

147. Electronic Absorption Spectra of Planar, Conjugated Biradicals in the Lowest Triplet State

by Markus Gisin¹⁾ and Jakob Wirz

Physikalisch-chemisches Institut der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

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Summary

The semiempirical PPP-SCF-SCI method has been adapted to even-electron, open-shell π -systems by performing the SCF calculation on the lowest triplet configuration and choosing a limited set of single electronic excitations from the latter for configuration interaction. The basic approximations and parameters of the standard PPP model were retained. The results were compared with experimental triplet-triplet absorption spectra of aromatic hydrocarbons and with more elaborate calculations available for selected systems. The reliability of the model was found to be comparable to its well-known performance in predicting the absorption spectra of closed-shell π -systems and of conjugated radicals. Triplet-state absorption spectra for various planar, conjugated biradicals were calculated and, where possible, compared with experimental data.

Introduction. – The aim of this report is to show that the triplet-triplet absorption spectra of planar conjugated biradicals can be predicted with useful reliability on the basis of simple π -electron calculations. Many efforts have been devoted in recent years to the spectroscopic detection of biradical intermediates and the direct monitoring of their reaction kinetics. Conjugated biradicals, in which the singly occupied orbitals are delocalized over a common π -system, are particularly attractive for studies by optical spectroscopy: due to the delocalization of their unpaired electrons, they may be expected to exhibit some kinetic stability and relatively long-wavelength absorption. Thus, readily available model calculations are desirable both as a guideline to decide between different conceivable assignments of an observed transient intermediate and to describe the electronic structure and, hence, the reactivity of such species.

Standard PPP-SCF-SCI²⁾ calculations are well-known to yield useful predictions for the absorption spectra of closed-shell conjugated hydrocarbons and heterocyclic

1) Present address: *Ciba-Geigy AG*, Postfach, 4002 Basel.

2) Semiempirical, π -electron, self-consistent field (SCF) calculations using the zero differential overlap (ZDO) approximation (*Pariser & Parr* [1] and *Pople* [2]), followed by configuration interaction (CI) using singly excited configurations only.

molecules [3] as well as for conjugated radicals or radical ions [4] at negligible computer cost. It is however dangerous to extend the use of semiempirical methods to new applications, unless the results can be tested extensively by comparison with experimental data. For example, it has been shown [5] that standard PPP-SCF-SCI predictions for the absorption spectra of benzenoid hydrocarbons in the excited triplet state are far from satisfactory, unless an entirely different parameter set is adopted for the triplet manifold. The unfortunate necessity to use different parameters for different multiplicities has been attributed to differences in electronic correlation which are not fully accounted for by limited CI. Indeed, satisfactory agreement with the experimental triplet spectra of a few benzenoid hydrocarbons has been achieved [6] [7], using standard parameters, by fairly extensive inclusion of multiply excited configurations.

It should be recalled that standard PPP-SCF-SCI calculations are biased to describe the electronic spectra of closed-shell singlet ground-state systems for two reasons: (i) The molecular orbitals are optimized by an SCF procedure for the closed-shell ground configuration Γ , and (ii) the choice to include only single-electron excitations (with respect to Γ) for CI is justifiable only when the initial state is well-described by Γ . Since only single excitations contribute to the transition moment connecting two states, we expected that an adequate model to predict the electronic spectra of triplet biradicals might be obtained by retaining the basic approximations, standard parameters, and simplicity of the PPP-SCF-SCI method, but replacing the above-mentioned bias by an equivalent one for open-shell triplets. Indeed, several authors [8] have found that PPP calculations with a single set of parameters can yield satisfactory predictions for the triplet energies E_T of benzenoid hydrocarbons, if separate SCF calculations are performed for the singlet ground configuration Γ and the lowest triplet configuration χ_0 . We now report the results of simple SCI calculations for the triplet state and test their reliability by comparison with the available electronic spectra.

