

THE PARISER-PARR-POPLE TYPE OF CALCULATION FOR SOME ELECTRON-DONOR ACCEPTOR COMPLEXES^{1,2}

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Electronic absorption spectra of a series of electron-donor acceptor complexes of tetracyanoethylene (TCNE) and 1,2,4,5-tetracyanobenzene (TCNB) with naphthalene and several substituted benzenes are interpreted by means of the SCF MO CI method within the Pariser-Parr-Pople approximation. The positions of the charge-transfer bands in the spectra of the complexes are predicted in a satisfactory way the calculation results.

1. Introduction

The understanding of the electron-donor acceptor interactions and of the electronic structure of a molecular complex formed from these interactions is very important from various points of view. For example, the electron-donor acceptor (EDA) complexes play an important role in biological systems [1, 2].

Among the various physicochemical properties of the EDA complexes, their electronic absorption spectra (and particularly the appearance of the charge-transfer bands) have most often been investigated experimentally and interpreted by means of semiempirical quantum-mechanical methods [3-12]. More recently some attempts were made to treat the EDA complexes as a single conjugated system of π -electrons and to calculate the π -electron states of this system by means of the semiempirical SCF MO CI method within the π -electron approximation [13, 14].

The aim of the present study is to calculate the electronic absorption spectra of com-

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plexes of TCNE and TCNB with naphthalene, benzene and several derivatives of benzene. For that purpose the Pariser-Parr-Pople method has been applied with some modifications similar to those made by Ohta *et al.* [13].

2. Calculation method

The π -electrons of a complex are treated as a single π -electronic system. Each π -electron in a complex is described by a linear combination of $2p\pi$ atomic orbitals of donor and acceptor atoms which contribute π -electrons to the conjugated system. Owing to the existence of the donor-acceptor interaction term in the Hamiltonian of a complex, the Hartree-Fock matrix elements within the standard approximations of the PPP method including the ZDO approximation contain among various integrals also the integrals γ_{pq} , β_{pq} , $\langle \varphi_p | U_A^{\text{core}}(D) | \varphi_p \rangle$ and $\langle \varphi_q | U_D^{\text{core}}(A) | \varphi_q \rangle$, where p and q indicate the donor and acceptor atoms respectively and, for example, $U_A^{\text{core}}(D)$ stands for the interaction between the acceptor core and π -electrons of the donor. The integrals of the last two kinds were approximated in a similar way as those in the case of single molecules, *i. e.* $\langle \varphi_p | U_A^{\text{core}}(D) | \varphi_p \rangle = -\sum_{q \neq p} Z_q \gamma_{pq}$. Then the H-F matrix elements have, in fact, the same form as those for isolated molecules.

All two-electron γ_{pq} ($p \neq q$) integrals (inter- and intramolecular) were evaluated from the Nishimoto-Mataga formula. The values of core integrals $W_p = \langle \varphi_p | T + U_p^{\text{core}} | \tau_p \rangle$ and the γ_{pp} integrals which were used in the calculations presented here are collected in Table I.

TABLE I
Semiempirical parameters used in the calculations

Atom	$-W_p^1$ (in eV)	γ_{pp} (in eV)	
Carbon (<i>tr tr tr</i> π)	11.16 ²	11.13 ²	
Carbon (<i>di² di</i> $\pi_y \pi_z$)	12.19 ^{2,3}	10.09 ^{2,3}	
Nitrogen ⁴ (<i>tr tr tr</i> π^2)	24.65	14.5 ^{4,5}	
in {	NH ₂		23.70
	NHCH ₃		23.50
	NHC ₂ H ₅		23.40
	NH(<i>n</i> -C ₄ H ₉)		23.50
	N(CH ₃) ₂		22.74
Nitrogen (<i>di² di</i> $\pi_y \pi_z$)	15.69 ^{2,3}	11.52 ^{2,3}	
Oxygen (<i>tr tr tr</i> π^2) in OCH ₃	28.85 ⁶	18.0 ⁵	

¹ $W_p = \langle \varphi_p | T + U_p^{\text{core}} | \varphi_p \rangle = -I_p - (Z_p - 1)\gamma_{pp}$

² Hinze and Jaffé [18]

³ According to the suggestion of Ohta *et al.* [13] the values of W_p and γ_{pp} are slightly modified in order to fit the calculated first excitation energy of TCNE to the observed value

⁴ See [16].

