The Application of MIM Method
to Spiroconjugated Systems

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The "Molecules in Molecules" method has been applied to spiroconnected systems. Energy, polarisation and intensity of electronic transitions of spiro(5,5)undeca-1,4,6,9-tetraene-3,8-dione have been compared with experimental data and PPP results. Through a "configuration analysis", PPP wave functions have been interpreted in terms of MIM configurations. The results show that the method is conveniently applicable to spiroconnected π systems.

Die "Molecules in Molecules"-Methode wurde auf Spiro-verbundene Systeme angewendet. Es wurden Energie, Polarisation und die Intensität der elektronischen Übergänge von Spiro(5,5)undeca-1,4,6,9-Tetraene-3,8-dione mit den experimentellen Werten und PPP-Ergebnissen verglichen. PPP-Eigenfunktionen wurden in MIM-Konfigurationen ausgedrückt. Die Ergebnisse zeigen, daß die Methode für Spiro-verbundene Systeme verläßlich ist.

La méthode "molecules in molecules" a été appliquée à molécules spiroconjugées. On a comparé les énergies, la polarisation et l'intensité des transitions électroniques de spiro (5,5)undeca-1,4,6,9-tetraene-3,8-dione avec les données expérimentales et les données PPP. Parmis un "Configuration Analysis" on a interprété les PPP fonctions d'onde en termes de MIM configurations. Les résultats indiquent que la méthode est applicable aux systémes spiroconjugées.

Introduction

The electronic spectrum of spiro(5,5)undeca-1,4,6,9-tetraene-3,8-dione [1] has recently been reported by Boschi, Dreiding, and Heilbronner and an interpretation both by naive orbital arguments and Pariser-Parr-Pople (PPP) CI calculations was given. The results were in agreement with the prediction derived from the molecular orbital model proposed by Simmons and Fukunaga [2] and by Hoffmann, Imamura and Zeiss [3], which describes spiroconjugation as mainly due to electron delocalisation.

In the present paper we use the "Molecules in Molecules" (MIM) method, that has been succesfully applied to a large number of hydrocarbons [4] and azines [5], for the interpretation of the electronic spectrum of spiro(5,5)undeca-1,4,6,9-tetraene-3,8-dione, to test the applicability of this approach to spiro-connected systems.

MIM method is particularly suitable for classifying electronic bands in terms of locally-excited and charge-transfer configurations, while the wave-functions obtained by PPP method for electronic states of a molecule are not immediately understandable in such terms, especially when the configuration interaction is included.

Following a procedure described by Baba, Suzuki and Takemura [6] a "configuration analysis" has been developed to analyze and interpret PPP wavefunctions in terms of MIM configurations and compare the euristic power of the two methods.

Calculations

Spiro(5,5)undeca-1,4,6,9-tetraene-3,8-dione represents an interesting situation: it can be considered as formed by two spiroconnected chromofores where there is no direct bond between π electron centers in the subsystems, but their distance is well below the distance between the molecules in organic crystals.

For the MIM treatment the idealized geometry D_{2d} has been assumed. The numbering of the atoms in the molecule and the reference axes are shown in Fig. 1. The distance of the central C atom in the spireo compound from one center of spiroconjugation (4 or 6) was assumed 1.54 Å. We assume that the dienone subsystem has C_{2v} simmetry. The bond lengths of all sp^2-sp^2 bonds have been set equal to 1.40 Å and the related bond angles equal to 120°.

The subsystem's molecular orbitals and the corresponding energies, calculated by the SCF-MO method within the PPP formalism, are reported in Table 1. The valence state ionisation potentials for C and O were taken as proposed by Hinze and Jaffé [7], and the one-centre repulsion integrals were approximated
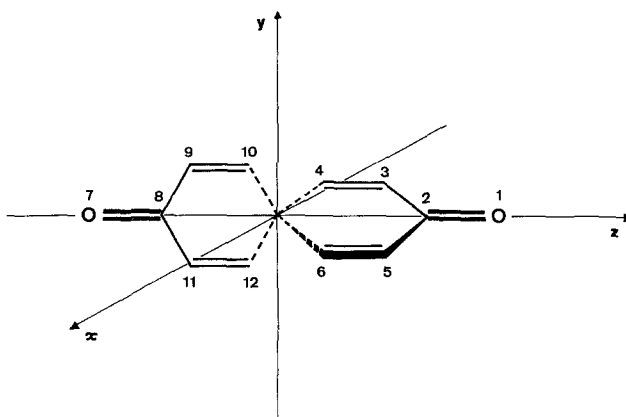

