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Transition Energies and Oscillator Strengths for Electronic Spectra of Non Planar Conjugated Molecules. I. Polyphenyls

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Ultraviolet spectra of terphenyls and quaterphenyls are theoretically investigated by "Molecules in Molecules" (MIM) method and compared with experiment. Oscillator strengths are evaluated using the gradient operator and the mixed dipole-gradient operator. The results are compared with those obtained by the dipole-length operator. The calculation of oscillator strengths *via* the gradient operator is shown to be in general the most successful. All the components of the "primitive integral", necessary for non planar π-electron systems, are reported.

Die Ultraviolettspektren von Terphenylen und Quaterphenylen wurden mit Hilfe der "Molekül im Molekül" (MIM) Methode theoretisch untersucht und mit den experimentellen Resultaten verglichen. Mit einem Gradient-Operator und einem gemischten Dipol-Gradient-Operator wurden die Oszillatorenstärken berechnet und mit Rechnungen mit Dipollängen-Operatoren verglichen. Es wird gezeigt, daß die Berechnung von Oszillatorenstärken mit dem Gradient-Operator im allgemeinen am erfolgreichsten ist. Es werden alle Komponenten des "primitiven Integrals", die für nicht planare π-Elektronensysteme nötig, angegeben.

Les spectres dans l'ultraviolet des triphényles et des quadriphényles sont étudiés théoriquement par la méthode «Molécules dans les molécules» (MIM) et comparés à l'expérience. Les forces oscillatrices sont évaluées en utilisant l'opérateur gradient et l'opérateur mixte gradient dipolaire. Les résultats sont comparés avec ceux obtenus avec l'opérateur longueur dipolaire. Le calculades, forces oscillatrices à l'aide de l'opérateur gradient s'avère plus convenable. On reproduit toutes les composantes de «l'intégrale primitive», nécessaires pour les systemes d'électrons π non plans.

1. Introduction

It has been shown that the use of "Molecules in Molecules" (MIM) method of calculation allows a quantitative interpretation of electronic spectra of hydrocarbons [1] and azines [2]. Calculated singlet-singlet, singlet-triplet and triplet-triplet transition energies and oscillator strengths are in excellent agreement with experimental data for all molecules and ions for which MIM calculation has been performed [1–3].

The MIM method has also been successful in the study of UV spectra of phenyl- and naphthyl-naphthalenes [4], spiroconjugated [5] and homoconjugated molecules [6] where the π-electron system is far from planarity.

The series of diphenyl, *ortho*, *meta*, *para* terphenyls and symmetric *ortho*, *meta*, *para* quaterphenyls seemed to us a particularly interesting case for a further test of this theory. To this aim the UV absorption spectra of these molecules in

