vitally interested in the identification and quantification of PACs in their source materials, final products, and intermediate process streams because these compounds interfere with petroleum refining operations by poisoning catalysts or building up in chemical reactors. They may also corrode refinery equipment and alter the odor and shelf lifetime of the final products. Environmental regulations to reduce toxic emissions also must be considered. This is of even greater importance in the oil sands industry because the aromatic content of these source materials is much higher than in most other forms of crude oil.

There are thousands of PACs in petroleum-related samples. Characterization of these compounds is extremely difficult because there are many similarities among them. Even if complete separation were possible, identification would still be difficult because in many cases standard compounds are not available for comparison and positive identification purposes. It has been proposed that PACs in oil sands samples are basically alkylated PAHs, mainly methyl- and ethyl-substituted PAHs, although it has also been suggested that partially hydrogenated PAHs (maybe with reduced rings as substituents) may be present as a consequence of the reduction process undergone by the samples during industrial treatment.[2] Furthermore, monoaromatic compounds with reduced rings have been found in chromatographic studies of heavy distillates.[3]

The presence of alkyl groups causes some problems in the identification of the species because the greater the number of rings the larger the number of possible alkylated isomers and the harder the labor of separation, identification, and quantification. State-of-the-art chromatographic methods are mainly used to separate and identify these compounds, incorporating UV−visible, laser fluorescence, and mass spectrometric detectors. However, all these isomers are indistinguishable from each other using mass spectrometry and there are few good reference electronic spectra available.

To complement our previous discussions[4] of the quadrupole moments of PAHs and their separation by chromatography, this paper focuses on the effect of alkyl substituents on the excited states of naphthalene, the smallest PAH. The effect of methyl and reduced-ring substituents (cyclic substituents that are completely reduced) on the electronic spectrum of naphthalene is examined. We are interested in studying the effect of the successive addition of methyl and reduced-ring substituents on the UV−visible spectrum of naphthalene. The calculated electronic spectra of all the reduced derivatives with two, three, and four substituents are compared with the spectra of their

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methylated analogues. The calculated excited states of several reduced derivatives with seven and eight substituents are also compared.

The electronic spectrum of naphthalene has been widely studied in both the vapor phase[5] and in solution.[6] Furthermore, a variety of theoretical calculations have been performed at different levels of theory: semiempirical[7] and ab initio.[8] Polymethylnaphthalenes have also been broadly studied in solution, but few UV−visible spectra of reduced-ring naphthalene derivatives have been reported.[9,6b−d] The effects of $-OH$, $-NH_2$, $-CN$, and $-CHO$ substituents on the electronic spectra of naphthalene have been theoretically analyzed and interpreted by the method of configuration analysis.[10] A systematic theoretical study of the effects of alkyl substituents on the excited states of naphthalene has not been previously reported.

We have also decided to use alkylated naphthalenes as a test case study to locate properties of the electronic spectra with respect to individual substituent positions. These results could prove useful in studies of larger systems where the wavelengths are longer and differences in wavelength due to changes in the positions of alkyl substituents are more likely to be detected and identified.

A total of 57 compounds, listed in Figure 1, were included in this study. For ease of identification these compounds were labeled in alphabetical order according to the number of substituents in the ring. Methylated isomers have also been identified with a number. To distinguish between a methylated naphthalene and its reduced analogues (a reduced naphthalene with the same number and position of substituents linked to the ring), the same letter and number is used, but a subscript is added to the label of the reduced compounds. Hence, labels such as **E2**, $\mathbf{E_r2}$ and $\mathbf{E_r2'}$ identify a methylated compound (**E2**) and its reduced analogues ($\mathbf{E_r2}$ and $\mathbf{E_r2'}$), all with four substituents connected to the ring in the same positions. For molecules of the series **H** and **I**, the same subscript is used for the reduced analogues, but the number in the label of the reduced compounds has no relation to the alkylated analogues.

Computational Details

Because of the size of the molecules chosen for this study (up to 32 heavy atoms), a semiempirical SCF-MO Hamiltonian was selected for the geometry optimizations of all substituted naphthalenes. Various semiempirical techniques have previously been used for the geometry optimization of naphthalene.[7e] The AM1[11] optimized geometry of naphthalene is closest to experiment, and therefore, all the naphthalene derivatives are optimized at the AM1 level as implemented in the MOPAC, v. 6.0, program package.[12]

Excited electronic states of naphthalene are calculated using the semiempirical methods for which the appropriate software is available: CNDO/S,[13] CNDOL,[14] and ZINDO/S (also known as INDO/S),[7b,15] employing the AM1 optimized geometry. For the CNDO/S and CNDOL methods, as implemented in the program NDOL,[16] 48 lowest-energy singly excited configurations (the maximum number of configurations possible due to constraints of the program) are considered in the CIS procedure. For the ZINDO/S method, as implemented in HyperChem, v. 5.0,[17] values of 1.267 and 0.585 are employed for the empirical overlap weighting factors f_σ and f_π,[7b] respectively. Moreover, an energy criterion of 13.0 eV for the maximum excitation energy (MEE) of the configurations included in the CIS procedure (this selection will be explained in the following section) is chosen.

Excited states of naphthalene are also calculated by means of ab initio CIS,[18,19] time-dependent Hartree−Fock (TD-HF), and density functional theory (TD-DFT),[20] as implemented in Gaussian 98,[21] with Pople's 6-31+G(d) basis set. The DFT calculations are performed using Becke's three-parameter exchange functional (B3)[22] in combination with the Lee, Yang, and Parr correlation functional (LYP).[23]

For the cases where experimental results are available, we have chosen to compare our results with experimentally determined $\bar{\nu}_{\max}$ (or $\lambda_{\max}$) rather than $\bar{\nu}_{o-o}$ (λ_{o-o}) values where possible.[7b]

For the substituted naphthalenes the calculation of excited states is performed with the ZINDO/S method using the specifications previously mentioned. The MEE is set to 12 eV for those compounds with more than three nonaromatic rings (series **F**, **G**, **H**, and **I**), and for the rest of the molecules the MEE is equal to 13 eV. This change is made in order to include approximately the same number of singly excited configurations for each compound.

To simplify the notation for the orbitals, the occupied MOs in the ground-state configuration will be called H, H1, H2, ... starting from the HOMO, and the unoccupied MOs will be called L, L1, L2, ... starting from the LUMO. Thus, H1 denotes the HOMO-1 orbital and L2 denotes the LUMO + 2 orbital.

Results and Discussion

1. Excited States of Naphthalene. All the singlet transitions calculated at several semiempirical levels with excitation energies (ΔE) smaller than 5.30 μm^{-1} are reported in Table 1, along with their intensities in terms of the oscillator strength (f). For the ab initio calculations the first eight singlet excited states are reported. Some experimental results in the vapor phase are also summarized.

The ab initio (CIS and TD-HF) calculations give higher excitation energies than the semiempirical methods. TD-DFT excitation energies are in good agreement with those from experiment, but the intensities are not well reproduced. Many more transitions than those observed are predicted with CNDO/S and CNDOL, and their agreement in position and intensity with experiment is not as good as those predicted with ZINDO/S. This is why the excited states of the alkylated naphthalenes are studied with the ZINDO/S method.