⁵ See [15]

⁶ The experimental value of ionization potential of the HOCH₃ (10.85 eV) molecule [19] was used to evaluate the W_p integral

As regards the resonance integrals $\beta_{pq}(p \neq q)$, all values of those were calculated from the formula $\beta_{pq} = -K \frac{A}{r_{pq}^6}$. The constants A in this formula have been evaluated in previous calculations for the component molecules of complexes [15, 16]. K is equal to 1, when p and q indicate neighbouring atoms in donor or acceptor molecules, while K is equal to 0 in the acceptor molecules, while K is equal to 0 in the case of p and q atoms not being neighbours in donor or acceptor molecules. When p and q indicate the donor or acceptor atoms respectively, we have tentatively selected the value of 10 for the K constant (cf. [10]).

As to the excited states, the lowest thirty five singly excited configurations were allowed to interact in our approximation.

A comparison of the present calculation scheme with that of Ohta *et al.* [13] shows that there is only a slight difference between both approaches. As a matter of fact they differ in the calculation of the resonance integrals and in the choice of some W_p and γ_{pp} integral values.

3. Calculation results and discussion

Before we get to the calculation results, here are a few words on the classification of the molecular orbitals and of electronic transitions in complexes (cf. [13]). Since the donor-acceptor interaction is not too strong in the complexes under study we can classify each molecular orbital (m. o.) of the complex as being mainly associated with the donor or acceptor. The classification can be made either by comparison of m. o. energies in the complex with those of the component molecules or by calculation of the weights of the complex m. o.'s as described in Ref. [13]. The calculations for all complexes show, for instance³, the highest occupied m. o. to be mainly localized on the donor and the lowest vacant m. o. to be mainly localized on the acceptor.

Similarly, singly excited configurations may be classified into two types:

(i) local excitations associated with a transition of donor or acceptor — denoted as LE(D^*) or LE(A^*) respectively,

(ii) charge-transfer excitations from the donor to the acceptor or *vice versa* — denoted as CT($D-A$) or CT($A-D$) respectively.

The nature of an excited state is specified by the type or excited configuration dominating in the wave function of the state. The specifications of the complexes for each excited state are presented further on the tables.

Calculations were performed on a series of complexes of TCNE and TCNB with naphthalene, benzene and some substituted benzenes (anisole, *p*-dimethoxybenzene, aniline and alkylaminobenzenes, *p*-phenylenediamine, *N,N,N',N'*-tetramethyl-*p*-phenylenediamine, toluene, hexamethylbenzene). The chosen geometrical structures used the experi-

³ A comparison between the characters of the molecular orbitals of TCNE: naphthalene complex obtained by Ohta *et al.* [13] and those obtained here shows that in the last case the complex m.o.'s are localized higher on the components than those in Ohta *et al.*'s approach. This seems to be due to the method of evaluation of the β_{pq} integrals in this calculation.

mental bond lengths and angles for the complex components, and the relative arrangement of the components (sandwich structure) was taken as shown in Fig. 1. For all calculations the distances between molecular planes were taken as equal to 3.4 Å. No rotation of donor relative to acceptor was taken into account.

