

Effect of Solvents on the Electronic Absorption Spectra of Some Substituted Diarylformazans

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Summary. The electronic absorption spectra of some substituted diarylformazans in organic solvents of varying polarities are studied. The absorption bands are assigned to the corresponding electronic transitions in the molecules. The solvent effects on the intramolecular charge transfer bands are discussed using various solvent parameters. The charge transfer nature of the bands was also confirmed by the solvent effects on the absorption spectra of some formazans. Molecular orbital calculations using MNDO-PM3 were performed and indicate a *trans* configuration as the favoured geometry.

Keywords. Electronic absorption spectra; Diarylformazans; Solvent effect; Charge transfer nature; Molecular orbital calculations.

Lösungsmiteleinflüsse auf die Absorptionsspektren einiger substituierter Diarylformazane

Zusammenfassung. Die Absorptionsspektren einiger substituierter Diarylformazane werden in organischen Lösungsmitteln unterschiedlicher Polarität untersucht. Die Absorptionsbanden werden den entsprechenden Elektronenübergängen in den Molekülen zugeordnet. Die Lösungsmittelleffekte auf die intramolekularen *charge-transfer*-Banden werden unter Verwendung verschiedener Lösungsmittelparameter diskutiert. Die *charge-transfer*-Natur der Banden wurde durch den Einfluß der Lösungsmittel auf die Absorptionsspektren einiger Formazane bestätigt. MO-Rechnungen (MNDO-PM3) wurden durchgeführt und bestätigen eine *trans*-Konfiguration als bevorzugte Geometrie.

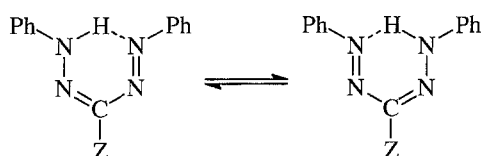
Introduction

In the course of the study of formazans it has been noted that they absorb strongly in the visible [1, 2] as well as in the UV range [3]. Absorption spectra of several derivatives of 1-phenyl-2-benzimidazolylformazans in dioxane, CHCl_3 , and EtOH [4] have been reported. Many spectroscopic studies have been performed in order to find an empirical assignment and to get information about the molecular structure [5]. The electronic absorption spectra of some *o*-arsonotriphenylformazans have been investigated in organic solvents of varying polarities [6]. Solvent influences on the electronic absorption spectra of some triphenylformazan derivatives have been studied [7]. The frequencies and oscillator strengths of the absorption bands of 1,5-diphenylformazans have been resolved into individual *Gaussian* components [8].

Results and Discussion

The electronic absorption spectra of the arylformazans were recorded after dissolution in organic solvents of different polarities. The wavelength maxima of the absorption bands and the corresponding molar absorptivities in ethanol and cyclohexane are listed in Table 1.

The spectra exhibit mainly four absorption bands (A, B, C, and D). The first band (A) observed in the wavelength range of 216–239 nm may be assigned to the medium energy π - π^* transition of the phenyl moiety (1L_a - 1_A). The second band (B, 240–285 nm) may be attributed to the low energy π - π^* transition of the phenyl moiety (1L_b - 1_A). The third band (C) within the 294–335 nm range is due to the π - π^* transition within the hydrogen chelate ring formed by the azo and hydrazo group and the tautomerization occurring within this ring:



In case of formazan **1b**, this band can be observed at 360–370 nm and is believed to arise from an intramolecular charge transfer from the hydrazo group to the COOH group on the phenyl ring.