It was previously shown that a singles-only CI calculation (CIS) using the ZINDO/S approximation accurately reproduces the optical spectrum of naphthalene.[7b,c,e] In refs 7b and 7c, single excitations that lie within ~6.50 μm^{-1} of the ground state were included in the CI calculation, as well as some additional selected configurations of the symmetry type of interest (50−70 configurations). In ref 7e a full CIS calculation (including all possible singly excited configurations within the 24 occupied and 24 unoccupied MOs of naphthalene) was performed, but results were in poorer agreement with the experiments (Table 2). The symmetry of the calculated excited states is also related to the number of configurations included.

Because of these differences, a study of the energy criterion for the selection of single excitations is performed in order to determine the best conditions (considering the quality of the results and the computational time) under which the ZINDO/S method gives results closest to experiment for the excited states of naphthalene. Thus, calculations are performed including singly excited configurations at 11 different maximum excitation energies (MEEs) and within 15−15 (15 occupied MOs and 15 unoccupied MOs) and 20−20 subsets of MOs. The number of configurations (no. conf) considered in each calculation has also been included in Table 3.

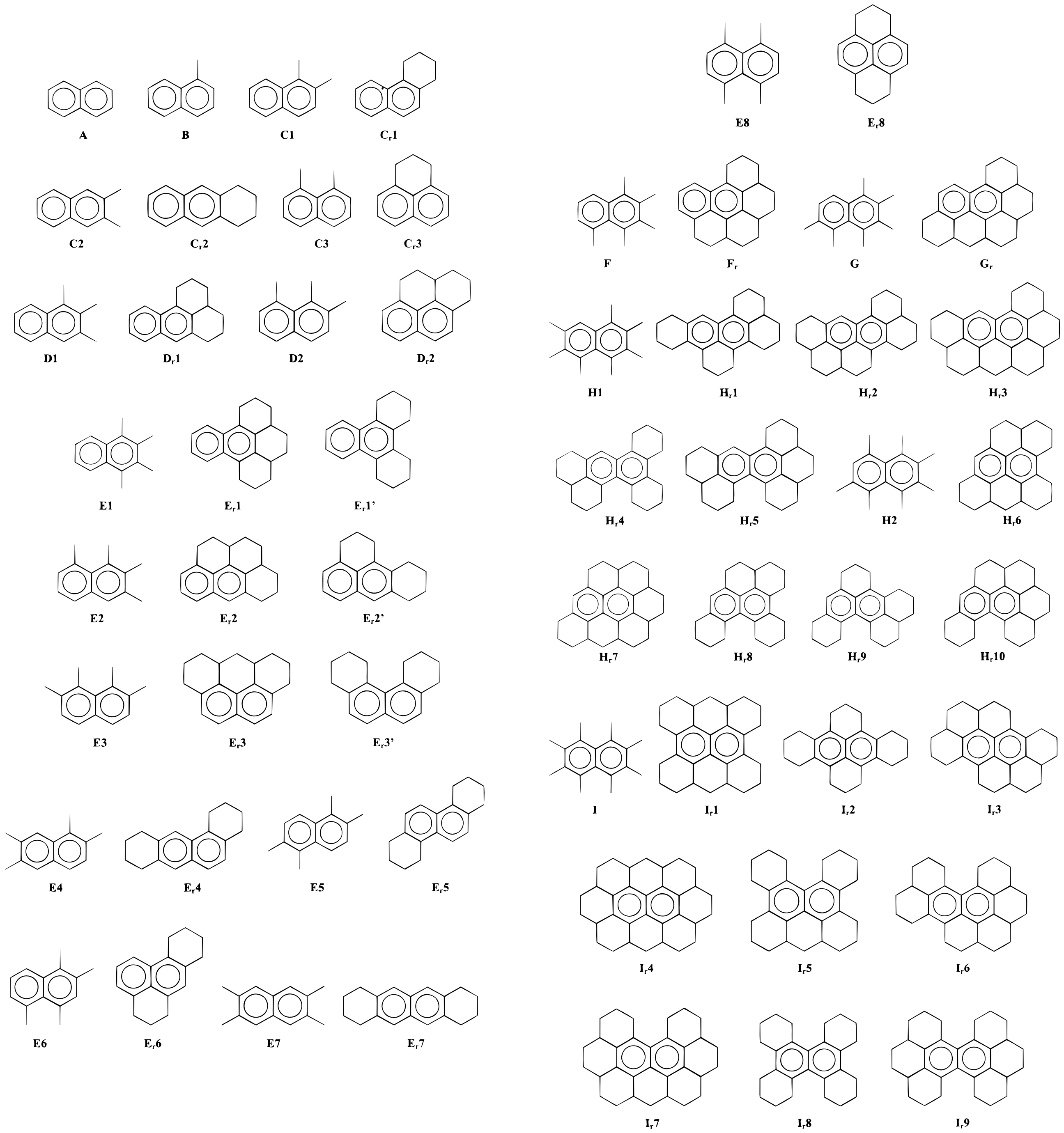


Figure 1. Molecules studied and their labels.

When the number of configurations included in the CIS procedure is increased, the calculated excitation energies decrease. However, the energy does not decrease variationally (i.e., excitation energies are not closer to the exact value when an improved procedure is used), since the ZINDO/S single-point calculation uses a parametrized (semiempirical) Hamiltonian. The inclusion of more than the "necessary" configurations is useless because the calculated excited states are in poorer agreement with experiment. Thus, it is important to determine the number of singly excited configurations that have to be included in the CIS procedure. It was also found in our study that the position and intensity of the calculated bands are very dependent on the values given to the overlap weighting factors, especially f_π.

The best agreement with experiment at the lowest computational cost was found to occur with a MEE of 13 eV. Details of the calculated spectrum with this MEE are reported in Table 2. These results are in excellent agreement with those reported by Ridley and Zerner[7b,c] and with the five $\pi-\pi^*$ transitions observed in the vapor spectrum.[5c] The calculations indicate a forbidden $\pi-\sigma^*$ band at 5.05 μm^{-1} ($^1B_{1g}$) and forbidden $\pi-\pi^*$ bands at 4.46 μm^{-1} (^1A_g), 4.62 μm^{-1} ($^1B_{3g}$), and 5.22 μm^{-1} ($^1B_{3g}$).

The only difference between experiment and calculation is the symmetry assigned to a band reported at 5.26 μm^{-1} by George and Morris.[5c] On the basis of PPP calculations[7a] and the intensity of the band, it was assigned as $^1B_{2u}$. However, Ridley and Zerner [7b] explain this band by suggesting that it is $^1B_{3g}$ and that it borrows intensity from the $^1B_{1u}$ band at 4.91 μm^{-1} through one of the b_{2u} modes.

Although Rydberg states have been identified to appear from 5.40 μm^{-1} for naphthalene,[5c] the assignment of the last two

TABLE 1: Position (ΔE in μm^{-1}) and Intensity (f) of Calculated and Experimental (in Vapor Phase) Excited States of Naphthalene

ΔE (f)							
calculated						experimental	
CIS(FC) 6-31+G(d)	TD-HF 6-31+G(d)	TD-DFT B3LYP/6-31+G(d)	CNDO/S (48 conf)[a]	CNDOL (48 conf)[a]	ZINDO/S (63 conf)[a]	absorption (vapor)[5c]	neon matrix[5f]
4.16 (0.090)	3.91 (0.015)	3.55 (0.009)	3.54 (0.006)	3.34	3.26 (0.006)	3.20 (0.002)	3.21 (0.07)
4.29	4.12	3.63	3.91 (0.101)	3.89	3.72 (0.162)	3.75 (0.102)	3.58 (0.13)
5.00	4.99	4.41	4.36	3.90	4.46		
5.20	5.08	4.44	4.44	3.92 (0.001)	4.60 (1.956)	4.75 (1.0)	4.73 (1.72)
5.30	5.29	4.66	4.74	3.93 (0.028)	4.62		
5.32	5.29 (0.301)	4.73	4.76	3.96	4.91 (0.676)	4.95 (0.3)	4.91 (0.60)
5.60 (2.154)	5.31	4.96	4.78 (0.902)	4.24 (0.002)	5.05		
5.62 (0.062)	5.50 (0.094)	5.02 (0.003)	4.86	4.46	5.22	5.26 (0.1)	
			4.87	4.50			
			5.03	4.60			
			5.18 (0.357)	4.63			
			5.25	4.81			
				4.91			
				4.93 (0.018)			
				5.02			
				5.18			
				5.28			

[a] Number of configurations included in the CIS calculation.