Fig. 1. Numbering of the atoms of spiro(5,5)undeca-1,4,6,9-tetraene-dione, and reference axes

Table 1. SCF *molecular orbitals and energies of cross-conjugated dienone*

	χ_1	χ_2	χ_3	χ_4	χ_5	χ_6	E (eV)
Φ_1	0.29677	0.54806	0.46320	0.30202	0.46320	0.30202	− 13.1051
Φ_2	0.0	0.0	−0.48629	−0.51334	0.48629	0.51334	− 11.1697
Φ_3	0.82241	0.22770	−0.19362	−0.31371	−0.19362	−0.31371	− 9.8266
Φ_4	0.44849	−0.52938	−0.14816	0.48720	−0.14816	0.48720	− 3.7092
Φ_5	0.0	0.0	−0.51335	0.48629	0.51335	−0.48629	− 1.3581
Φ_6	−0.18556	0.60625	−0.47540	0.27020	−0.47540	0.27020	0.8924

Table 2

	I (eV)	$\gamma_{\mu\mu}$ (eV)
C^+	11.16	11.13
O^+	17.70	15.32

Table 3. *Energies and wavefunctions for cross-conjugated dienone excited states*

	Dominating configurations	E (eV)
L_1	$0.9657\,A_2^4 - 0.2597\,A_3^5$	4.47[a]
L_2	$-0.1865\,A_2^5 + 0.9825\,A_3^4$	5.318[a]
L_3	$0.2575\,A_2^4 + 0.9663\,A_3^5$	6.035[b]
L_4	$0.9104\,A_1^4 + 0.3288\,A_2^5$	6.522[b]
	$+ 0.1056\,A_3^4 + 0.2279\,A_3^6$	
L_5	$-0.5397\,A_2^5 + 0.8419\,A_3^6$	7.115[a]
L_6	$-0.4179\,A_1^4 + 0.7630\,A_2^5$	7.852[b]
	$+ 0.4931\,A_3^6$	

[a] Values from experiment [1].
[b] Interpolated values.

A_i^k is the wavefunction for the configuration in which one electron has been excited from the i-th to the k-th molecular orbital.

according to well known prescriptions [8], namely as $\gamma_{\mu\mu} = I - A$, where I and A are the valence state ionisation potential and electron affinity, respectively, of μ-*th* atom. The numerical values are summarized in Table 2.

The two-centre repulsion integrals $\gamma_{\mu\nu}$ were obtained using the Nishimoto-Mataga approximation [9]. The two-centre core integrals β_{CC} and β_{CO} were taken as -2.32 eV and -1.17 eV respectively, as calculated semiempirically by the Kon formula [10].

Interactions between ground and singly-excited configurations built by the above mentioned molecular orbitals were considered. The energies of the locally-excited states of the two fragments were taken from the electronic spectrum of the dienone chromofore present in spiro(5,5)undeca-1,4-dien-3-one [1]. We needed several energy values which cannot be obtained from the spectrum; these have been calculated through a CI treatment on the SCF orbitals of Table 1 and an interpolation procedure as shown in Ref. [4]. The energies and the corresponding wavefunctions are reported in Table 3.

The first ionisation potential for the subsystem is – at this time – unfortunately not available. Related chromofores present values [11] which fall between 9.0 and 10.0 eV. Since the ionisation potential for the dienone chromofore is calculated to be 0.26 eV lower than of p-benzoquinone and the experimental I value of p-benzoquinone is 9.68 eV [11], we performed MIM calculation for $I = 9.0$; 9.5; 10.0 eV.

First electron affinity was evaluated from ionisation potential through an empirical relationship [12].

Higher ionisation potentials and electron affinities were calculated from the values of first ionisation potentials and electron affinities using the differences in the energies of the relevant orbitals, shown in Table 1.

Following the assumption made in Ref. [1] the value $|\beta'| = |\beta|/3 = 0.773$ eV proposed by Simmons and Fukunaga was assigned to the resonance integrals between the spiroconjugating centers 4 and 6 of one subsystem with the corresponding center in the other.

Results and Discussion

MIM energies compared with the experimental and PPP ones are reported in Table 4. Oscillator strength values (f) and polarisation direction are also reported.