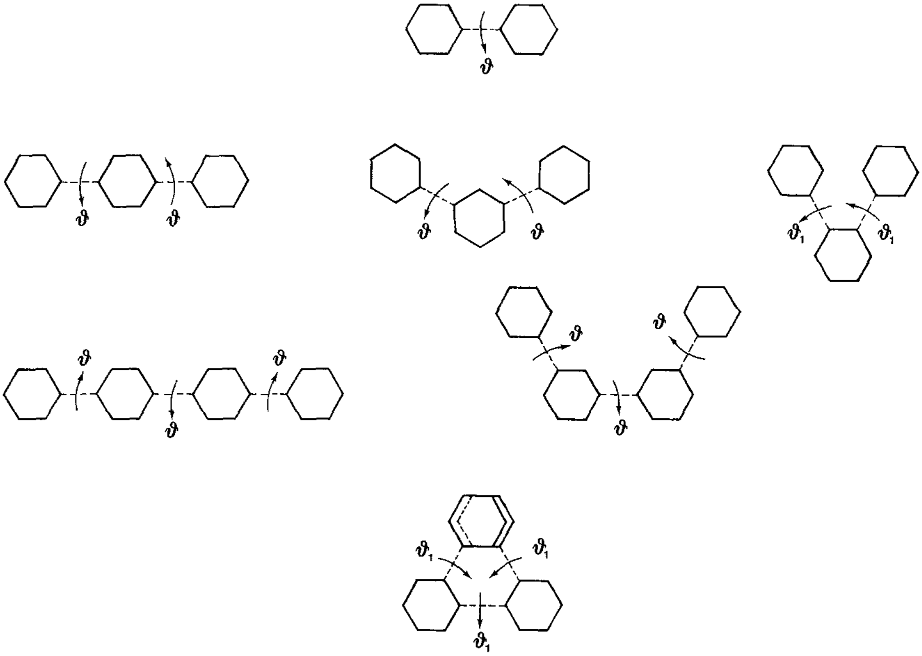

Fig. 1. Molecular geometry and fragmentation scheme for considered molecules $\vartheta = 40°$, $\vartheta_1 = 53°$

different solvents have been measured.[1] A complementary problem was the choice of the best operator to be used in calculating oscillator strengths when the MIM wavefunctions are the basis functions. As usual [4, 7] preliminary to excitation energy calculations a conformational analysis has been carried out to determine the ground-state geometry.

Fig. 1 shows the geometries of all molecules considered in the present paper as well the fragmentation scheme.

2. Experimental

2.1. Materials

Terphenyls and quaterphenyls were pure KEK products. For ultraviolet absorption measurements, spectrograde solvents were used.

2.2. Ultraviolet Spectra

Ultraviolet absorption spectra in the wavelength region 1750–3500 Å were measured at room temperature by a recording ultraviolet spectrophotometer Beckman DK–2A. In the far ultraviolet region short-path cells with suprasil silica windows were employed: their optical path was fixed at 0.02 cm. Recording was carried out in a purified nitrogen stream (oxygen content ≤ 0.2 ppm). In the near ultraviolet region standard cell with optical path of 1 cm were used.

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[1] Except for *o*-quaterphenyl, for which a sample of sufficient high purity was not available.

Table 1. Excitation energies, oscillator strengths calculated through dipole moment operator (f_1), gradient operator (f_2) and their mean ($\sqrt{f_1 \times f_2}$), and corresponding experimental values for diphenyl[a]

ΔE_{calc}(eV)	ΔE_{exp}(eV)			f_1	f_2	$\sqrt{f_1 \times f_2}$	f_{exp}	
	sol.	vap.	solid				sol.	vap.
$^1A_1$ 5.959								
6.310								
6.530								
7.350								
$^1B_1$ 4.900	5.02	5.22	5.08	0.871	0.419	0.604	0.33	0.31
6.115	6.19	6.43		1.121	0.517	0.761	0.90	
6.577				0	0	0		
7.200				0.160	0.157	0.158		
$^1B_2$ 4.531				0	0	0		
6.047	6.05			0.448	0.227	0.319	shoulder	
6.556				0	0	0		
7.362		7.40		1.487	0.554	0.945		0.70
$^1B_3$ 4.533		4.16	4.27	0	0.0002	0	0.0004[b]	
5.842				0.100	0.055	0.074		
6.578				0	0	0		
6.996				0.152	0.055	0.092		

[a] Energy values and experimental oscillator strengths are taken from Table 6 in Ref. [7].

[b] $\varepsilon_{max} = 20$ [7]; f evaluated from the relationship: $f = 2 \cdot 10^{-5}\ \varepsilon_{max}$.