TABLE 2: ZINDO/S Calculations on Naphthalene

this work (MEE = 13 eV) (63 conf)[a]						ref 7b,c (50−70 conf)[a]		ref 7e (full-CIS) (1153 conf)[a]		experiment[5c]	
state	configurations	conf[b] (c^2)	type	λ (nm)	ΔE[c] (f)[d]	state	ΔE[c] (f)[d]	state	ΔE[c] (f)[d]	state	ΔE[c] (f)[d]
$^1B_{2u}$	$1a_u \rightarrow 2b_{2g}$ $2b_{3u} \rightarrow 2b_{1g}$	H−L1 (0.55) H1−L (0.43)	$\pi\pi^*$	307.2	3.26 (0.006)	$^1B_{2u}$	3.25 (0.002)	$^1B_{3u}$	3.23 (0.003)	$^1B_{2u}$	3.20 (0.002)
$^1B_{1u}$	$1a_u \rightarrow 2b_{1g}$	H−L (0.88)	$\pi\pi^*$	268.6	3.72 (0.162)	$^1B_{1u}$	3.77 (0.148)	$^1B_{2u}$	3.39 (0.166)	$^1B_{1u}$	3.75 (0.102)
$1A_g$	$2b_{3u} \rightarrow 3b_{3u}$ $1b_{2g} \rightarrow 2b_{2g}$	H1−L2 (0.56) H2−L1 (0.28)	$\pi\pi^*$	224.1	4.46	^1A_g	4.48	$^1B_{3u}$	4.28 (1.590)		
$^1B_{2u}$	$1a_u \rightarrow 2b_{2g}$ $2b_{3u} \rightarrow 2b_{1g}$	H−L1 (0.42) H1−L (0.55)	$\pi\pi^*$	217.5	4.60 (1.956)	$^1B_{2u}$	4.58 (1.866)	$^1B_{1g}$	4.29	$^1B_{2u}$	4.75 (1.0)
$^1B_{3g}$	$1a_u \rightarrow 3b_{3u}$	H−L2 (0.80)	$\pi\pi^*$	216.6	4.62	$^1B_{3g}$	4.67	^1A_g	4.45		
$^1B_{1u}$	$2b_{3u} \rightarrow 2b_{2g}$	H1−L1 (0.87)	$\pi\pi^*$	203.7	4.91 (0.676)	$^1B_{1u}$	4.86 (0.672)	$^1B_{2u}$	4.53 (0.563)	$^1B_{1u}$	4.95 (0.3)
$1B_{1g}$	$1a_u \rightarrow 5b_{1u}$	H−L4 (0.95)	$\pi\sigma^*$	198.1	5.05	$^1B_{1g}$	5.27	$^1B_{3g}$	4.93		
$^1B_{3g}$	$1b_{2g} \rightarrow 2b_{1g}$	H2−L (0.96)	$\pi\pi^*$	191.5	5.22	$^1B_{3g}$	5.27	$^1B_{1g}$	4.95	$^1B_{2u}$	5.26 (0.1)

[a] Number of configurations included in the CIS calculation. [b] Dominant configurations of each CIS state. [c] Units are μm^{-1}. [d] f is intensity.

excited states (Table 2) in terms of dominant singly excited configurations could change if more flexible and computationally expensive ab initio methods with proper one-electron basis sets including Rydberg functions are used. Even the assignment to the other excited states would change if other levels of theory are employed[8c,d] or if more singly excited configurations are included in the CIS procedure.[7e] This situation would also be applicable to the excited states of the naphthalene derivatives studied.

2. Effects of Alkyl Substituents on the Excited States of Naphthalene. Since the degree of reproducibility of the excited states of naphthalene with the chosen method was excellent, it is expected that calculations on alkylated naphthalenes will also be in good agreement with experiment if a similar number of singly excited configurations is included in the CIS procedure because the π framework is the same. Hence, the main characteristics of the UV−visible spectrum of naphthalene, in terms of the dominant configurations in each CIS state, should be reproduced.

Vapor-phase spectra have not been reported for any of the naphthalene derivatives included in our study. Experimental results for polymethylnaphthalenes in hydrocarbons[9] have been reported, and we have used some of them to compare the quality of our calculations. In Table 4 the absorption band maxima reported for some di- and trimethylnaphthalenes are shown along with our ZINDO/S results.

The ZINDO/S calculations are in very good agreement with experimental results. Small differences can be attributed to the presence of solvent (even nonpolar solvents can alter slightly the spectra of PAHs). Qualitative changes in the position and intensity of the maxima reported are very well described. The bathochromic and hyperchromic displacements exhibited due to increasing the number of substituents in α positions (see Figure 2a) are very well reproduced.[9b,24] The excited states of alkylated naphthalenes can also be calculated accurately with the ZINDO/S method.

2.1. Methylated and Reduced Series of Substituents. The first eight singlet excited states of the series of methylated and reduced-ring naphthalenes were calculated. Alkylation starts from position 1 and continues successively to position 8 (see Figure 2b). The displacement of the calculated UV−visible bands when increasing the number of alkyl substituents on the naphthalene ring is shown in Figures 3 and 4 for both series. Every transition has been identified in terms of the dominant singly excited configurations (e.g., H−L1/H1−L, H−L, etc.).

To obtain more information about the effects of alkyl substituents on the MOs of naphthalene, the ZINDO/S orbital energies of H2, H1, H, L, L1, L2, L4, and L5 of both series are plotted, as well as the calculated transition energies (based on orbital energy differences) of the dominant configurations of the excited states (the transition H−L5 is also included). This information appears in Figures 5 and 6.

TABLE 3: ZINDO/S Excited States of Naphthalene Using Various Energy Criteria for the Selection of the Singly Excited Configurations

MEE[a] (eV)	9.0	9.5	10.0	10.5	11.0	11.5	12.0
no. conf[b]	7	11	11	17	23	29	41
ΔE (f)[c] (in μm^{-1})	3.31 (0.002)	3.31 (0.002)	3.31 (0.002)	3.31 (0.002)	3.31 (0.002)	3.30 (0.004)	3.30 (0.004)
	3.89 (0.501)	3.75 (0.185)	3.75 (0.185)	3.75 (0.185)	3.75 (0.185)	3.75 (0.185)	3.74 (0.163)
	4.64 (2.068)	4.64 (2.068)	4.64 (2.068)	4.62	4.53	4.53	4.46
		4.64	4.64	4.64 (2.068)	4.62	4.60 (1.968)	4.60 (1.968)
		4.95 (0.932)	4.95 (0.932)	4.89	4.64 (2.068)	4.62	4.62
				4.95 (0.932)	4.95 (0.932)	4.95 (0.932)	4.91 (0.676)
				5.23	5.09	5.09	5.05
					5.23	5.23	5.23