The electronic spectrum of spiro(5,5)undeca-1,4,6,9-tetraene-3,8-dione in n-hexane solutions exhibits three bands, whose absorption maxima lie at 3.67, 5.43, and 6.20 eV, respectively, and a shoulder concealed under the band at 5.43 eV. The band at 3.67 eV has been classified as due to a $\pi^* \leftarrow n$ transition, while other bands are due to $\pi^* \leftarrow \pi$ transitions.

From the data reported in Table 4 it is evident that MIM and PPP results allow an anambiguous good interpretation of the spectrum. The low intensity shoulder can be safely ascribed to a $E^* \leftarrow A_1$ transition, while the two strong bands are z-polarized ($B_2^* \leftarrow A_1$ transition). MIM calculations suggest that a second z-polarized transition contributes to the short-wavelength band. The weakest point of this method is the relatively low f value for the same band.

In Table 5 the dominating configurations contributing to the wavefunctions of more interest, are compared with the configurations of the corresponding wavefunctions, obtained with a SCF-PPP-CI treatment, and expressed by "reference" MIM locally-excited and charge-transfer configurations, through the procedure previously mentioned [6]. Again the two methods reach the same conclusions. Locally-excited configurations essentially contribute to the wavefunction associated to the low-energy absorption bands, while a little amount of charge-transfer configurations is present in the wavefunction associated to

Table 4. *Energies (eV), intensities, and polarisations for spiro(5,5)undeca-1,4,6,9-tetraene-3,8-dione*

	Irred. repr.	pol.	MIM ($I = 9.0$ eV)	MIM ($I = 9.5$ eV)	MIM ($I = 10.0$ eV)	PPP (Ref. [1])	Exp (Ref. [1])
ψ_0	A_1	—	-0.242	-0.221	-0.202		
ψ_1	E	xy	4.270 (0.10)	4.315 (0.10)	4.334 (0.10)	4.128 (0.04)	
ψ_2	B_2	z	5.046 (1.96)	5.046 (1.98)	5.046 (2.00)	5.045 (1.90)	5.45 (4.34)[a]
ψ_3	A_1	—	5.499 —	5.499 —	5.499 —	5.407 —	
ψ_4	E	xy	5.863 (0.04)	5.904 (0.05)	5.929 (0.05)	6.100 (0.00)	
ψ_5	B_2	z	6.211 (0.69)	6.330 (0.52)	6.399 (0.35)	6.519 (2.30)	6.20 (4.71)[a]
ψ_6	A_1	—	6.523 —	6.523 —	6.523 —	6.560 —	
ψ_7	B_2	xy	6.596 (0.27)	6.622 (0.41)	6.654 (0.56)		
ψ_8	A_1	—	7.038 —	7.145 —	7.145 —		

[a] $\log \varepsilon$.

Table 5. *Dominating configurations for ψ_2 and ψ_5 (Table 4)*

	(a)			(b)
	$I = 9.0$ eV	$I = 9.5$ eV	$I = 10.0$ eV	
ψ_2	$0.6991\,(L_2 - L_2')$	$0.6988\,(L_2 - L_2')$	$0.6986\,(L_2 - L_2')$	$0.5825\,(L_2 - L_2')$ $+0.1055\,(L_5 - L_5')$
ψ_5	$0.4158\,(L_4 - L_4')$ $+0.3673\,(L_6 - L_6')$ $-0.3337\,(L_5 - L_5')$ $+0.2783\,(T_2^{5'} - T_{2'}^5)$	$0.5094\,(L_4 - L_4')$ $+0.3188\,(L_6 - L_6')$ $-0.3018\,(L_5 - L_5')$ $+0.2119\,(T_2^{5'} - T_{2'}^5)$	$0.5879\,(L_4 - L_4')$ $+0.2548\,(L_6 - L_6')$ $-0.2503\,(L_5 - L_5')$ $+0.1581\,(T_2^{5'} - T_{2'}^5)$	$0.1440\,(L_4 - L_4')$ $+0.3307\,(L_6 - L_6')$ $-0.2156\,(L_5 - L_5')$ $+0.1440\,(T_2^{5'} - T_{2'}^5)$

(a) MIM method.
(b) PPP method and configuration analysis.

the short-wavelength band. These facts confirm the previous predictions (2, 3), that spiroconjugation is mainly due to electron delocalisation. On the base of these results it can be argued that MIM method, using an amount of computational time that is much less (roughly 1/10) than for the PPP method, can give the same correct interpretation of the electronic spectrum of a spiro-connected compound. Moreover, the nature of MIM wavefunctions (a combination of locally-excited and charge-transfer configurations) is particularly suitable to obtain informations about the spiroconjugative process.

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