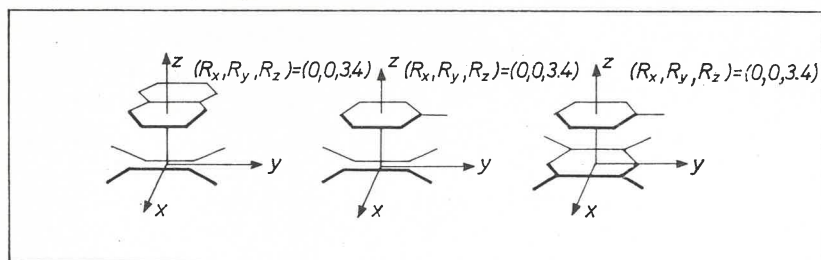


Fig. 1. Geometrical structures of complexes

Tables II and III give the calculation results together with the experimental data for the acceptor and donor molecules respectively. This shows that the predicted band positions of isolated molecules are in good agreement with the observed ones.

TABLE II

Electronic spectra of TCNE and TCNB

Transition energy (in eV) and oscillator strength ¹		
Theoretical	Experimental	
Tetracyanoethylene (TCNE)		
4.60(0.795)	4.55 [13]	
5.87(0.000) forb. ²		
5.89(0.484)		
6.85(0.000) forb.		
1,2,4,5-Tetracyanobenzene (TCNB)		
3.85(0.111)	4.02 [29]	3.93(0.03) [10]
4.31(0.470)		
4.98(1.697)	4.84	4.66(0.34)
5.45(0.231)	5.56	5.56

¹ In parentheses. ² forb. = forbidden transition in the present calculation

The next tables compile the transition energies, oscillator strengths, π -electronic charge transferred from donor to acceptor on excitation (ΔQ) and π -electronic dipole moments in excited states calculated for the complexes in question. The figures presented in Tables IV to VII show that the calculation results predict the absorption band positions of the complexes in agreement with the measurements. It is worth noting that, although

TABLE III

Electronic spectra of donors

Transition energy (in eV), oscillator strength ¹			
Theoretical		Experimental	
Benzene			
		[30]	[31]
4.72 (forb.) ²		4.7	4.9
6.01 (forb.)		6.0	6.2
6.84	} (1.2)	} 6.8	7.0
6.84			
Naphthalene			
		[30, 33, 34]	
3.78 (forb.)		4.0	
4.36(0.233)		4.3(0.10)	
5.64(1.998)		5.6(1.70)	
6.27(0.587)		6.5(0.21)	
Methoxybenzene			
		[32]	
4.47(0.029)		4.59	
5.53(0.231)		5.78	
6.49(0.786)	} (0.991)	} 6.68	
6.55(0.991)			
<i>p</i> -Dimethoxybenzene			
		[34]	
4.20(0.078)		4.25	
5.25(0.409)		5.51	
6.50(0.775)			
6.55(1.005)			
Aniline			
		[31]	
4.40(0.037)		4.40(0.028)	
5.34(0.316)		5.39(0.140)	
6.35(0.614)		6.31(0.510)	
6.48(0.847)			
Methylaminobenzene			
		[31]	
4.26(0.051)		4.37(0.031)	
5.13(0.393)		5.20(0.190)	
6.16(0.400)		6.31(0.478)	
6.44(0.736)		6.88(0.556)	

TABLE III (continued)

Transition energy (in eV), oscillator strength ¹	
Theoretical	Experimental
Ethylaminobenzene	
	[31]
4.22(0.053)	4.34(0.048)
5.08(0.407)	5.17(0.230)
6.11(0.361)	6.28(0.451)
6.43(0.717)	6.88(0.779)
<i>n</i> -Butylaminobenzene	
	4[31]
4.20(0.055)	4.32
5.06(0.415)	5.17
6.09(0.343)	} 6.27
6.42(0.708)	
Dimethylaminobenzene	
	[31]
4.18(0.056)	4.30(0.044)
5.04(0.422)	5.12(0.256)
6.07(0.325)	6.25(0.350)
6.42(0.699)	6.88(0.575)
Diethylaminobenzene	
	4[31]
4.07(0.064)	4.21
4.92(0.459)	5.00
5.97(0.241)	} 6.25
6.40(0.657)	
<i>p</i> -Phenylenediamine	
	[30]
4.07(0.090)	4.05
5.03(0.504)	5.08
6.43(0.656)	6.14
6.45 (forb.)	
N,N,N',N'-Tetramethylaminobenzene	
	[34]
3.73(0.111)	3.87
4.68(0.634)	4.77
5.71(forb.)	
6.13 forb.)	