MEE[a] (eV)	13.0	14.0	15.0	16.0	15−15[d]	20−20[d]
no. conf[b]	63	85	123	171	451	801
ΔE (f)[c] (in μm^{-1})	3.26 (0.006)	3.22 (0.003)	3.21 (0.003)	3.21 (0.003)	3.21 (0.003)	3.21 (0.004)
	3.72 (0.162)	3.72 (0.161)	3.71 (0.163)	3.70 (0.164)	3.65 (0.183)	3.53 (0.176)
	4.46	4.46	4.46	4.46	4.41 (1.711)	4.33 (1.723)
	4.60 (1.956)	4.60 (1.966)	4.54 (1.837)	4.53 (1.833)	4.46	4.43
	4.62	4.62	4.62	4.61	4.53	4.45
	4.91 (0.676)	4.91 (0.677)	4.86 (0.646)	4.86 (0.643)	4.71 (0.623)	4.61 (0.630)
	5.05	4.98	4.98	4.94	4.92	4.91
	5.22	5.22	5.22	5.21	5.09	5.01

[a] Maximum excitation energy. [b] Number of configurations considered. [c] f is intensity. [d] Occupied and unoccupied MOs included in the production of singly excited determinants.

TABLE 4: Absorption Band Maxima of Some Di- and Trimethylnaphthalenes: ZINDO/S Calculations and Experimental Results[d]

		calculated		experimental	
substitution	compound	λ (nm)[c]	f[e]	λ_{max} (nm)	log ϵ
αα	1,4-dmn[a]	286	0.217	289	3.88
	1,5-dmn	280	0.218	287	3.96
	1,8-dmn	283	0.226	285	3.85
αβ	1,2-dmn	275	0.157	285	3.77
	1,3-dmn	278	0.176	283	3.78
	1,6-dmn	278	0.173	281	3.80
	1,7-dmn	280	0.185	280	3.80
$\beta\beta$	2,3-dmn	275	0.126	278	3.71
	2,6-dmn	274	0.149	274	3.67
	2,7-dmn	276	0.130	275	3.69
ααα	1,4,5-tmn[b]	291	0.251	292	3.90
ααβ	1,4,6-tmn	287	0.202	290	3.82
α$\beta\beta$	1,3,6-tmn	279	0.149	284	3.70
$\beta\beta$α	2,3,5-tmn	280	0.150	283	3.87
α$\beta\beta$	1,3,7-tmn	281	0.178	280	3.74
$\beta\beta\beta$	2,3,6-tmn	277	0.116		

[a] dmn = dimethylnaphthalene. [b] tmn = trimethylnaphthalene. [c] H−L transition. [d] Reference 9a,b,d. [e] f is intensity.

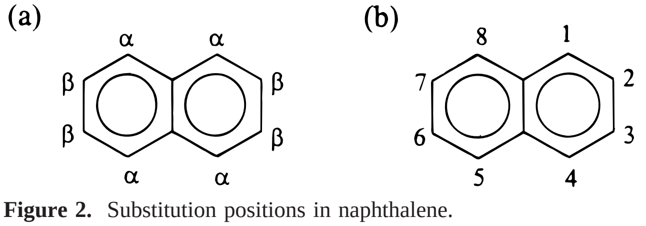


Figure 2. Substitution positions in naphthalene.

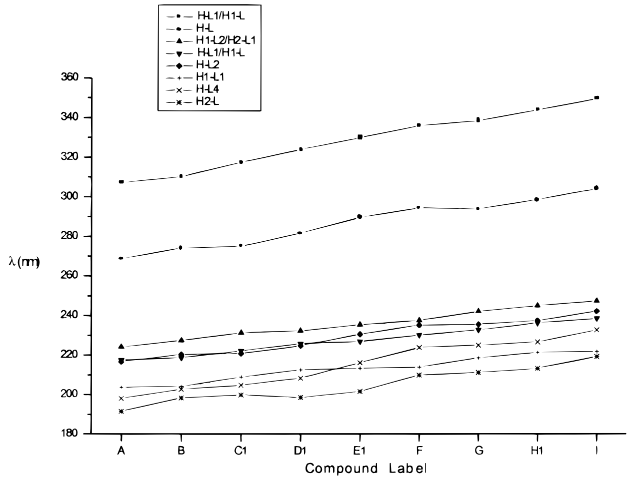


Figure 3. Displacement of the calculated transitions of the methylated series of naphthalenes.

The composition of the calculated CIS states for all the compounds studied is basically the same as that obtained for naphthalene, although there are some differences in position, intensity, and CIS coefficients, as expected. This situation made possible the comparative study of the excited states of naphthalene upon substitution.

As the number of substituent alkyl groups increases, there is a general shift toward longer wavelengths, in accordance with observations of Mosby[9b] and Laszlo[9c] on methylnaphthalenes and of Askew on methylphenanthrenes.[25] The greatest bathochromic change is obtained in the long-wavelength bands of the spectra, as reported from experiments.[6d]

In these substituents all C atoms have sp^3 hybridization. The atom connected to the naphthalene ring is linked to an sp^2 C atom. The latter is more electronegative than the former because the "s" content in sp^2 hybrid orbitals is higher than in sp^3 orbitals. Hence, a positive inductive effect transfers electronic density from the substituents to the ring, increasing the energy of the MOs and destabilizing the molecule from a kinetic point of view; e.g., reactivity toward electrophilic aromatic substitution reactions is increased.

As can be seen from Figures 5a and 6a, the energy of the occupied MOs (H, H1, and H2) increases with the number of substituents. The unoccupied MOs L, L1, and L2 (of π symmetry) also increase in energy but not by as much as the occupied orbitals, and L4 and L5 (unoccupied MOs of σ symmetry) show a slight decrease in energy.

As a consequence of the changes produced in the energy of the MOs of these molecules with an increase in the number of

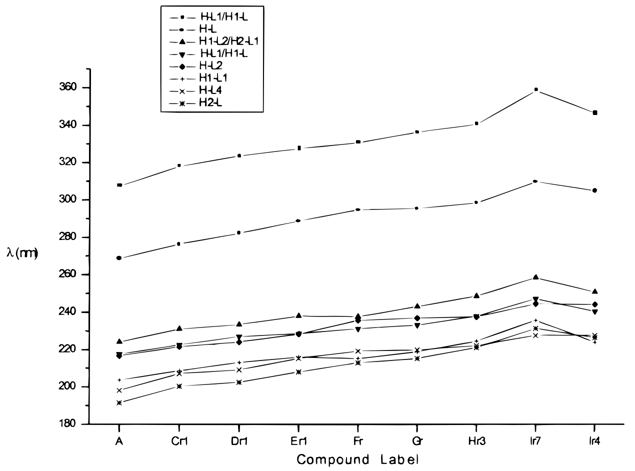


Figure 4. Displacement of the calculated transitions of the reduced series of naphthalenes.