Table 2. Excitation energies, oscillator strengths calculated through dipole moment operator (f_1), gradient operator (f_2), and their mean ($\sqrt{f_1 \times f_2}$), and corresponding experimental values for terphenyls

	ΔE_{calc}(eV)	ΔE_{exp}(eV)[a]	f_1		f_2		$\sqrt{f_1 \times f_2}$		f_{exp}[a]
o-terphenyl	4.995	4.998	0.383		0.198		0.275		0.29
	5.243	5.332	1.204		0.552		0.815		0.56
	5.962		0.288		0.149		0.207		
	6.028	6.003	0.589	1.314	0.284	0.649	0.409	0.923	0.91
	6.154		0.437		0.216		0.307		
	6.230		0.478		0.222		0.326		
	6.236	6.357	0.090	0.706	0.039	0.294	0.060	0.453	0.62
	6.366		0.138		0.033		0.067		
m-terphenyl	4.777	5.019	0.337	1.839	0.169	0.950	0.239	1.322	0.96
	4.912		1.502		0.781		1.083		
	5.888		0.195		0.108		0.145		
	5.948	6.076	0.316	1.203	0.166	0.635	0.229	0.874	1.01
	5.973		0.692		0.361		0.500		
	6.342	6.390	0.185	0.783	0.055	0.275	0.102	0.464	0.62
	6.528		0.598		0.220		0.363		
p-terphenyl	4.480	4.491	1.430		0.790		1.063		0.80
	5.855		0.125		0.118		0.159		
	5.926	6.032	0.435	2.013	0.228	1.055	0.315	1.457	1.21
	5.995		1.363		0.709		0.983		
	6.963		0.226		0.088		0.141		
	7.010	6.457	0.120	1.015	0.185	0.518	0.149	0.699	0.37
	7.071		0.660		0.245		0.405		

[a] Solvent: *n*-hexane.

Table 3. Excitation energies, oscillator strengths calculated through dipole moment operator (f_1), gradient operator (f_2), and their mean ($\sqrt{f_1 \times f_2}$), and corresponding experimental values for quaterphenyls

	ΔE_{calc}(eV)	ΔE_{exp}(eV)	f_1		f_2		$\sqrt{f_1 \times f_2}$		f_{exp}
o-quaterphenyl	5.076		0.987		0.494		0.698		
	5.249		1.330		0.598		0.882		
	5.892		0.471		0.228		0.328		
m-quaterphenyl	4.664		0.324		0.196		0.252		
	4.819	5.008	1.156	2.759	0.652	1.528	0.868	2.053	1.30
	4.886		1.279		0.680		0.933		
	5.732		0.159		0.102		0.127		
	5.939	6.046	0.509	1.005	0.275	0.544	0.374	0.739	
	6.098		0.337		0.167		0.238		
p-quaterphenyl	4.242	4.216	2.258		1.282		1.606		0.93
	5.902	5.988	1.392		0.799		1.054		

[a] In cyclohexane.

[b] In CH_2Cl_2. In cyclohexane the compounds exhibit low solubility.

Spectra were recorded in several solvents: spectra for the same molecule in different solvents were so close to each other that only the data relative to measurements in *n*-hexane for terphenyls and cyclohexane for quaterphenyls have been reported (see Tables 1–3): apparently the influence of the solvent is not relevant. Transition intensities were calculated according to the relationship

$$f = 4.32 \times 10^{-9} \cdot \int \varepsilon(v)\, dv\,.$$

Owing to the low solubility of quaterphenyls in *n*-hexane and cyclohexane, f values for these molecules have been obtained from spectra measured in CH_2Cl_2.

3. Calculations

3.1. Conformational Analysis

The geometry of the ground state of diphenyl has been the subject of several investigations [7, 8]. We used in the present paper the following geometry [7]: all C–$\hat{\mathrm{C}}$–C angles equal to 120°; intra-ring C–C distance 1.40 Å; C–C inter-ring distance equal to 1.48 Å; inter-ring twist angles 40°. For terphenyls the same values for geometrical parameters were assumed except for the twist angle. The total energy has been calculated as the sum of π-electron energy (obtained by MIM calculations) and non-bonded interactions, and has been minimized with respect to the two inter-ring twist angles. However the minimum in all cases was obtained for a geometry showing C_2 symmetry.