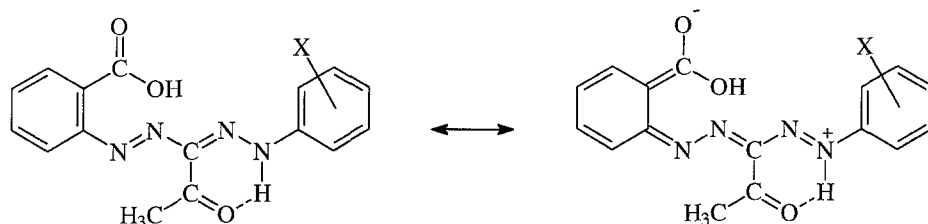


Table 1. Electronic absorption bands of formazans in ethanol and cyclohexane

	Solvent	Band A		Band B		Band C		Band D	
		λ (nm)	$\epsilon \times 10^{-4}$	λ (nm)	$\epsilon \times 10^{-4}$	λ (nm)	$\epsilon \times 10^{-4}$	λ (nm)	$\epsilon \times 10^{-4}$
1a	Ethanol	233	0.32			307	1.19	437	2.40
	Cyclohexane					298	1.44	416	2.26
1b	Ethanol	234	0.725			368	1.34	428	1.58
	Cyclohexane			283	1.68	363	1.33	418	1.45
1c	Ethanol			243	1.34	299	1.10	437	0.78
	Cyclohexane	222	1.21	285	1.74			429	0.67
2a	Ethanol	235	0.29			314	0.62	458	2.78
	Cyclohexane					284	1.07	412	2.67
2b	Ethanol					310	0.84	453	1.77
	Cyclohexane					283	1.91	420	2.17
2c	Ethanol					286	1.72	425	2.69
	Cyclohexane	222	0.41			285	1.47	425	1.00
2d	Ethanol	232	6.79			317	0.57	480	1.97

In connection with formazan **2b** it is of interest to notice that this band (C) shows a blue shift indicating that the high electron withdrawing effect of the $-C\equiv N$ group ($\sigma = +1.00$) will decrease the strength of the hydrogen bond between the NH group and N₅. It also antagonizes and therefore weakens the charge transfer.

Band D located at 395–444 nm, is assigned to the π - π^* transition within the N=N group influenced by charge transfer within the whole molecule [14].

It is well known that the bands due to local transitions are solvent insensitive, whereas the charge transfer bands are sensitive to environmental changes. Thus, the solvent effects may lead to substantial changes in the optical properties molar absorptivity (ϵ) and absorption maximum (λ_{\max}). Accordingly, the absorption spectra are influenced by the physical properties of the solvent, *e.g.* dipole moment, dielectric constant, and refractive index. *Nagakura* and *Baba* [15] have explained solvent shifts in aromatic compounds by assuming the occurrence of hydrogen bonding which assists electron migration in the molecules. Some solvent effects may be attributed to the stabilization of preferred resonance structures due to their dielectric constant or electron donor character [16, 17]. *Coggeshall* and *Lang* [18] showed the importance of dipole-dipole interaction, hydrogen bonding, and the change in the dipole moment during the solute transition on the solvent effect.

Kosower [19] proposed that the transition energies (E_T) for 1-alkylpyridinium iodide calculated from the position of the absorption maximum can be adopted as empirical measures of solvent polarity (Z values)

$$E_T(\text{kcal/mol}) = 2.859 \times 10^{-3} \bar{\nu}(\text{cm}^{-1}) \equiv Z$$

1-Methyl-4-carbomethoxypyridinium iodide was chosen for further investigations because of its deep orange colour in contrast to the colourless appearance of 1-methylpyridinium iodide. It was found that the 1-ethyl salt is more suitable for this investigation due to its higher solubility, especially in non-polar media. High Z values correspond to high transition energies. The stronger the stability effect of the solvent on the ion pair in the ground state as compared with that on the less polar excited state, the lower the wavelength of the intermolecular CT band. Therefore, Z values provide an empirical measure of solvent polarity based on CT bands. Since Z values reflect the dipole-dipole solute-solvent interaction, poor correlations are obtained in nonpolar solvents.

In earlier papers [20–22] information obtained by solvatochromic comparisons was used to construct an α scale of solvent HBD (hydrogen bond donor) acidities, a β scale of solvent HBA (hydrogen bond acceptor) basicities, and a π^* scale which is related to single valued solvent polarity/polarizability parameters [10]. Recently, a unified scale of solvent polarities for specific and non specific interactions has been reported [23]. An experimental procedure which leads to the separation into specific and non-specific components has been described. Therefore, the total solvent effect is composed of three independent contributions: polarity (π^*), acidity (α), and basicity (β). These contributions can be combined into one equation:

$$\bar{\nu}_{\max} = \nu_0 + s\pi^* + a\alpha + b\beta,$$

where s , a , and b range from 0 to 1 according to the extent of contribution of each parameter.

E_T values [24, 25] are sensitive to polar and hydrogen interactions; other interactions such as dispersion forces are probably also operative. They are known for 62 pure solvents and some solvent mixtures.