Method of Calculation. – *Definition of Symbols* (cf. the Figure). Small greek suffixes (μ, ν) label atomic p_z -orbitals (ϕ_μ), small roman suffixes (i, j) molecular orbitals (ψ_i), large roman suffixes (L, J) state wave functions (ψ_L). The configurations $\chi(i \rightarrow j)$ are constructed from the lowest triplet configuration χ_0 by excitation of an electron from ψ_i to ψ_j . To distinguish closed-shell, open-shell and virtual orbitals, the general labels (i, j) are replaced by (k, l), (m, n), and (r, s) for orbitals which are doubly, singly, and un-occupied, respectively, in χ_0 . In integrals which are abbreviated by brackets and in *Slater*-determinants the sole labels μ , i, and (i \rightarrow j) are used to represent the functions ϕ_μ , ψ_i , and $\chi(i \rightarrow j)$, respectively.

$$\begin{aligned} \psi_i &= \sum_{\mu} c_{i\mu} \phi_{\mu} \\ \chi_0 &= | \dots k \bar{k} \dots mn | \\ \chi(k \rightarrow n) &= | \dots k \bar{n} \dots mn |, & \chi(m \rightarrow s) &= | \dots k \bar{k} \dots sn | \\ (\mu\mu | \nu\nu) \equiv \gamma_{\mu\nu} &= \int \int \phi_{\mu}^2(1) \frac{e^2}{r_{12}} \phi_{\nu}^2(2) dv(1) dv(2) \\ [ij | i'j'] &= \int \int \psi_i(1) \psi_{i'}(2) \frac{e^2}{r_{12}} \psi_j(1) \psi_{j'}(2) dv(1) dv(2) \end{aligned}$$

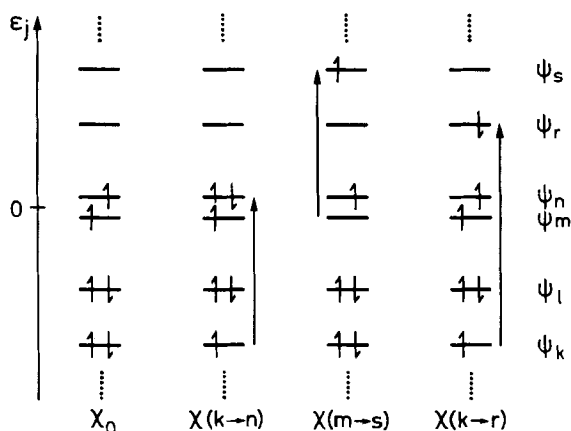


Figure. Orbital occupation schemes showing the lowest triplet configuration χ_0 and different types of singly excited configurations

$$\begin{aligned} \langle (i \rightarrow j) | (i' \rightarrow j') \rangle &= \int \chi(i \rightarrow j) \mathbf{H} \chi(i' \rightarrow j') dv \\ \mathbf{H} &= \sum_i h_i^c + \sum_i \sum_j \frac{e^2}{r_{ij}} \\ \vec{\mathbf{M}}(i \rightarrow j; i' \rightarrow j') &= \int \chi(i \rightarrow j) \vec{\mathbf{M}} \chi(i' \rightarrow j') dv \\ \vec{\mathbf{M}} &= e(\sum \vec{r}_i - \sum_{\mu} Z_{\mu}^c \vec{r}_{\mu}) \end{aligned}$$

SCF Calculations. Starting from *Hückel* MO's, a restricted open-shell SCF calculation is performed for the lowest triplet configuration χ_0 using the 'zero differential overlap' [1] [2] and 'half-electron' [9] approximations. Thus the SCF part of a closed-shell PPP computer program can be easily adapted by modifying only the occupation numbers b_j in the density matrix $p_{\mu\nu}$ (Eqn. 1) of the *Pople* equations (Eqn. 2 and 3) [2].

$$p_{\mu\nu} = \sum_j b_j c_{j\mu} c_{j\nu} \begin{cases} b_j = 2 \text{ for } j = k, l \\ b_j = 1 \text{ for } j = m, n \\ b_j = 0 \text{ for } j = r, s \end{cases} \quad (1)$$

$$F_{\mu\mu} = I_{\mu} + \frac{1}{2} p_{\mu\mu} \gamma_{\mu\mu} + \sum_{\nu \neq \mu} (p_{\mu\nu} - Z_{\mu}^c) \gamma_{\mu\nu} \quad (2)$$

$$F_{\mu\nu} = \beta_{\mu\nu} - \frac{1}{2} p_{\mu\nu} \gamma_{\mu\nu} \quad (3)$$

Idealized molecular geometries (regular planar polygons, bond lengths 140 pm) are assumed throughout and the standard parameter set used in closed-shell calculations ($\gamma_{\mu\nu} = 1439.5 / (132.8 + R_{\mu\nu} / \text{pm})$ eV [10], $I_{\mu} \equiv 0$ eV, $\beta_{\mu\nu} = -2.318$ eV, and $Z_{\mu}^c = 1$ for hydrocarbons) is retained. Minor deviations of the approximate 'half-electron' MO's from the proper SCF-MO's determined by the *Rootaan* procedure [11] are likely [12] to be wiped out by the subsequent CI calculation.