Computations were carried on following exactly the same line as in previous work [4, 7]. The results are shown in Fig. 2. To save a large amount of computing time the geometry of quaterphenyls was assumed, namely C_2 symmetry with inter-ring distances and twist angles equal to values of the corresponding terphenyls. This assumption is supported by the results obtained for *para* and *meta* terphenyl as compared with diphenyl.

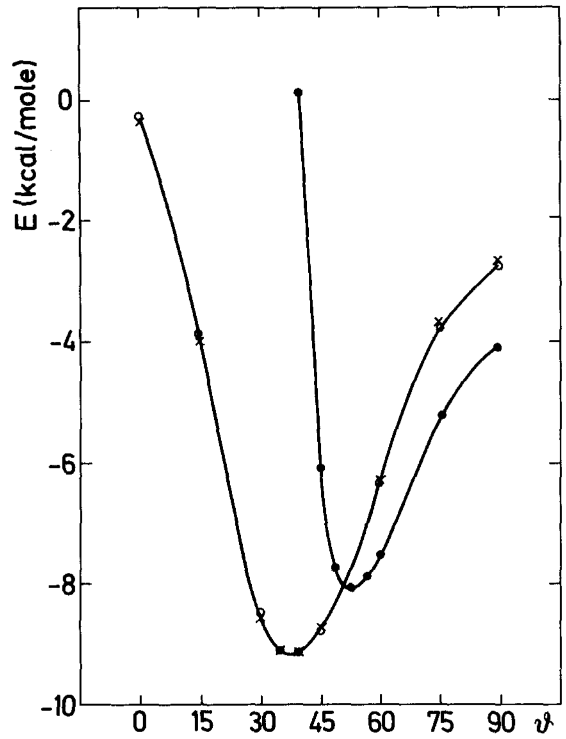

Fig. 2. Total energy *vs* twist angle ○ *p*-terphenyl, × *m*-terphenyl, ● *o*-terphenyl (π-electron energy calculated by MIM method). Curves for *p*- and *m*-terphenyls are practically coincident

3.2. MIM *Calculations*

These calculations were performed following the fragmentation scheme reported in Fig. 1. Details of the method have been described before [1] and are not reported here.

Only ground state and singly excited configurations have been included. Excitation energies are reported in Tables 1–3.

MIM wavefunctions have been used in the calculation of oscillator strengths. There is some discussion on the choice of the operators to be used in such calculations. Namely the use of transition moment, transition gradient and the geometric mean of the two alternative values have been recommended [9–11]. The relative merits of the different operators as well as of different values for the $2p_z$ carbon orbital exponent have been discussed [12, 13], but no definitive criterium to justify a choice on practical or theoretical grounds has been offered. For this reason we report in Table 1, 2, 3 oscillator strengths obtained by the three different methods using a Slater orbital exponent $\xi = 1.625$.

3.3. Primitive Integrals

In the calculation of transition gradient, primitive integral such as $I_{pq} = \langle \chi_p | \text{grad} | \chi_q \rangle$ on the atomic orbitals χ centered on p and q atoms are necessary. Owing to non-planarity of π-electron systems considered in this paper, all the components of the primitive integrals are necessary. They have been calculated according to the following formulae:

$$\begin{array}{cccc}
 & k=x & k=y & k=z \\
\left\langle p_x^P \middle| \frac{\partial}{\partial k} \middle| p_x^Q \right\rangle & 0 & 0 & -\xi F(\varrho) \\
\left\langle p_x^P \middle| \frac{\partial}{\partial k} \middle| p_y^Q \right\rangle & 0 & 0 & 0 \\
\left\langle p_x^P \middle| \frac{\partial}{\partial k} \middle| p_z^Q \right\rangle & -\xi F(\varrho) & 0 & 0 \\
\left\langle p_y^P \middle| \frac{\partial}{\partial k} \middle| p_y^Q \right\rangle & 0 & 0 & -\xi F(\varrho) \\
\left\langle p_y^P \middle| \frac{\partial}{\partial k} \middle| p_z^Q \right\rangle & 0 & -\xi F(\varrho) & 0 \\
\left\langle p_z^P \middle| \frac{\partial}{\partial k} \middle| p_z^Q \right\rangle & 0 & 0 & -\xi G(\varrho)
\end{array}$$