¹ In parentheses. ² forb. = forbidden transition in the present calculation.

the π -electrons of a complex are treated as a single conjugated system, a great amount of π -charge transfers from donor to acceptor on excitation to lower energy states of the complex (see ΔQ -values). Then the absorption bands corresponding to transitions to states with $\Delta Q \approx 1$ may be really named the "charge-transfer" (CT) bands.

TABLE IV
Electronic spectra of complexes of TCNB with substituted benzenes

Transition energy (in eV), oscillator strength ¹		ΔQ^2	μ^3	Character of transition ⁴
Theoretical	Experimental [10]			
TCNB: Aniline				
2.95(0.001)	2.89	0.995	17.12	CT(D-A)
3.77(0.001)	3.76	0.994	16.51	CT(D-A)
3.90(0.013)		0.960	15.78	CT(D-A)
3.93(0.100)		0.009	1.49	LE(A*)
TCNB: Dimethylaminobenzene				
2.49(<10 ⁻³)	2.27	0.998	17.90	CT(D-A)
3.30(<10 ⁻³)	3.10	0.999	16.92	CT(D-A)
3.82(0.006)		0.978	16.76	CT(D-A)
3.91(0.005)		0.982	17.77	CT(D-A)
TCNB: <i>p</i> -dimethoxybenzene				
2.52(<10 ⁻³)	2.85	0.998	16.28	CT(D-A)
3.56(<10 ⁻³)		1.008	16.30	CT(D-A)
3.81(0.010)		0.968	15.80	CT(D-A)
3.86(<10 ⁻³)		0.999	16.30	CT(D-A)
TCNB: N,N,N',N'-Tetramethyl- <i>p</i> -phenylenediamine				
1.61(<10 ⁻³)	1.69	0.999	16.31	CT(D-A)
2.45(<10 ⁻³)	2.43	1.000	16.32	CT(D-A)
2.94(<10 ⁻³)		0.999	16.31	CT(D-A)
3.58(<10 ⁻³)		0.999	16.30	CT(D-A)

¹ In parentheses. ² π -electronic charge transferred from donor to acceptor on excitation. ³ π -dipole moment in an excited state. ⁴ See text.

The position of the 1-st CT bands in TCNB: substituted benzenes as well as that of the 2-nd CT bands is correctly predicted in the calculation results. In the case of the TCNE: substituted benzene complexes (Tab. V) the theory also predicts the appearance of more than one CT band, the result being experimentally confirmed in the case of complexes of TCNE: methoxybenzene and TCNE: hydrocarbons (see *e. g.* [17]).

It is noteworthy that the origin of the multiple CT bands in the complexes with TCNB as acceptor is quite different from that in the complexes with TCNE as acceptor. Iwata *et al.* [10] have found the separation between the two CT bands to be almost constant