CI Calculation. For convenience, the total π -electron energy of χ_0 [11],

$$E(\chi_0) = \sum_j b_j \varepsilon_j - \sum_k \sum_{j=l,m} (2 J_{kj} - K_{kj}) - \frac{1}{2} \sum_m \sum_n J_{mn}, \quad (4)$$

$$\varepsilon_j \equiv F_{jj}, \quad F_{ij} = \sum_{\mu} \sum_{\nu} c_{i\mu} c_{j\nu} F_{\mu\nu},$$

$$J_{ij} \equiv [ii | jj] = \sum_{\mu} \sum_{\nu} c_{i\mu}^2 c_{j\nu}^2 \gamma_{\mu\nu},$$

$$K_{ij} \equiv [ij | ij] = \sum_{\mu} \sum_{\nu} c_{i\mu} c_{j\mu} c_{i\nu} c_{j\nu} \gamma_{\mu\nu},$$

is chosen as the origin for the computation of the energies of the singly excited configurations. Only configurations corresponding to single excitations to or from the singly occupied orbitals ψ_m and ψ_n , i.e. $\chi(k \rightarrow m)$ and $\chi(m \rightarrow r)$, respectively, are considered for CI. The elements of the CI matrix are given in Table 1.

Transition Densities and Bond Orders. The oscillator strength f_{LJ} for an electronic transition from the lowest triplet state ψ_L to an excited state ψ_J and the bond orders $P_{\mu\nu, J}$ are calculated as follows [13]:

$$f_{LJ} = 1.085 \cdot 10^{-5} \Delta E_{LJ} \cdot |\vec{M}_{LJ}|^2 / e^2$$

where $[\Delta E_{LJ}] = \mu m^{-1}$ and $[|\vec{M}_{LJ}|^2 / e^2] = \text{pm}^2$.

$$\begin{aligned} \vec{M}_{LJ} &\equiv \int \psi_L \vec{M} \psi_J \, dv = \sum_{(i \rightarrow j)} \sum_{(i' \rightarrow j')} C_{L(i \rightarrow j)} C_{J(i' \rightarrow j')} \vec{M}(i \rightarrow j; i' \rightarrow j') \\ P_{\mu\nu, J} &\equiv \int \psi_J \sum_{\mu} e_{\mu} \psi_J \, dv = \sum_{(i \rightarrow j)} \sum_{(i' \rightarrow j')} C_{J(i \rightarrow j)} C_{J(i' \rightarrow j')} P_{\mu\nu}(i \rightarrow j; i' \rightarrow j') \end{aligned}$$

The matrix elements $\vec{M}(i \rightarrow j; i' \rightarrow j')$ are given in Table 1 in terms of integrals \vec{m}_{ij} , where

$$\vec{m}_{ij} \equiv e \int \psi_i(1) \xi \psi_j(1) \, dv = e \sum_{\mu} c_{i\mu} c_{j\mu} \xi_{\mu}, \quad \xi_{\mu} = (x_{\mu} \, y_{\mu} \, z_{\mu})$$

and the elements $P_{\mu\nu}(i \rightarrow j; i' \rightarrow j')$ are derived from the elements of the transition moment matrix $\vec{M}(i \rightarrow j; i' \rightarrow j')$ by replacement of \vec{m} with d and Z_{μ}^2 with zero, where

$$d_{ij} \equiv e \int \psi_i(1) \psi_j(1) \, dv = \frac{e}{2} (c_{i\mu} c_{j\nu} + c_{j\mu} c_{i\nu}).$$

The dipole moment of the ground configuration,

$$\vec{M}(\chi_0, \chi_0) = 2 \sum_k \vec{m}_{kk} + \vec{m}_{mm} + \vec{m}_{nn},$$

is arbitrarily set to zero to allow for the calculation of transition moments in charged systems.