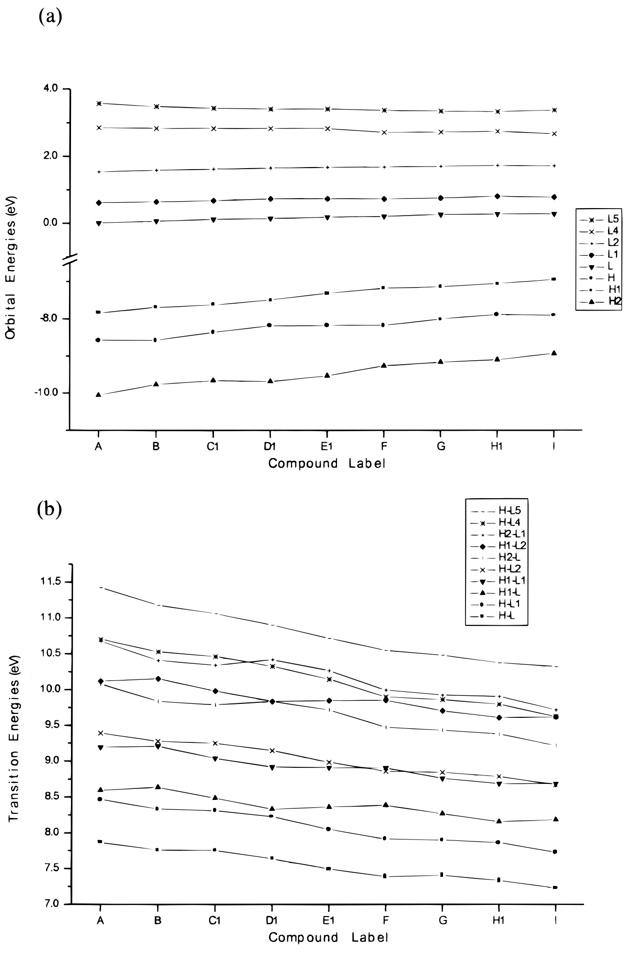


Figure 5. Orbital (a) and transition energies (b) of the methylated series of naphthalenes.

substituents (Figures 5a and 6a), the energy of the electronic transitions decreases (Figures 5b and 6b) and bathochromic displacements of the calculated UV−visible bands are obtained (Figures 3 and 4).

In the methylated series, it can also be seen (Figure 3) that the addition of methyl groups to positions 2 and 6 provokes less pronounced (or almost zero) red shifts in those states where H and H2 are the only dominant initial MOs (transitions H−L, H−L2, H−L4, and H2−L). Something similar occurs in the reduced series (Figure 4) when position 6 is occupied (when going from $\mathbf{F_r}$ to $\mathbf{G_r}$). The same situation is observed when the transition energies are analyzed (Figures 5b and 6b). Transitions from H and H2 show very little change in energy, while a much greater decrease in energy is obtained for transitions from H1. This is very important because it could be possible to determine from some absorption bands if position 2 or 6 is alkylated even in molecules with different numbers of alkyl substituents, e.g., 2,6,7-trimethylnaphthalene (equivalent to 2,3,6-trimethylnaphthalene) and 2,7-dimethylnaphthalene (see the calculated transitions in Table 4). This situation corroborates the fact that the strength of the electronic interaction between a substituent and the aromatic ring, as well as the perturbation of MOs, is very dependent on the position being substituted.[9b,24]

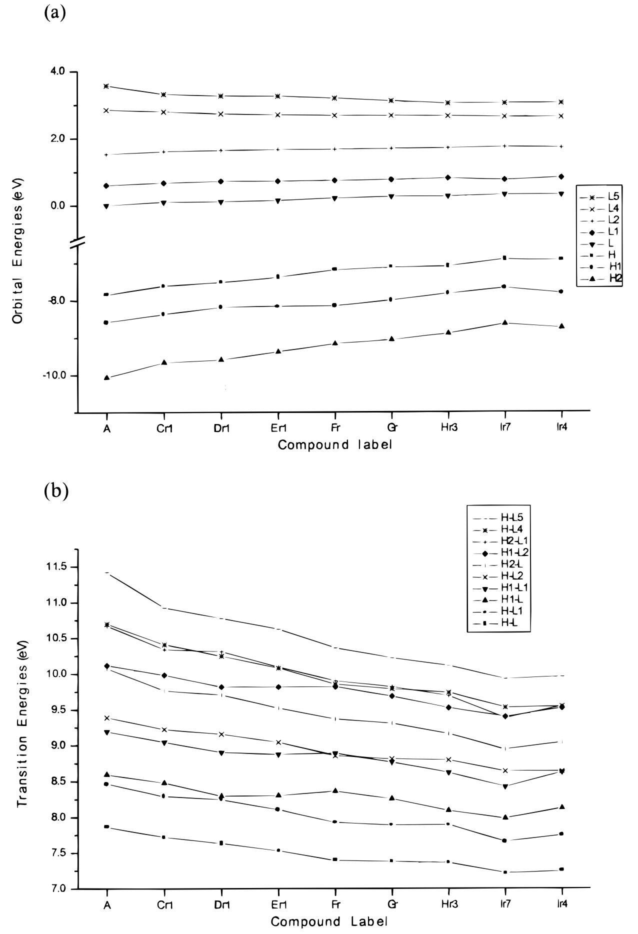
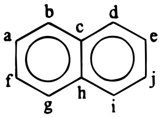


Figure 6. Orbital (a) and transition energies (b) of the reduced series of naphthalenes.

Another important observation is the difference found between $\mathbf{I_r7}$ and $\mathbf{I_r4}$ (Figure 4). It is expected that the wavelengths of $\mathbf{I_r7}$ will be smaller (following the trends noted above) or equal (since they have the same number of substituents on the naphthalene ring) to the values obtained for $\mathbf{I_r4}$. The only structural difference between these compounds is the planarity of the aromatic area. Four dihedral angles can be defined to characterize the coplanarity (or noncoplanarity) of the fused rings in naphthalene. These angles and their absolute values for the reduced series of compounds are displayed in Table 5. All the methylated naphthalenes included in this study are assumed to be planar. From these results it can be inferred that the contrasting distortion from planarity in $\mathbf{I_r7}$ (maximum of 17°) is the cause of the “anomalous” (higher than expected) wavelength values. In $\mathbf{I_r7}$ orbital energies of occupied MOs are higher than in $\mathbf{I_r4}$ and the overall effect causes the reduction of the transition energy values and CIS energies. It seems that the presence of the alkyl bridge between the fused rings in

TABLE 5: Dihedral Angles *d* (in Degrees) of the Optimized Structures of the Reduced Series



label	C_r1	D_r1	E_r1	F_r	G_r	H_r3	I_r7	I_r4
d(a,b,c,d)	179.7	179.2	177.4	179.4	178.4	179.2	163.0	176.1
d(b,c,d,e)	177.9	179.2	179.3	178.9	176.8	176.6	169.0	172.9
d(f,g,h,i)	179.3	178.6	177.5	179.5	176.7	173.2	172.9	174.0
d(g,h,i,j)	179.3	179.8	178.9	175.6	175.5	167.3	178.7	175.0

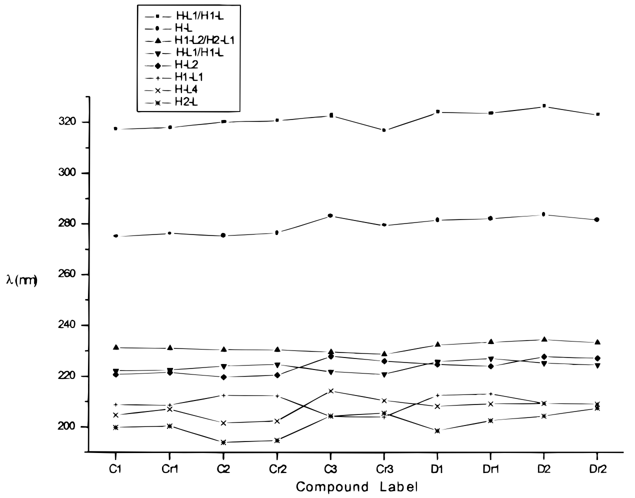


Figure 7. Displacement of the calculated transitions of the series **C** and **D**.

naphthalene (in $\mathbf{I_r4}$) equilibrates the tensions provoked by the six-member rings and favors a more planar conformation of the aromatic skeleton. In cases where greater distortions from planarity are obtained, greater differences between the positions of the UV−visible bands should be found. This will be discussed further in the next section.