where:

$$p_k^Q = \pi^{-1/2} \cdot \xi^{5/2} \cdot k_Q \cdot e^{-\xi r_Q} \qquad (k = x, y, z)$$

$$F(\varrho) = \varrho e^{-\varrho}(\varrho^2 + 3\varrho + 3)/15\,,$$

$$G(\varrho) = \varrho e^{-\varrho}(\varrho^3 - 2\varrho^2 - 9\varrho - 9)/15\,,$$

$$\varrho = \xi R\,.$$

The not reported matrix elements can be obtained by using the antihermitian property of the gradient operator. The relationship between local and external coordinates systems is shown in Fig. 3.

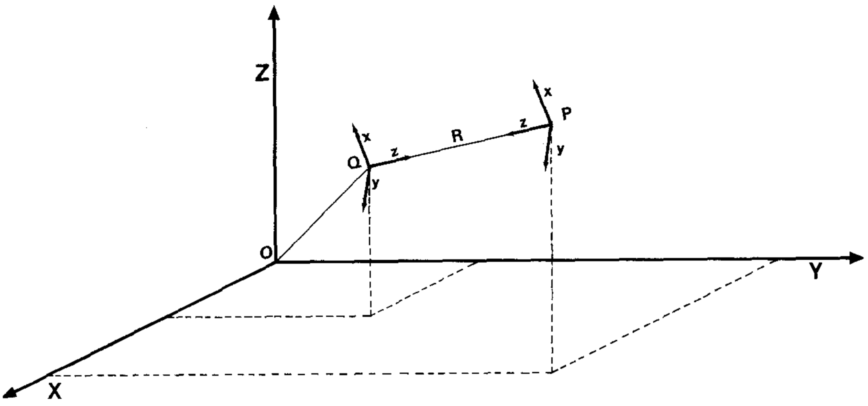

Fig. 3. Local and external coordinate systems for the calculation of transition gradients

Table 4. Calculated $T_1 \leftarrow S_0$ and most intense $T_j \leftarrow T_1$ transitions for quaterphenyls

		ΔE(eV)	f_1	f_2[a]	$\sqrt{f_1 \times f_2}$[a]
o-quaterphenyl	$T_1 \leftarrow S_0$	3.377			
	$T_j \leftarrow T_1$	1.854	0.001	0.	0.
		2.496	0.044	0.001	0.001
		2.586	0.099	0	0.003
		2.737	0.239	0.002	0.021
		2.936	0.030	0.001	0.004
m-quaterphenyl	$T_1 \leftarrow S_0$	3.206			
	$T_j \leftarrow T_1$	1.885	0.010	0	0.001
		1.899	0.002	0	0.001
		2.742	0.395	0.003	0.003
		2.844	0.240	0.002	0.002
		2.897	0.030	0	0
p-quaterphenyl	$T_1 \leftarrow S_0$	3.111			
	$T_j \leftarrow T_1$	*2.544*	0.884	0.006	0.075
		2.838	0.004	0	0
		2.993	0.029	0	0.002

[a] 0 means $<10^{-3}$.

3.4. Excitation Involving Triplet States

MIM calculations for excitations involving triplet states in diphenyl and the three terphenyls have been reported before [3, 7].

In Table 4 we collected the calculated values for excitation energies and oscillator strengths of $T_1 \leftarrow S_0$ and $T_j \leftarrow T_1$ transitions in quaterphenyls. Unfortunately no experimental data are available for comparison.