The interactions between solvents of different polarities and formazans are illustrated in Table 2. Studying the solvent effect on the position of the intramolecular CT band reveals that this band acquires a blue shift in cyclohexane relative to ethanol (Table 1). This can be mainly attributed to the fact that solvation by a polar solvent stabilizes π and π^* orbitals, the latter ones to a higher degree, presumably because they are more polar. The net result is the decrease of the π - π^* transition energy (red shift). From the data in Table 2, it can be concluded that band (D) of most of the formazans under investigation appears at longer (λ_{nm}) in DMF and/or DMSO, thus indicating the cleavage of the hydrogen bond $NH\dots N=N$ by the action of these polar solvents which are considered as hydrogen acceptors.

The plots of λ_{max} of the formazans under investigation as a function of Z , π^* , α , and β deviate from linearity within the same solvent class; however linear relations were obtained between different solvent classes (Fig. 1), thus confirming it to be difficult to obtain single solvent parameters.

Absorption spectra in various solvents are influenced by solvation and/or dielectric constants of the solvents. The relation which governs this behaviour was given by *Gati and Szalay* [26] as

$$\bar{\nu} = (a - b) \cdot \frac{n^2 - 1}{2n^2 + 1} + b \left(\frac{D - 1}{D + 1} \right)$$

where a and b are constants depending on the nature of the solute, n is the refractive index, and D is the solvent dielectric constant. D is an important contributing factor which should have a substantial influence on the transition energy [27]:

$$F(D) = \frac{2(D - 1)}{2D + 1}; \varphi(D) = \frac{D - 1}{D + 1}$$

David and Hallem [28] derived a multiparametrical equation containing the following functions:

$$F(n) = \frac{n^2 - 1}{n^2 + 2} \quad \text{and} \\ F_2(D) = \frac{D - 1}{D + 1}$$

For nonpolar solvents, the following equation was derived:

$$F(D, n) = \left(\frac{D - 1}{D + 1} - \frac{n^2 - 1}{n^2 + 2} \right)$$

Plots of $D - 1/D + 1$, $f(D)$, $\varphi(D)$, $F(n)$, and $F(D, n)$ vs. λ_{max} deviate from linearity, indicating that the dielectric constant is not the sole parameter governing the solvent shift.

Table 2. Charge transfer bands of diarylformazans in different solvents

Solvent	1a		1b		1c		2a		2b		2c		2d	
	λ_{\max}	$\epsilon \times 10^{-4}$	λ_{\max}	$\epsilon \times 10^{-4}$	λ_{\max}	$\epsilon \times 10^{-4}$	λ_{\max}	$\epsilon \times 10^{-4}$	λ_{\max}	$\epsilon \times 10^{-4}$	λ_{\max}	$\epsilon \times 10^{-4}$	λ_{\max}	$\epsilon \times 10^{-4}$
Water	440	0.81	397	1.61	436	1.10	n.o.	—	439	2.60	428	3.80	424	2.08
MeOH	443	0.42	442	1.44	437	0.78	458	2.78	453	1.77	425	2.69	428	1.28
EtOH	437	2.40	428	1.58	437	0.78	427	2.20	442	1.75	425	2.60	480	1.97
Glacial acetic acid	436	2.43	412	1.51	428	0.83	424	2.05	432	1.74	413	3.12	419	1.15
1-Propanol	439	2.52	424	1.38	443	0.72	434	2.12	456	1.71	434	2.57	442	0.99
<i>n</i> -Butanol	440	2.65	421	1.56	440	0.78	431	2.16	454	1.77	n.o.	—	445	2.57
Isopropanol	438	2.54	n.o.	—	443	0.70	440	2.41	455	1.74	438	2.58	453	0.91
Isobutanol	440	2.40	423	1.48	438	0.64	433	2.22	455	1.84	429	0.90	445	0.40
Cyclohexanol	441	2.47	420	1.42	434	0.70	434	2.10	441	1.67	423	1.13	426	0.79
1-Pentanol	441	2.41	425	1.43	443	0.67	434	2.10	455	1.69	434	2.47	429	0.55
<i>DMSO</i>	442	2.11	430	1.35	445	0.62	438	2.20	455	1.76	493	5.42	504	1.69
<i>DMF</i>	440	2.20	442	1.32	441	0.67	479	2.04	483	3.82	488	5.22	503	2.41
Acetone	436	2.41	423	1.40	440	0.72	446	2.15	464	2.01	461	2.62	494	0.38
Ethyl acetate	437	2.43	420	1.40	421	0.70	419	2.18	432	1.89	414	1.19	396	0.69
Dioxane	440	2.37	422	1.34	439	0.65	414	2.43	428	2.16	418	2.51	n.o.	—
Benzene ^a	446	2.14	422	1.23	440	0.53	426	1.92	431	1.70	427	0.77	399	0.47
Toluene ^a	446	2.13	420	1.36	440	0.67	424	2.05	431	1.96	425	0.91	398	0.59
<i>n</i> -Hexane	438	2.39	410	1.19	429	0.56	408	2.58	416	1.53	422	0.79	n.o.	—
CCl_4	442	2.26	418	1.54	438	0.58	415	2.60	425	2.39	422	0.90	397	0.46
Cyclohexane	443	2.26	418	1.45	429	0.67	412	2.67	420	2.17	425	1.00	n.o.	—
CH_2Cl_2	441	2.58	418	1.51	429	0.74	432	2.14	430	1.87	423	1.00	395	0.64
CHCl_3^b	442	2.27	416	1.44	427	0.71	432	2.15	432	1.92	423	0.94	403	0.61