2.2. Comparison of the Effects of Methyl and Reduced Substituents. To compare the effects of methyl and reduced substituents on the excited states of naphthalene, the absorption spectra of all possible reduced derivatives with two, three, and four substituents on the aromatic ring, as well as their methylated analogues, were calculated.

The wavelengths of the calculated bands are shown in Figures 7 and 8. The values of the dihedral angles that define the fusion of the benzene rings in naphthalene are shown in Table 6.

It can be seen from the series **C**, **D**, and **E** (in the methylated and reduced derivatives) that an increase in the number of α substituents leads to longer wavelengths, especially in those transitions where H and H2 are the only dominant initial MOs, e.g., in the order **C2**, **C1**, **C3**, with their respective reduced derivatives, also from **D1** to **D2**, and in the order **E7**, **E4**, **E5**, **E6** to **E8**. This situation has been experimentally observed for methylnaphthalenes,[9b] and it has been explained in terms of the conjugating power[26] of the various positions.

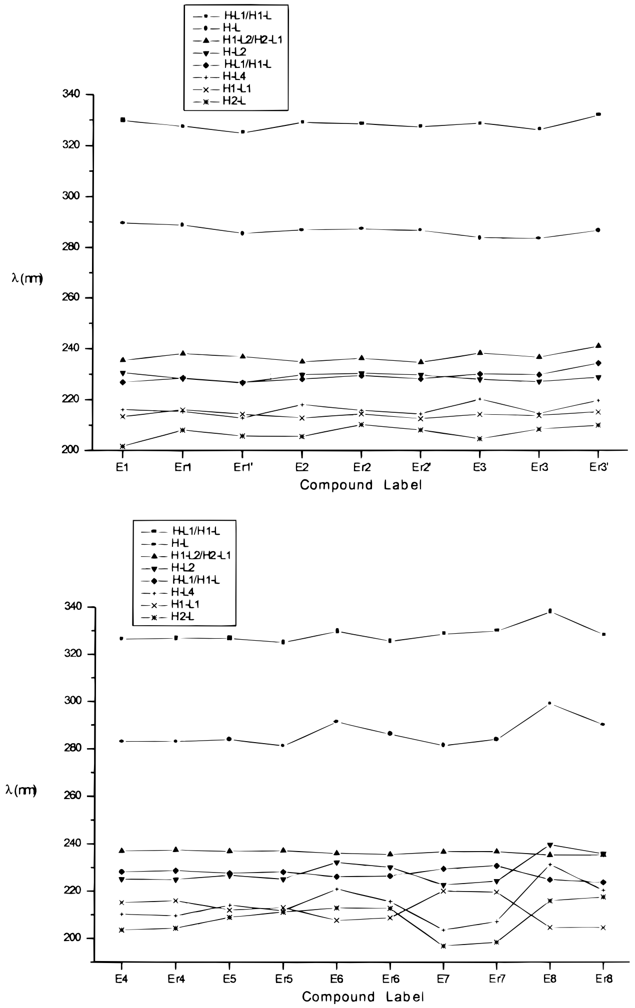
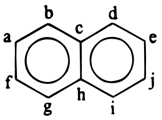


Figure 8. Displacement of the calculated transitions of the series **E**.

TABLE 6: Dihedral Angles *d* (in Degrees) of the Optimized Structures of the Reduced Series C, D, and E



label	C_r1	C_r2	C_r3	D_r1	D_r2	E_r1	E_r1'	E_r2
d(a,b,c,d)	179.7	179.9	179.7	179.2	179.7	177.4	178.9	179.8
d(b,c,d,e)	177.9	180.0	179.7	179.2	177.2	179.3	177.8	175.7
d(f,g,h,i)	179.3	179.8	179.8	178.6	179.1	177.5	178.9	179.9
d(g,h,i,j)	179.3	179.9	179.8	179.8	179.1	178.9	177.8	178.5

label	E_r2'	E_r3	E_r3'	E_r4	E_r5	E_r6	E_r7	E_r8
d(a,b,c,d)	179.6	177.3	169.0	179.3	179.8	179.8	179.7	179.9
d(b,c,d,e)	177.6	177.3	169.0	177.7	176.7	177.4	179.8	179.8
d(f,g,h,i)	179.4	178.0	177.7	179.4	176.7	178.9	179.8	179.9
d(g,h,i,j)	179.0	178.0	177.7	179.8	179.9	178.9	179.8	179.9

When an energy cutoff is used to determine the number of configurations to include, the smaller the difference in energy between the occupied and virtual orbitals, the greater the number of configurations that will be considered important. The excited states of the reduced compounds of the series **C**, **D**, and **E** are calculated with more configurations than their methylated analogues, using the same energy criterion (MEE = 13 eV). It could be expected that the MOs in the former are closer in energy and that the transition energies also are smaller. However, there are no significant differences or trends in the wavelengths of methylated and reduced derivatives in these series (Figures 7 and 8). It shows us that there are no major shifts of the energies of the π MOs and that the σ MOs become closer in energy because of the presence of reduced substituents. Moreover, small distortions from planarity are observed in the reduced molecules (Table 6), especially in the series **C** and **D** (maximum distortion of 2.8°). In the molecules with greater distortion: $\mathbf{E_r5}$ (3.3°), $\mathbf{E_r2}$ (4.3°), and $\mathbf{E_r3'}$ (11°), longer wavelengths are obtained in most of the calculated transitions (although the differences are small). The greater the distortion, the greater the red shift of the calculated bands.

In those cases where a reduced cycle forms a bridge between the fused benzene rings (e.g., **C_r3**, **D_r2**, **E_r2′**, **E_r3**, **E_r6**, and **E_r8**), the wavelengths are slightly shorter than in the methylated analogues. In **E_r8** the change is greater because reduced cycles are present in both bridge positions. In **E_r2** this situation is not observed perhaps because of the slight distortion from planarity.

The wavelengths of the reduced analogues of the same methylated compound, with more cycles (**E_r1**, **E_r2**), are longer than the wavelengths of their partners (**E_r1′**, **E_r2′**). For **E_r3** and **E_r3′** this situation is inverted because of the distortion from planarity observed in **E_r3′** (11°).

For the reduced molecules with two, three, and four substituents significant distortions from planarity are not observed (except for **E_r3′** where up to 11° of distortion is obtained). To explore the possible relationship between the planarity of the substituted naphthalene skeleton and the bathochromic displacement of the calculated UV−visible bands upon substitution, derivatives with seven and eight substituents (series **H** and **I**) were studied. The greater the number of methyl groups, the greater the number of reduced analogues that can be found. Moreover, the greater the number of reduced substituents, the greater the probability of distortion from planarity of the aromatic skeleton. Only a subset of all possible reduced compounds with seven and eight substituents was examined. It is expected that the degree of distortion will depend on the number and positions of the reduced substituents present.

The calculated transitions for the series **H** (**H1** and **H2**) and **I** are shown in Figures 9 and 11. Orbital energies are displayed in Figures 10 and 12. Dihedral angles that define the degree of planarity of the naphthalene center and the distances between the farthest points in naphthalene (another criterion to measure distortion from planarity) are reported in Table 7.