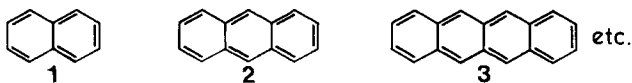
It is important to note that the SCF calculations described above are inadequate for molecules with degenerate triplet ground configurations (e.g. benzene or

triphenylene) [14]. However, such cases will hardly be encountered in biradicaloid systems.

Table 1. Elements of the Configuration Interaction and Transition Moment Matrices in MO Basis
(The symbols are defined in the text)

Configurations (i → j)	(i' → j')	Configuration interaction (i → j) (i' → j')	Transition moment $\vec{M}(i \rightarrow j; i' \rightarrow j')$
χ_0	χ_0	0 (arbitrarily)	$\vec{0}$ (arbitrarily)
k → n	k → n	$e_n - e_k - J_{kn} + 1/2(J_{nn} + K_{kn} + K_{mn} - K_{km})$	$\vec{m}_{nn} - \vec{m}_{kk}$
m → s	m → s	$e_s - e_m - J_{sm} + 1/2(J_{mm} + K_{sm} + K_{mn} - K_{sn})$	$\vec{m}_{ss} - \vec{m}_{mm}$
χ_0	k → n	$F_{kn} + 1/2([nn nk] + [mk nm])$	\vec{m}_{kn}
χ_0	m → s	$F_{ms} - 1/2([mm ms] + [ns mn])$	\vec{m}_{ms}
k → n	m → s	$[kn ms]$; if $m = n$: $[km ms]$	$\vec{0}$
k → n	k → m	$F_{nm} - [kk nm] + [kn km] + 1/2([nn nm] + [mm nm])$	\vec{m}_{nm}
k → n	l → n	$-F_{kl} - [nn kl] + 1/2([nk nl] - [mk ml])$	$-\vec{m}_{kl}$
k → n	l → m	$[kn lm] - [nm kl]$	$\vec{0}$
m → s	m → r	$F_{sr} - [mm sr] + 1/2([ms mr] - [ns nr])$	\vec{m}_{sr}
m → s	n → s	$-F_{mn} - [mn ss] + [ms ns] + 1/2([mm mn] + [nn mn])$	$-\vec{m}_{mn}$
m → s	n → r	$[ms nr] - [sr mn]$	$\vec{0}$

Triplet Absorption Spectra of Aromatic Hydrocarbons. – Although the open-shell PPP program was conceived for biradicals, it should also be adequate for predicting triplet-triplet absorption spectra of molecules with a singlet ground state, since the spacial part of the lowest triplet state T_1 is usually well-described by the lowest open-shell configuration χ_0 [15]. To test the reliability of our model, we have performed calculations for more than sixty aromatic hydrocarbons. The results agree fairly well with the experimental data [16] [17], *i.e.* the transition energies are on the average overestimated by 5–10%, but it must be realized that such a comparison is somewhat arbitrary, since in most cases only the positions and approximate intensities of the strongest triplet absorption bands are known experimentally. A more stringent test is possible only by comparison with high-quality triplet spectra including weak absorption bands and with reliable symmetry assignments, corroborated by polarization data. We thus restrict the present discussion to the linear polyacenes naphthalene (1), anthracene (2), tetracene (3), pentacene (4), and hexacene (5) [7] [18–23].



Meyer et al. [7] have performed PPP-type calculations with extensive CI, including all singly and doubly excited configurations with respect to χ_0 , to interpret their outstanding spectral data for 1 to 3. Our calculations for the triplet absorption spectra of the linear polyacenes are summarized in Table 2. A comparison with the experimental and theoretical data of *Meyer et al.* leads to the following conclusions. (i) The two calculations suggest the same symmetry assignments for all observed

transitions and the accuracy (energy, oscillator strength) is comparable; both calculations tend to overestimate the transition energies. (ii) Starting at fairly low energies ($\Delta E \geq 2 \mu\text{m}^{-1}$), the calculations by Meyer *et al.* predict a number of excited states which are missing in our calculations. The transitions to these states are invariably calculated to be weak; they have not been detected experimentally and a comparison with the related results by Pancir & Zahradnik [5] reveals that their leading configurations are doubly excited with respect to χ_0 . Indeed, doubly excited configurations of the type $\chi(k \rightarrow m, n \rightarrow r)$, which are ignored by our model, may be expected to occur at rather low energies when the energy gaps between the orbitals ψ_k and ψ_m and between ψ_n and ψ_r are small (*cf.* the *Figure*).