n.o.: not observed; ^a these aromatic solvents are usually weak hydrogen bond acceptors, but sometimes behave as non-hydrogen bonding solvents; ^b usually acts as non-hydrogen bonding solvent, but has shown weak hydrogen bond donor abilities

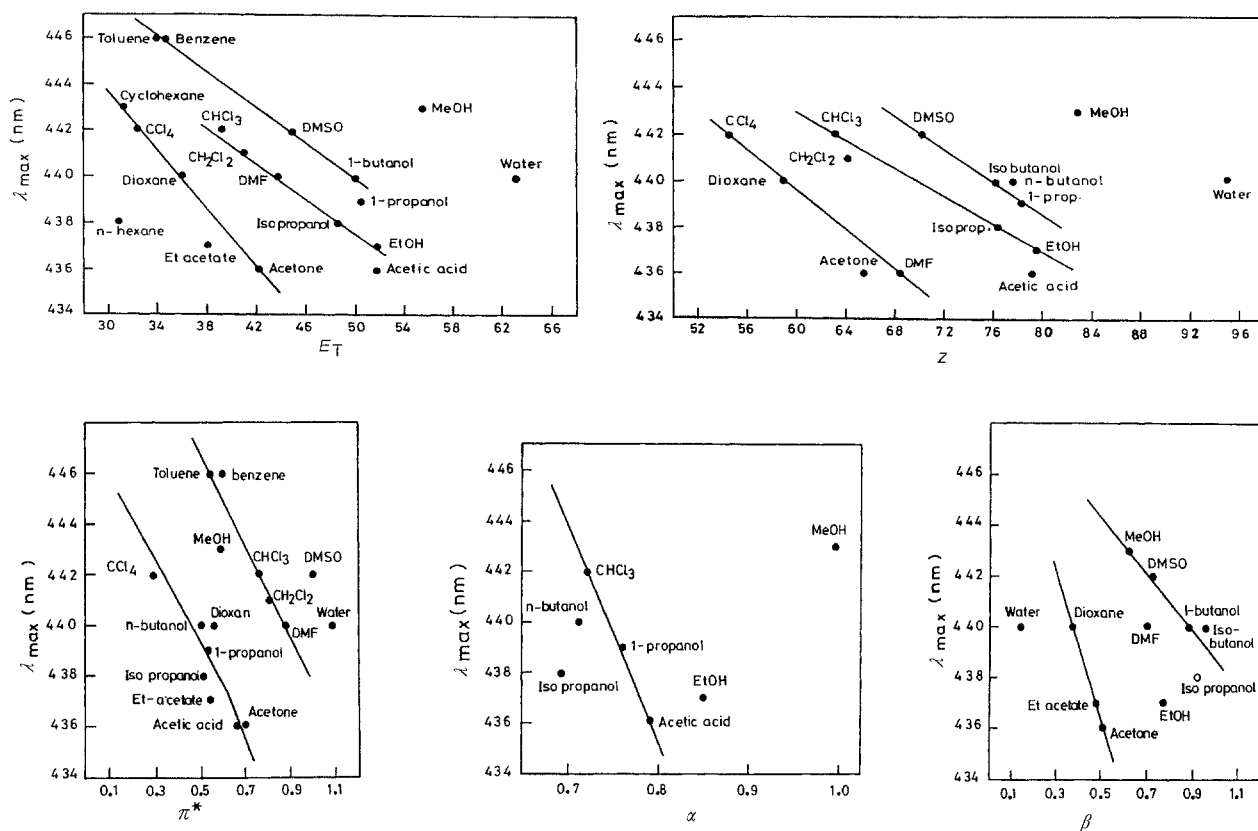


Fig. 1. Effect of solvent parameters on the absorption band D of formazan **1a**

The observed transition energies (E_{obs} (eV) = $h\nu_{\text{max}}$) of the absorption bands were calculated from the experimental data using the following relation [29]:

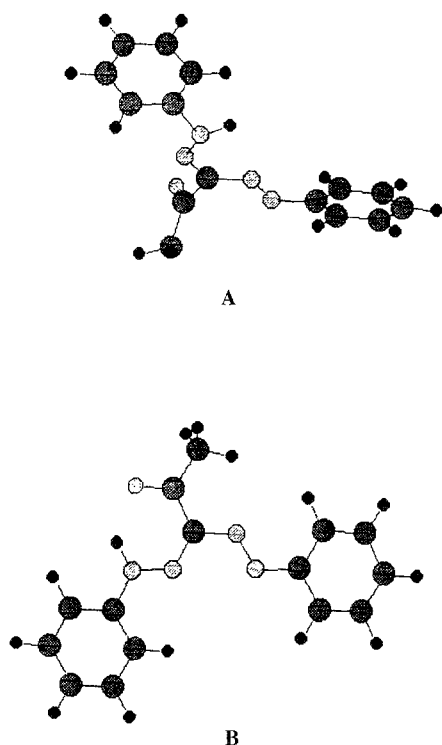
$$E_{\text{obs}} = \frac{1241.7121}{\lambda_{\text{max}}}$$

According to *Koopman's* theorem [30], the ionization potential (I_p) can be approximated by the highest occupied molecular orbital energy (HOMO). Ionization potentials were calculated applying the relation

$$I_p = a + b \cdot h \cdot \nu_{\text{max}}$$

where a and b are constants amounting to 5.110 and 0.701 [31].

The following is an attempt to correlate the observed ionization potential with that calculated applying the MNDO-PM3 method. Consideration of the total energy and dipole moment of the *cis* and *trans* forms (Fig. 2) suggests that the *trans* form is the more favoured one on the basis of its high polarity. For the cyanoforzans, both the total energy and the dipole moment are mostly of the same magnitude.

Fig. 2. A: *trans* form, B: *cis* form of diarylformazans

	<i>Trans</i>		<i>Cis</i>	
	Total energy (eV)	Dipole moment (D)	Total energy (eV)	Dipole moment (D)
1a	-2932.30	3.217	-2932.25	0.448
2a	-2634.83	2.350	-2634.85	2.672

$I_p(\text{calc})$, $I_p(\text{obs})$, electron affinities and dipole moments for the investigated compounds in organic solvents are given in Table 3. I_p values correlate reasonably with the HOMO energy whereas electron affinities correlate with the LUMO energy.

The theoretical calculations indicate that similar charge densities are present, the charge density on the nitrogen atoms of the formazan skeleton being the highest. Hence, electrophilic attack is to be expected most probably at these centers [32].

Although there are some differences between the calculated and observed ionization potentials, these differences may be due to solvolysis of the formazans and the solute-solvent interaction liable to occur in solution.

Based on the above results, the shift in the band positions and the differences in $I_p(\text{obs})$ and $I_p(\text{calc})$ can be attributed to the change in the strength of solute-solvent hydrogen bonding governed by proton donor-acceptor interaction between solute and solvent molecules, to the change in the solvation energy upon going from the ground to the excited state which depends on the properties of both the solute and

Table 3. Ionization potentials, electron affinities and dipole moments of diarylformazans