Compounds of the series **H1**, **H2**, and **I** are labeled from the shortest to the longest wavelengths. The geometrical parameters that characterize the degree of planarity of the aromatic center show that, in general, the greater the distortion, the greater the red shift of the calculated transitions.

Deviations of the dihedral angles far from the planar value of 180° or values of the distances between the farthest points in naphthalene smaller than those found in the methylated analogues (**H1**, **H2**, and **I**) are measures of the distortion from planarity of these compounds. There are cases where the comparison of the distortions is not evident, but in general, greater distortions are accompanied by greater bathochromic displacements and higher energies of the occupied orbitals.

The biggest wavelength changes are found in the series **I**, as expected, since all available positions in naphthalene are occupied and greater distortions are possible. Bathochromic displacements of up to 35 nm (0.27 μm^{-1}) were calculated for the most affected transition of the compound with the greatest distortion.

Another important observation is that greater distortions are obtained in those molecules where a maximum of one reduced ring is located in the bridge positions. Reduced substituents in the bridge positions lead to less distortion of the aromatic backbone of the molecule, resulting in shorter wavelengths in comparison with compounds that have reduced groups in other positions. The loss of planarity could be a consequence of the torsional strain in the reduced substituents. The instability provoked by strained substituents is not compensated for by the stability of a completely planar π system.

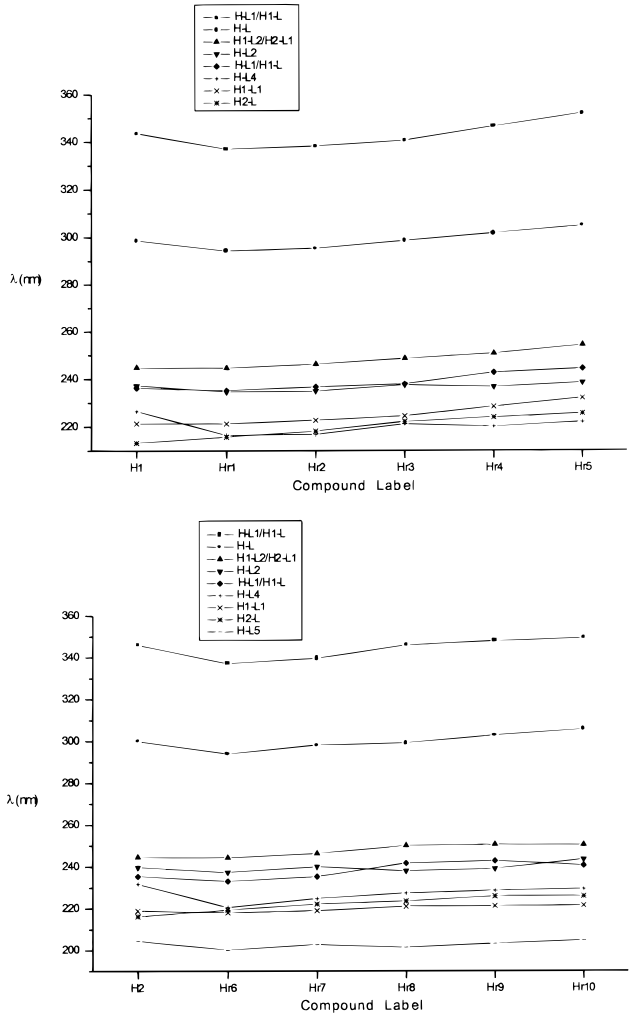


Figure 9. Displacement of the calculated transitions of the series **H**.

In some of these compounds (e.g., **H_r9**, **I_r5**, **I_r6**, **I_r9**, etc.) the composition of some of the CIS states is slightly changed. New configurations become dominant, making the selection of the transitions to be followed difficult. This could be a reason for the nonuniform change in the displacement of some excited states. The most intense excited states in naphthalene (usually the most intense excited states of the substituted compounds), i.e., the first, second, fourth, and sixth transitions, increase in wavelength (decrease in energy) with increasing distortion from planarity. To find an explanation for this situation, the ground states of the molecules of series **H** and **I** were examined.

To compare the thermodynamic stability of different molecules, their total energies must be compared. But this comparison is only correct when considering molecules with the same type and number of atoms, that is, isomers. In the series **H** and **I** there are three sets of isomers, without mixing molecules of different series. These are **H_r1/H_r8/H_r9**, **H_r2/H_r10**, and **I_r1/I_r3**. Their total energies as calculated by MOPAC (AM1) and HyperChem (ZINDO/S) are reported in Table 8. Although ZINDO/S is not a method designed to obtain ground-state energies, we have decided to include these values in order to show that the AM1 order of stability is also reproduced at the ZINDO/S level.

AM1 and ZINDO/S results are in agreement. Both show that the greater the distortion from planarity, the higher the ground-state energy of these molecules. This increase in ground-state energy is a consequence of the higher orbital energies of the occupied orbitals.

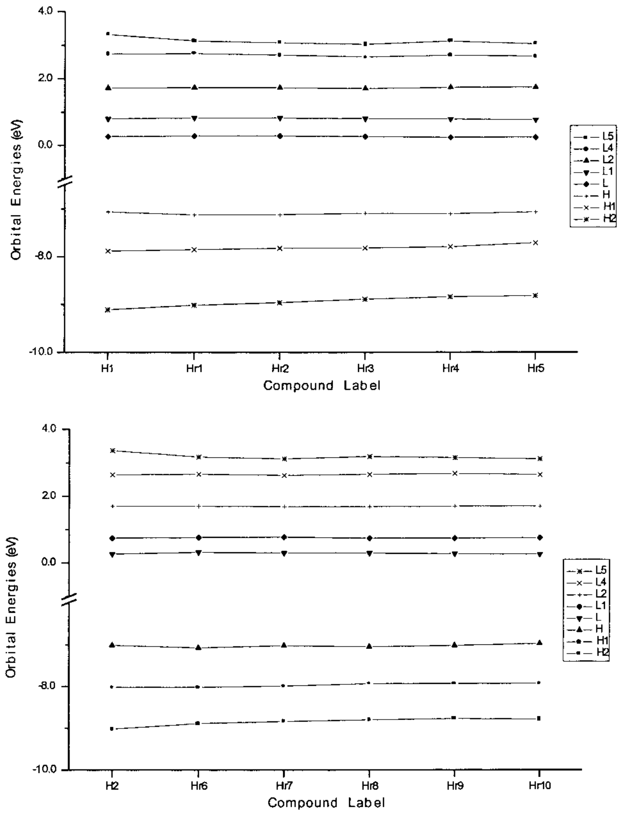


Figure 10. Orbital energies of the series **H**.

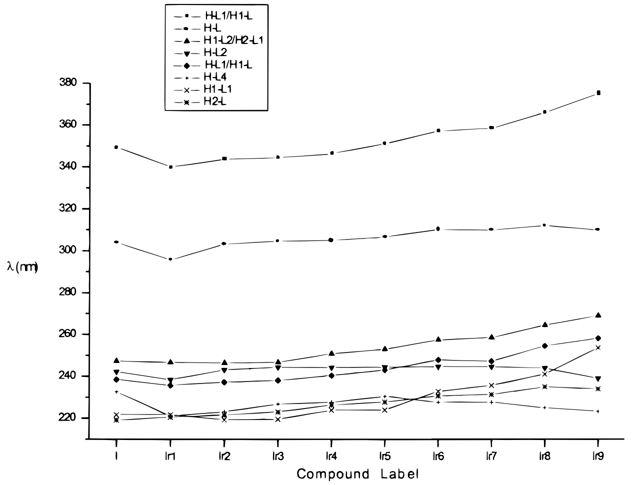


Figure 11. Displacement of the calculated transitions of the series **I**.