Electronic spectra of the complexes of TCNE with substituted benzenes

Transition energy (in eV), oscillator strength ¹		ΔQ^2	μ^3	Character of transition ⁴	
Theoretical	Experimental				
TCNE: Methoxybenzene					
	[23, 24]	[25]			
2.50(0.007)	2.42	2.43	1.000	16.89	CT(D-A)
3.28(<10 ⁻³)	3.25	3.20	1.001	16.39	CT(D-A)
4.31(0.003)			0.963	15.85	CT(D-A)
4.47(0.023)			0.126	3.93	LE(D*)+CT(D-A)
TCNE: Aniline					
	[25]	[23]			
2.28(0.006)	2.07	2.10	1.000	17.22	CT(D-A)
3.25(<10 ⁻³)			0.901	16.21	CT(D-A)
4.07(0.002)			0.996	16.41	CT(D-A)
4.35(0.020)			0.617	13.55	CT(D-A)+LE(D*)
TCNE: Methylaminobenzene					
	[25]	[23]			
1.96(0.006)	1.93	1.95	1.000	17.70	CT(D-A)
3.21(<10 ⁻³)			1.001	16.45	CT(D-A)
3.72(0.001)			0.998	16.29	CT(D-A)
4.09(0.007)			0.955	20.68	CT(D-A)
TCNE: Ethylaminobenzene					
	[25]	[23]			
1.89(0.007)	1.89	1.93	1.001	17.82	CT(D-A)
3.20(<10 ⁻³)			1.002	16.47	CT(D-A)
3.64(0.001)			0.999	16.31	CT(D-A)
4.03(0.006)			0.967	21.09	CT(D-A)
TCNE: <i>n</i> -Butylaminobenzene					
	[23]				
1.86(0.006)	1.91		1.000	17.87	CT(D-A)
3.19(<10 ⁻³)			1.001	16.47	CT(D-A)
3.60(0.001)			0.999	16.32	CT(D-A)
4.00(0.006)			0.972	21.28	CT(D-A)
TCNE: Dimethylaminobenzene					
	[25]	[23]			
1.82(0.006)	1.76	1.84	1.000	17.93	CT(D-A)
3.19(<10 ⁻³)			1.002	16.48	CT(D-A)
3.56(0.001)			0.009	16.33	CT(D-A)
3.92(0.006)			0.975	21.45	CT(D-A)

TABLE V (continued)

Transition energy (in eV), oscillator strength ¹		ΔQ^2	μ^3	Character of transition ⁴
Theoretical	Experimental			
TCNE: Diethylaminobenzene				
	[23]			
1.60(0.006)	1.47	1.000	18.25	CT(D-A)
3.15($<10^{-3}$)		1.002	16.51	CT(D-A)
3.33(0.001)		1.001	16.42	CT(D-A)
3.76(0.005)		0.988	22.23	CT(D-A)
TCNE: <i>p</i> -Phenylenediamine				
	[25]			
1.56(0.009)	1.54	1.001	16.33	CT(D-A)
3.11($<10^{-3}$)		1.003	16.37	CT(D-A)
3.45($<10^{-3}$)		1.004	16.35	CT(D-A)
3.50(0.006)		0.996	16.25	CT(D-A)

¹ In parentheses. ² π -electronic charge transferred from donor to acceptor on excitation. ³ π -dipole moment in an excited state. ⁴ See text.

for complexes of TCNB. They have determined that the appearance of these bands is due to the transitions from the highest occupied m.o. to the two vacant m.o.'s of TCNB. The analysis of the s.c.f. m.o.'s and wave functions of the calculated complexes of TCNB confirms this conclusion. Namely, the first two CT bands in the complexes are mainly due to transitions from the highest occupied m.o. ψ_{11} localized on the donor to the vacant m.o.'s ψ_{12} and ψ_{13} both being localized on TCNB. By contrast, the calculations on a series of complexes of TCNE suggest that two CT maxima should be due to the transitions from the two highest occupied m.o.'s ψ_9 and ψ_8 localized mainly on the donor, to the vacant m.o. ψ_{10} mainly localized on TCNE. Then the separation, in energy terms, between the first two CT band maxima is dependent on the donor (*cf.* experimental data for complexes of TCNE listed in [17]).

The figures presented in Tab. IV show the appearance of the two CT bands in the spectra of complexes on TCNE and TCNB with naphthalene. Similarly as in TCNE: substituted benzenes, the 1-st and 2-nd CT bands in TCNE: naphthalene are mainly due to the respective transitions from m.o. ψ_{10} and ψ_9 , both localized on naphthalene, to m.o. ψ_{11} localized on TCNE.