Solvent	I_p (observed) (eV)						
	1a	1b	1c	2a	2b	2c	2d
Water	7.09	7.30	7.11	–	7.09	7.14	7.16
Methanol	7.07	7.08	7.10	7.01	7.03	7.16	7.14
Ethanol	7.10	7.14	7.10	7.15	7.08	7.16	6.93
Acetic acid	7.11	7.22	7.14	7.16	7.12	7.21	7.18
<i>n</i> -Propanol	7.09	7.16	7.07	7.11	7.02	7.11	7.08
<i>n</i> -Butanol	7.09	7.18	7.09	7.13	7.03	–	7.07
Isopropanol	7.09	–	7.07	7.09	7.02	7.09	7.03
Isobutanol	7.09	7.17	7.09	7.09	7.12	7.14	7.07
Cyclohexanol	7.09	7.18	7.11	7.11	7.02	7.11	7.14
<i>n</i> -Pentanol	7.09	7.17	7.07	7.11	7.02	7.11	7.14
<i>DMSO</i>	7.08	7.14	7.07	7.07	7.02	6.88	6.84
<i>DMF</i>	7.09	7.08	7.09	6.93	6.91	6.89	7.12
Acetone	7.10	7.17	7.09	7.06	6.99	7.00	7.21
Ethyl acetate	7.10	7.18	7.18	7.18	7.18	7.12	7.31
Dioxane	7.09	7.17	7.09	7.21	7.14	7.19	–
Benzene	7.06	7.17	7.09	7.15	7.13	7.15	7.29
Toluene	7.06	7.18	7.09	7.16	7.13	7.15	7.29
Hexane	7.09	7.23	7.14	7.24	7.19	7.17	–
CCl_4	7.08	7.19	7.09	7.21	7.16	7.17	7.30
Cyclohexane	7.07	7.19	7.14	7.14	7.22	7.16	–
CH_2Cl_2	7.09	7.19	7.14	7.12	7.14	7.17	7.31
$CHCl_3$	7.07	7.19	7.15	7.12	7.12	7.17	7.27
I_p (calculated) (eV)	8.68	8.78	8.95	8.93	9.09	9.20	9.73
EA	1.12	1.44	1.74	1.24	1.27	1.75	2.04
Dipole moment (D)	3.217	7.15	4.79	2.67	5.54	5.78	3.87

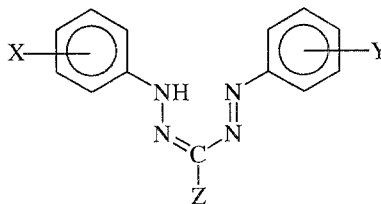
solvent, and to combined effects of dielectric constant and refractive index. This leads to the conclusion that several superimposed individual effects contribute to the observed change, confirming that there is a difficulty in obtaining a single solvent parameter.

Experimental

The 1,5-diarylformazans studied are

- i) symmetric 1,5-diary-3-acetyl- or 1,5-diary-3-cyano-formazans which were prepared by coupling of the corresponding aryldiazonium chloride with acetylacetone or ethylcyanoacetate in a molar ratio of 2:1 in alkaline medium [9] and
- ii) asymmetric formazans which were prepared by coupling of the corresponding aryldiazonium chloride with acetylacetone or ethylcyanoacetate arylhydrazones in a molar ratio of 1:1 in alkaline medium [9].

The formula of the 1,5-diarylformazan is given below.



1:	Z = COCH ₃		2:	Z = CN	
	X	Y		X	Y
a	H	H	a	H	H
b	H	<i>o</i> -COOH	b	H	<i>o</i> -COOH
c	H	<i>p</i> -AsO(OH) ₂	c	H	<i>p</i> -AsO(OH) ₂
			d	<i>p</i> -AsO(OH) ₂	<i>p</i> -AsO(OH) ₂

The organic solvents used include [10]

- i*) amphiprotic hydrogen bond acceptor-donor solvents (α and $\beta \neq 0$) such as methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol, isobutanol, water, glacial acetic acid, and cyclohexanol,
- ii*) hydrogen bond acceptors ($\beta \neq 0$) such as *DMSO*, *DMF*, acetone, benzene, dioxane, ethyl acetate, and toluene, and
- iii*) non hydrogen bonding solvents ($\alpha = \beta = 0$) including *n*-hexane, CCl₄, cyclohexane, methylene chloride, and chloroform.

They were either spectral grade (BDH or Aldrich) or purified by recommended methods [11]. The absorption spectra were scanned using a Perkin-Elmer SP Lambda 4 spectrophotometer using 1 cm quartz cells.

MO calculations

The MNDO-PM3 method (modified neglect of diatomic overlap parametric method 3) is a semi-empirical quantum chemical method [12]. In this method, only valence electrons are considered explicitly, and they are assumed to move in a fixed framework formed by the nuclei and inner shell electrons. Valence electrons are treated using a minimum basis set simplified by neglecting some electron repulsion integrals involving differential overlap. The remaining integrals are equated to parametric functions which contain numerical parameters obtained by fitting some experimental data. The calculations have been performed using MNDO-PM3 as implemented in an improved version of MOPAC6.0 [13].

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