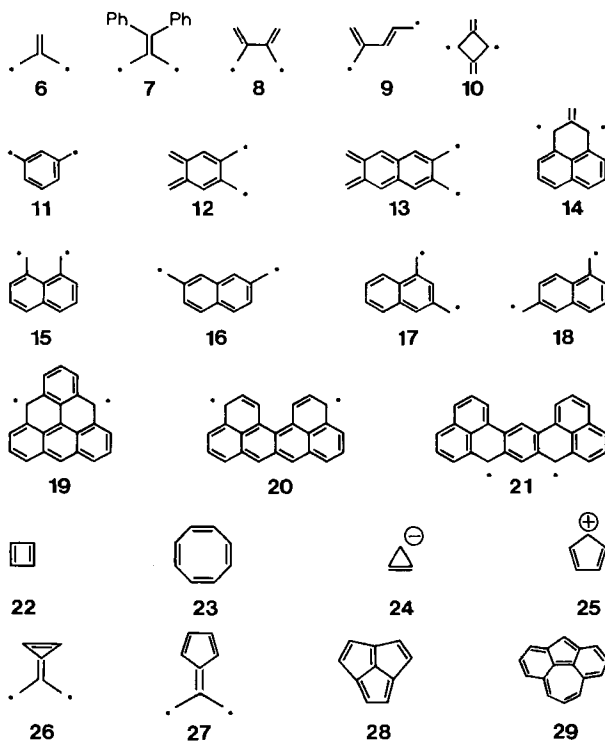
Table 2. Calculated and Observed [7] [18–23] Triplet-Triplet Transitions of the Linear Polyacenes 1–5 (Forbidden or weak ($f \leq 0.1$) calculated transitions are quoted only, if they are lower in energy than the first allowed transition)

Column entries: a) symmetry species of the excited triplet state (long axis: x, short axis: y), b) calculated transition energy in μm^{-1} , c) calculated oscillator strength f_{1J} , d) experimental transition energy in μm^{-1} , e) experimental oscillator strength, f) questionable assignments marked (?).

a	b	c	d	e	f	a	b	c	d	e	f
Naphthalene (1)						Tetracene (3)					
B_{1g}^+	0.69	0				B_{1g}^+	0.87	0	1.04	0.002	
B_{3u}^+	1.11	0				B_{3u}^+	1.96	0	2.08	0.2	?
B_{3u}^-	1.46	0	1.59	0.002	?	B_{3u}^-	2.14	0			
A_g^+	2.14	0				B_{1g}^-	2.25	0.96	2.16	0.45	
B_{1g}^-	2.52	0.47	2.42	0.12		A_g^-	3.40	0.36	3.14	0.15	?
A_g^-	3.47	0.54	3.64	0.13	?	B_{1g}^-	4.24	2.37	3.50	0.85	
B_{1g}^-	4.88	1.54	4.24	0.5							
Anthracene (2)						Pentacene (4)					
B_{1g}^+	1.28	0	1.13	0.002		B_{1g}^+	0.80	0			
B_{3u}^+	1.75	0				B_{1g}^-	2.09	1.20	1.98	0.7	
B_{3u}^-	1.95	0				A_g^-	3.38	0.30	2.68	0.03	?
B_{2u}^+	2.04	0	1.94	0.04	?	B_{1g}^-	4.07	2.62	3.28	2.1	
A_g^+	2.50	0				Hexacene (5)					
B_{1g}^-	2.51	0.59	2.35	0.25		B_{1g}^+	0.66	0			
A_g^-	3.49	0.43	3.04	0.03	?	B_{1g}^-	1.95	1.48	1.82	~1	
B_{1g}^-	4.55	1.85	3.81	0.8		A_g^-	3.36	0.25			
						B_{1g}^-	3.93	2.69			

Fortunately, the mixing of singly and doubly excited configurations appears to be of minor importance. A similar situation applies to closed-shell SCI calculations; the SCI model is quite successful in predicting the absorption spectra of, *e.g.*, the linear polyacenes [24], in spite of the fact that it completely ignores the presence of numerous forbidden states in the spectral region of interest [25]. The further omission of singly excited configurations with four unpaired electrons, type $\chi(k \rightarrow r)$, is likely to be a serious limitation of our model in perimeter-like closed-shell systems, but should not interfere in open-shell biradicals where the lowest $k \rightarrow r$ excited configurations are relatively high in energy (*cf.* the *Figure*).