Since the energy difference between the ground and excited states becomes smaller with greater distortions from planarity (UV−visible bands are displaced to longer wavelengths) and since it has been shown that the ground-state energy increases with distortion, it can be inferred that excited states do not increase in energy relative to the ground state as a consequence of the distortion from planarity.

From the calculations presented in this section it can be said that distortions from planarity of the aromatic center (due to the number and position of the reduced substituents) increase the ground-state energy of the naphthalene derivatives more than the corresponding excited states. This is translated into bathochromic displacements of their UV−visible bands with respect to the position of the corresponding bands of other nondistorted derivatives.

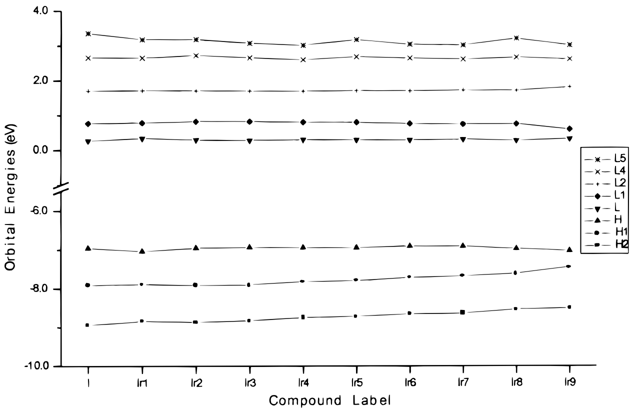
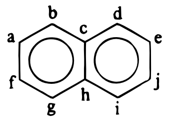


Figure 12. Orbital energies of the series **I**.

TABLE 7: Dihedral Angles *d* (in Degrees) and Distances *r* (in Angstroms) of the Optimized Structures of the Series H and I



label	**H1**	**H_r1**	**H_r2**	**H_r3**	**H_r4**	**H_r5**
d(a,b,c,d)	180.0	177.7	179.7	179.2	174.4	176.3
d(b,c,d,e)	180.0	178.5	177.7	176.6	171.9	170.7
d(f,g,h,i)	180.0	177.7	175.4	173.2	166.2	160.1
d(g,h,i,j)	180.0	177.9	177.8	174.6	167.3	172.7
r(a,j)	5.100	5.079	5.079	5.081	5.073	5.055
r(f,e)	5.118	5.084	5.083	5.092	5.082	5.084

label	**H2**	**H_r6**	**H_r7**	**H_r8**	**H_r9**	**H_r10**
d(a,b,c,d)	180.0	179.1	178.4	178.6	176.0	173.5
d(b,c,d,e)	180.0	177.8	177.6	170.7	173.2	178.1
d(f,g,h,i)	180.0	177.2	176.4	163.0	164.0	169.4
d(g,h,i,j)	180.0	178.9	175.5	175.3	169.7	163.9
r(a,j)	5.085	5.070	5.069	5.044	5.053	5.068
r(f,e)	5.122	5.088	5.084	5.085	5.083	5.073

label	**I**	**I_r1**	**I_r2**	**I_r3**	**I_r4**
d(a,b,c,d)	180.0	179.0	176.9	176.4	176.1
d(b,c,d,e)	180.0	179.0	176.8	176.1	172.9
d(f,g,h,i)	180.0	179.0	174.7	176.2	174.0
d(g,h,i,j)	180.0	179.0	174.7	176.3	175.8
r(a,j)	5.125	5.093	5.091	5.082	5.078
r(f,e)	5.121	5.093	5.091	5.092	5.088

label	**I_r5**	**I_r6**	**I_r7**	**I_r8**	**I_r9**
d(a,b,c,d)	161.7	159.4	163.0	154.3	163.0
d(b,c,d,e)	170.1	171.1	169.0	175.8	163.0
d(f,g,h,i)	179.9	178.1	172.9	175.8	163.0
d(g,h,i,j)	174.6	177.1	178.7	154.3	163.0
r(a,j)	5.081	5.084	5.072	5.070	5.025
r(f,e)	5.088	5.066	5.079	4.986	5.025

Conclusions

The effects of methyl and reduced-ring substituents on the electronic excited states of naphthalene have been studied at a semiempirical level. Successive addition of alkyl substituents on naphthalene leads to bathochromic displacements of its UV−visible bands because of the greater increase of energy of the occupied MOs relative to the unoccupied orbitals. The red shifts of these bands are a consequence of a relative destabilization of the ground state with respect to the excited states. This slow and steady increase in wavelength with the number of substituents may help to distinguish between a long alkyl chain at one position and several short alkyl substituents.

TABLE 8: Total Energies of the Isomers of the Series H and I

label	E_T (AM1)[a]	E_T (ZINDO/S)[a]
$\mathbf{H_r1}$	−3460.814	−4241.487
$\mathbf{H_r8}$	−3460.508	−4241.108
$\mathbf{H_r9}$	−3460.489	−4241.069
$\mathbf{H_r2}$	−3744.724	−4592.775
$\mathbf{H_r10}$	−3744.377	−4592.276
$\mathbf{I_r1}$	−4028.838	−4944.488
$\mathbf{I_r3}$	−4028.684	−4944.114

[a] Units are eV.

Analysis of substituent effects on absorption bands corroborates the fact that substituent positions in naphthalene are not equivalent.[9b] Certain substituent positions have zero (or near-zero) effect on important bands. Red shifts obtained when positions 2 and 6 (or only 6 for the reduced derivatives) are occupied are smaller than in other positions in excited states where the only dominant initial MO is H or H2. This may help to identify the substituent positions of an unknown alkylated PAH.

In those cases where no significant distortion from planarity is produced in the aromatic center of the reduced compounds, very small differences are found between the calculated electronic spectra of these compounds and their methylated analogues. Where the number and position of the reduced substituents affect the planarity of the naphthalene skeleton, the calculated position of the absorption bands among derivatives with the same number of substituents (with methyl or reduced rings) differs greatly. Distorted rings lead to unusually longer wavelengths. The greater the distortion, the greater the bathochromic displacement of the bands. This displacement is a consequence of the destabilization of the ground state with respect to the excited states. This situation can also be extended to larger PAHs; the bigger the PAH the greater the distortion from planarity to be expected because of the presence of reduced-ring substituents. PAHs with reduced rings at bridgehead positions are not as distorted as ones with reduced rings at other positions. These theoretical observations may be useful criteria to assist with the separation and identification of PACs in complex oil-sands samples, in combination with other analytic techniques, e.g., mass spectrometry. Moreover, the retention behavior of electron acceptor and electron donor charge-transfer phases for the separation of PAH isomers and methyl-substituted PAHs has been previously studied,[27] and in all cases planar compounds were retained in preference to corresponding nonplanar analogues.

The conclusions derived from alkylated naphthalenes could be transferred to larger PAHs for which absorption bands occur at longer wavelengths, and these effects are more likely to be detected. Small changes in the energy of the transitions will result in a large change in the (observable) wavelength of the absorption spectrum.

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Supporting Information Available: Calculated ZINDO/S spectra in terms of position (λ), intensity (f), and composition of the calculated transitions above 200 nm of the compounds included in the present study and tables with the plotted magnitudes (orbital, transition energies, and wavelengths of the calculated bands). This material is available free of charge via the Internet at http://pubs.acs.org.

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