4. Discussion

A recent X-ray determination of the molecular structure of *para*-terphenyl has shown this molecule to be nearly planar [14]. However this finding is not in contrast with our results. The nearly planar configuration given by X-ray results may correspond to a mean configuration and not to equilibrium configuration. Besides it has been shown in the case of diphenyl [8] that the planar configuration in the crystal is due to the action of packing forces. In the case of p, p'-bitolyl the packing of molecules in the crystal is such that twist angle for the molecule in the crystal is 36° and 40° for the two molecules in the asymmetric unit [15]. A similar angle of twist ($\vartheta = 33°$) is found in 4,4'-dinitrobiphenyl [16] and 4-nitrobiphenyl [17]. As usual in the MIM method the agreement of calculated and experimental singlet-singlet transition energy is excellent for all molecules. This is evident from Fig. 4, where a regression line is shown to correlate the experimental transition energies of all known bands with the corresponding calculated values for the whole series of molecules. Oscillator strengths have been calculated by means of the dipole-length, dipole-velocity expressions and their geometrical mean. Our systems differ from the ones that have been previously used for a

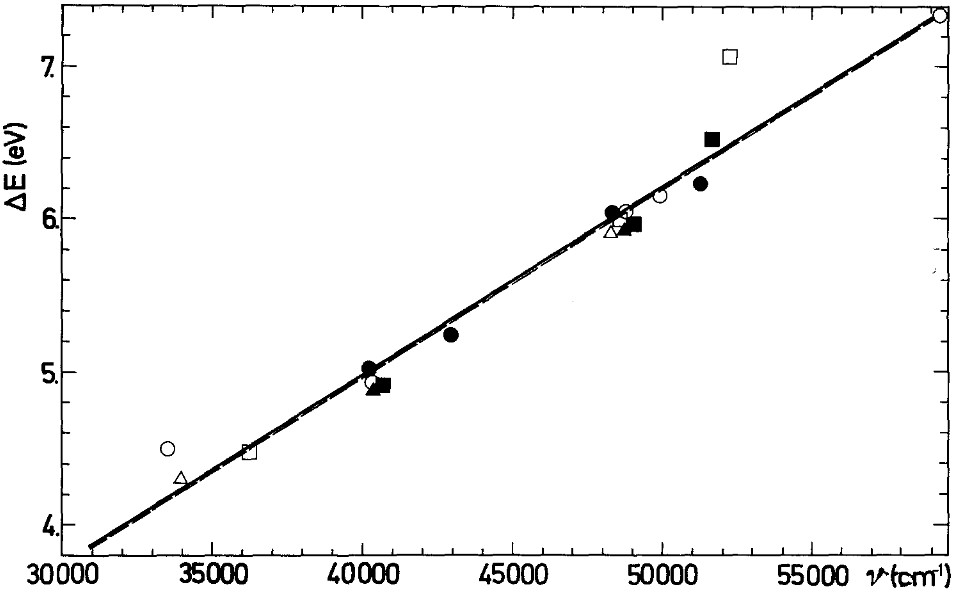

Fig. 4. Regression line for theoretical excitation energy of the first bands versus observed frequencies in polyphenyls (solid line). The dotted line corresponds to exact agreement between theory and experiment. Correlation coefficient $r = 0.997$, $n = 18$. ○ diphenyl, ● *o*-terphenyl, □ *p*-terphenyl, ■ *m*-terphenyl, △ *p*-quaterphenyl, ▲ *m*-quaterphenyl

test of this kind in two aspects: we are using MIM wave-functions and we consider non planar conjugated molecules, where σ-π interactions may be particularly significant.

It may be pointed out that in general a better agreement is obtained when the gradient operator is used. This rule is not without exception as for example in the fourth band of *ortho*-terphenyl. However it is worthwhile to point out that the agreement between experimental and calculated oscillator strengths when using gradient operator is always good even in cases when dipole operator does a better job, while the f_1 values may sometimes be far off the experimental values. On the basis of the small series of molecules which has been used in the present test it seems that the use of gradient operator together with MIM wavefunctions may be recommended.

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