Triplet Absorption Spectra of Conjugated Biradicals. – The transition energies and oscillator strengths f calculated for the biradicals **6** to **29** are listed in *Table 3*.



Discussion. – *General.* The chemical behavior of biradicaloid reaction intermediates is complicated by the existence and possible involvement of several low-lying electronic states. It is difficult to determine experimentally the energy difference between the lowest singlet and triplet state of such transient species and the corresponding rates of intersystem crossing. *Ab initio* calculations have become an important tool to predict the ground-state multiplicity and structure of prototype biradicaloids such as methylene [26], cyclobutadiene (**22**) [27], or ‘trimethylene-methane’ (**6**) [28]. For each of these species the best available experimental evidence was at one time in the last decade considered to be in serious contradiction with the most trustworthy theoretical predictions. Remarkably, in each case further work has strongly favored the original theoretical predictions and it is likely (or proven) that the discrepancies arose by misinterpretation of the spectroscopic data. For larger systems, qualitative guidelines are available [29] to answer such questions from theory. It appears that conjugated π, π -biradicals tend to favor planar, ‘aromatic’ structures in the triplet state and distorted geometries in the singlet state. In this work we have simply assumed that the π, π -biradicals **6–29** are (essentially) planar in the lowest triplet state which may or may not be the electronic ground

Table 3. Calculated Triplet-Triplet Transitions of the Conjugated Hydrocarbon Biradicals 6-29

 (Symmetry axis convention for C_{2v} and D_{2h} point groups: y = horizontal, z = vertical)

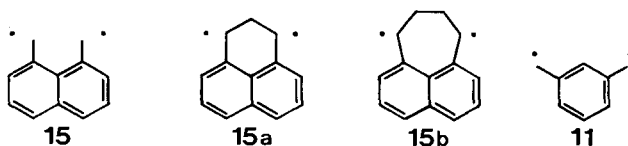
 Column entries: a) compound number, b) assumed molecular symmetry, c) symmetry species of the lowest triplet state, d) sequence of excited triplet states; symmetry species and transition energy in μm^{-1} (oscillator strength f_{LJ}). Forbidden or weak ($f_{LJ} \leq 0.1$) transitions are usually omitted, unless they are lower in energy than the first allowed transition.