In TCNE: naphthalene the 1-st CT band is due to the transition from the highest occupied m.o. localized on naphthalene to vacant m.o.'s localized on TCNE. The nature of the 2-nd CT band in this complex seems to be interesting. Iwata *et al.* [11] have analyzed the absorption spectra of the TCNE: naphthalene complex and found the absorption band at 30600 to 32700 cm^{-1} to appear at the wavelength region of absorption of TCNB itself. The band in the complex spectrum has quite a different structure from the first

absorption band of TCNB — in the first case the broad band has three indistinct peaks at 30600, 31800 and 32700 cm^{-1} (3.79, 3.94 and 4.05 eV, respectively), while the band of TCNE is much more distinct than the former one. From the figures presented in Tab. VI it may be seen that the calculation gives three electronic transitions (two CT transitions and one local transition in TCNB) which correspond to absorption at 30600 to 32700 cm^{-1} in the complex spectrum. However, it should be remembered that the calculations presented

TABLE VI

Electronic spectra of the complexes of naphthalene with TCNE and TCNB

Transition energy (in eV), oscillator strength ¹		ΔQ^2	μ^3	Character of transition ⁴
Theoretical	Experimental			
TCNE: Naphthalene				
2.36(0.002)	[20] [21] [22]	1.001	17.06	CT(D-A)
3.33($<10^{-3}$)	2.22 2.26 2.26			
4.10($<10^{-3}$)	2.9 2.9			
4.21(0.006)				
4.28($<10^{-3}$)				
4.35(0.026)				
4.48(0.002)				
4.67(0.895)				
TCNB: Naphthalene				
2.98(0.001)	[10, 11, 17]	0.997	16.70	CT(D-A)
3.87(0.002)	3.05-3.1			
3.94(0.008)	} 3.8-4.05			
4.02(0.082)				
4.11($<10^{-3}$)	} 3.8-4.05			
4.31(0.001)				
4.31(0.019)				
4.46(0.622)				
		0.993	16.75	CT(D-A)
		0.968	16.13	CT(D-A)
		0.062	0.46	LE(A*)
		0.000	0.78	LE(D*)
		0.987	17.58	CT(D-A)
		0.025	0.65	LE(A*)+LE(D*)
		0.014	1.04	LE(D*)+LE(A*)

¹ In parentheses. ² π -electronic charge transferred from donor to acceptor on excitation. ³ π -dipole moment in an excited state. ⁴ See text.

here cannot be treated as evidence indicating that three separate electronic bands really appear in the absorption region mentioned above. The π -electron SCF MO CI calculations have limited significance for prediction of the sequence of the higher excited electronic states, and the three peaks mentioned above may be only a vibrational structure of one (or two) electronic transitions.

The predicted and observed spectra of TCNE and TCNB complexes with benzene are compared in Tab. VII. The table also contains tentative results for complexes with

TABLE VII

Electronic spectra of complexes of benzene, toluene, hexamethylbenzene with TCNE and TCNB

Transition energy (in eV), oscillator strength ¹		Character of transition ²
Theoretical	Experimental	
TCNE: Benzene		
3.41($< 10^{-3}$)	} [24] [26, 27] 3.2 3.67 ³	CT(D-A)
3.42(0.007)		CT(D-A)
4.62(0.630)		LE(A*)
4.71($< 10^{-3}$)		LE(D*)
5.36(0.001)		CT(D-A)
5.37($< 10^{-3}$)		CT(D-A)
5.38(0.008)		CT(D-A)
5.41(0.003)		CT(D-A)
TCNE: Toluene		
3.16($< 10^{-3}$)	} [24] [26, 27] 3.0 3.35 ³	CT(D-A)
3.17(0.007)		CT(D-A)
4.61(0.624)		LE(A*)
4.71($< 10^{-3}$)		LE(D*)
5.11(0.002)		CT(D-A)
5.12($< 10^{-3}$)		CT(D-A)
5.14(0.011)		CT(D-A)
5.16(0.003)		CT(D-A)
TCNE: Hexamethylbenzene		
2.17($< 10^{-3}$)	} [24] [26, 27] 2.3 2.44 ³ 2.3 ⁴ 4.0-4.15	CT(D-A)
2.19(0.011)		CT(D-A)
4.12(0.002)		CT(D-A)
4.13($< 10^{-3}$)		CT(D-A)
4.14(0.001)		CT(D-A)
4.16(0.004)		CT(D-A)
4.58(0.559)		LE(A*)
4.72($< 10^{-3}$)		LE(D*)
TCNB: Benzene		
3.88(0.092)	} [10] 3.97	LE(A*)+CT(D-A)
4.05(0.031)		CT(D-A)
4.15(0.010)		CT(D-A)
4.40(0.356)		LE(A*)
4.71(0.001)		CT(D-A)
4.91(0.269)		CT(D-A)+LE(A**)
4.94(0.012)		CT(D-A)
5.14(1.049)		LE(A*)+CT(D-A)

TABLE VII (continued)

Transition energy (in eV), oscillator strength ¹		Character of transition
Theoretical	Experimental	
TCNB: Toluene		
3.78(0.043)	} [10] } 3.94	CT(D-A)+LE(A*)
-3.81(0.010)		CT(D-A)
4.00(0.059)		LE(A*)+CT(D-A)
4.38(0.373)		LE(A*)
4.67(0.048)		CT(D-A)+LE(D*)
4.70(0.012)		CT(D-A)
4.72(0.019)		LE(D*)+CT(D-A)
5.11(0.208)	CT(D-A)+LE(A*)	
TCNB: Hexamethylbenzene		
2.82(0.001)	} [10] [29] } 2.91 2.90 } 3.71	CT(D-A)
2.85(0.002)		CT(D-A)
3.68(<10 ⁻³)		CT(D-A)
3.70(<10 ⁻³)		CT(D-A)
3.95(0.110)		LE(A*)
4.18(<10 ⁻³)		CT(D-A)
4.22(<10 ⁻³)		CT(D-A)
4.32(0.427)		LE(A*)

¹ In parentheses. ² See text. ³ Gaseous phase. ⁴ Evaluated from the absorption curve [28].

model donors which here correspond to toluene or hexamethylbenzene (HMB). Predicted spectra of complexes with methylbenzenes as donors seem to be, in the first place, dependent on the relative energy difference between m.o.'s of component molecules of the complex.

Thus the existence of the methyl groups in the compounds was indirectly taken into account by decreasing of the ionization potential of the valence state of carbon atoms. The $-W_p$ integral value was decreased from the value of 11.16 eV in the case of benzene to the value of 10.91 and 9.91 eV in the case of the model toluene and HMB, respectively⁴.

A comparison of the figures presented in Table VII shows a good agreement between the calculation results and experimental data. It is worth noting that in the case of the TCNB: HMB complex the theory predicts an appearance of the CT bands in the 33200–33600 cm⁻¹ ($\Delta E = 4.12$ – 4.16 eV) absorption region. This is in accordance with experiment [28] showing two absorption maxima in this complex which are not connected with the absorption of the component molecules.

⁴ Of course, m.o.'s of both toluene and HMB are the same as those of benzene. The energies of m.o.'s in the first two cases are higher by about 0.25 and 1.25 eV respectively than the corresponding m.o.'s of benzene. Thus the ionization potentials of model toluene and HMB are lower than that of benzene by about 0.25 and 1.25 eV, respectively.

The results presented in this paper deserve an additional comment. As we see, in all cases the calculated absorption band positions are in agreement with the experimental data. However, the theoretical oscillator strengths for transitions having CT character are too lower. This is a deficiency of the method. Another remark concerns the influence which the intermolecular interactions occurring in the complexes have upon the positions of the local excitation bands of the component molecules. The theory shows that the LE bands in the complexes under study are, in general, affected slightly by these interactions. On the other hand, the LE bands occur in the absorption region in which the spectra are usually not measured. It is then difficult to discuss the effect, and the present calculations may be, in fact, applied only for the purpose of interpreting the CT bands in complexes.

Finally, it should be noted that the both Ohta *et al.* [13] scheme and the present one contain a few unjustified approximations. Japanese workers have mentioned about them in their paper and we will not discuss the failings of the method. We think both schemes should be treated as the first step of modification of the PPP method for the study of the EDA spectra.

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