a	b	c	d
6	D_{3h}	A_2^+	E^+ 3.24 (0), E'^- 5.12 (0.54).
7	C_{2v}	B_2^+	A_1^+ 2.55 (0), A_1^+ 2.68 (0), B_2^+ 2.83 (0), B_2^+ 3.03 (0), A_1^+ 3.04 (0), B_2^- 3.36 (0.43), A_1^- 3.37 (0.49), A_1^- 3.46 (0.10), B_2^- 3.54 (0.36), A_1^- 4.83 (0.59).
8	D_{2h}	B_{3u}^+	B_{1g}^+ 1.43 (0), B_{2u}^+ 1.49 (0), B_{2u}^- 3.53 (0), B_{1g}^- 3.72 (0.53).
9	C_s	A'^+	A'^+ 2.05 (0), A'^+ 2.52 (0), A'^+ 3.83 (0), A'^- 3.85 (1.07), A'^- 4.47 (0.31).
10	D_{2h}	B_{2u}^+	B_{3g}^+ 1.55 (0), B_{1u}^+ 2.91 (0), B_{1u}^- 2.91 (0), B_{3g}^- 4.15 (1.80).
11	C_{2v}	B_2^+	B_2^+ 2.49 (0), A_1^+ 2.51 (0), A_1^+ 3.27 (0), B_2^+ 3.43 (0), A_1^- 3.64 (0.17), B_2^- 4.14 (0.11), B_2^- 4.44 (0.44), A_1^- 4.58 (1.26).
12	D_{2h}	B_{1u}^+	B_{3g}^+ 0.98 (0), B_{2u}^+ 1.12 (0), B_{2u}^- 2.55 (0), B_{1u}^+ 2.55 (0), A_g^+ 2.66 (0), B_{3g}^- 2.77 (0.93), B_{3g}^- 4.84 (1.85).
13	D_{2h}	B_{1u}^+	B_{3g}^+ 0.57 (0), B_{2u}^+ 0.81 (0), B_{2u}^- 1.98 (0), B_{3g}^- 2.22 (1.35), A_g^- 3.43 (0.01), B_{3g}^- 4.04 (0.04), B_{3g}^- 4.33 (2.59).
14	C_{2v}	B_2^+	B_2^+ 1.98 (0), A_1^+ 2.25 (0), B_2^+ 2.70 (0), A_1^+ 2.73 (0), A_1^- 2.94 (0.03), B_2^- 3.31 (0.85), A_1^- 3.40 (0.62), A_1^- 3.80 (0.30), B_2^- 4.10 (0.33), B_2^- 4.42 (0.84).
15	C_{2v}	B_2^+	A_1^+ 1.97 (0), B_2^+ 2.06 (0), A_1^+ 2.46 (0), B_2^+ 3.04 (0), A_1^- 3.28 (0.43), B_2^- 3.31 (0.51), B_2^- 3.71 (0.22), A_1^- 4.31 (0.15), B_2^- 4.92 (1.14).
16	C_{2v}	B_2^+	A_1^+ 1.96 (0), B_2^+ 2.15 (0), A_1^- 3.16 (0.50), B_2^- 3.42 (0.07), B_2^- 3.97 (0.21), A_1^- 4.21 (1.65).
17	C_s	A'^+	A'^+ 1.86 (0), A'^+ 2.60 (0), A'^+ 2.96 (0), A'^+ 3.21 (0), A'^- 3.22 (0.32), A'^- 3.50 (0.35), A'^- 3.88 (0.52), A'^- 4.39 (0.47), A'^- 4.53 (0.47).
18	C_s	A'^+	A'^+ 1.85 (0), A'^+ 2.22 (0), A'^+ 2.72 (0), A'^+ 3.04 (0), A'^- 3.29 (0.40), A'^- 3.32 (0.09), A'^- 3.59 (0.44), A'^- 4.16 (1.18), A'^- 4.45 (0.48).
19	D_{3h}	A_1^+	E^+ 1.93 (0), E^+ 2.26 (0), A_2^+ 2.41 (0), A_2^+ 2.67 (0), E'^- 2.76 (0.04), E'^- 3.30 (2.26).
20	C_{2v}	B_2^+	A_1^+ 1.71 (0), B_2^+ 1.78 (0), A_1^+ 2.17 (0), B_2^+ 2.18 (0), A_1^+ 2.49 (0), A_1^- 2.55 (0.60), A_1^- 2.80 (0.39), A_1^- 3.14 (1.40), B_2^- 3.53 (0.47).
21	C_{2v}	B_2^+	A_1^+ 1.52 (0), B_2^+ 1.61 (0), B_2^+ 2.26 (0), A_1^- 2.27 (1.16), B_2^- 2.59 (0.18), A_1^- 2.85 (0.37), A_1^- 3.15 (1.22), B_2^- 3.22 (1.12).
22	D_{4h}	A_{2g}^+	E_u^+ 2.43 (0), E_u^- 5.05 (0.54).
23	D_{8h}	A_{2g}^+	E_{1u}^+ 2.16 (0), E_{3u}^+ 2.16 (0), E_{3u}^- 3.13 (0), E_{2g}^+ 3.73 (0), E_{1u}^- 4.40 (1.60).
24	D_{3h}	A_2'	E' 5.61 (0.20).
25	D_{5h}	A_2'	E_1' 2.01 (0.04), E_2' 4.18 (0), E_1' 5.21 (0.71).
26	C_{2v}	B_2	A_1 0.92 (0.01), B_2 2.88 (0.11), A_1 3.01 (0.02), B_2 4.53 (0.55).
27	C_{2v}	B_2	A_1 0.46 (0.00), B_2 2.47 (0.18), B_2 3.68 (0.21), B_2 4.00 (0.58), A_1 4.72 (0.35).
28	D_{3h}	A_2'	E' 0.27 (0.00), A_2' 2.08 (0), E' 2.09 (0.03), E' 3.50 (0.73).
29	C_{2v}	B_2	A_1 1.32 (0.01), A_1 1.66 (0.01), B_2 2.21 (0.02), B_2 2.59 (0.07), A_1 2.80 (0.08), A_1 3.25 (0.10), A_1 3.64 (1.10), B_2 3.96 (0.67).

state. Our results indicate that, under these premises, the triplet-triplet transitions predicted by a simple open-shell version of the PPP-SCF-CI procedure (Table 3) are sufficiently reliable to be helpful for the assignment of optical spectra obtained at low temperature and/or by flash photolysis.

Before we discuss a few particular examples, we wish to point out some *general rules, applicable to the lowest triplet state of alternant hydrocarbons* (AH's), which follow directly from the *Coulson-Rushbrooke* pairing theorem [30]. The far-reaching consequences of orbital pairing on the electronic spectra of AH's (closed-shell systems, radicals, radical ions, polyions) are well-known. In particular, the electronic states are partitioned into two sets ('plus' and 'minus' states [24], or states of 'odd' and 'even parity' [31]) and only transitions between states of different parity are allowed, irrespective of symmetry. In practice, parity-forbidden transitions are very weak ($\epsilon \approx 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, e.g. the first absorption band of naphthalene, labelled α or 1L_b). It is shown in the *Appendix* that the first triplet-triplet absorption band of neutral even AH's is necessarily forbidden by the parity rule. In the case of *triplet biradical AH's, the first two (or more) transitions are forbidden by the parity rule*. Furthermore, as predicted and extensively documented for neutral AH's in general, *transition energies will be rather insensitive to inductive perturbation by substituents, whereas the intensity of parity-forbidden transitions should be very susceptible to such perturbations*. Variations in the resonance integrals β due to deviations from planarity should not impair the rules but, of course, will affect the transition energies in explicit calculations.

Specific Examples. The number of authentic, experimental triplet absorption spectra of conjugated triplet biradicals is obviously limited. The best-documented example of a neutral hydrocarbon is 1,8-naphthoquinodimethane (**15**) and its methylene- and dimethylene-bridged derivatives **15a** and **15b**, all of which are known [32] [33] to have a triplet ground state. The close similarity between the triplet-triplet absorption spectra of **15** [32], **15a** [34], and **15b** [32] indicates either that all three molecules are essentially planar, or that the absorption spectrum is insensitive to deviations from planarity. The agreement between the experimental absorption spectra and the calculation (*Table 3*) for planar **15** is quite satisfactory³). As predicted by the general rule and the explicit calculation, the first absorption band near $2 \mu\text{m}^{-1}$ consists of two closely-spaced, very weak transitions of opposite polarization [32] [35].



Methylated *m*-xylylenes **11** were tentatively identified in 1968 by *Migirdicyan* [36] among the photolysis products of polymethylbenzenes at 77 K by using the sensitive technique of fluorescence excitation and emission. The author has since corroborated her innovating proposal by further work and calculations [37]. Recently, *Wright & Platz* [38] have prepared the parent biradical **11** by low-temperature photolysis of a different precursor. In this work the species was detected by ESR spectroscopy and was found to have triplet multiplicity in the

³) In fact, the result of this calculation has been one of the major early indications leading us to doubt the original assignment of the optical spectra of **15a** to singlet-singlet transitions [32].

ground state. It remains to be established that the optical and ESR spectra arise from the same species⁴). The present calculations are in fair agreement with the observed optical spectra (Table 3). The calculations performed by Migirdicyan & Baudet [37] predict two weak transitions near $2.5 \mu\text{m}^{-1}$ in agreement with our results.

Optical spectra for two trimethylenemethane derivatives **6a** and **7a** have been reported by Turro *et al.* [39]. Their analysis was based on the tacit assumption that the substituent effects on the spectrum of **6** should be of minor importance (spectral features in a given spectral region were associated with related transitions in the two molecules and compared with the *ab initio* predictions for parent **6** by Davis & Goddard [28]). This approach should be legitimate with respect to alkyl substituents in accordance with the rules for inductive perturbation and the experimental findings with the alkyl derivatives of **11** and **15**. However, the phenyl groups should not be treated in this cavalier manner (*cf.*, *e.g.*, the spectra of ethylene and stilbene). Indeed, the present calculation predicts large differences between the spectra of **6** and **7** (Table 3).

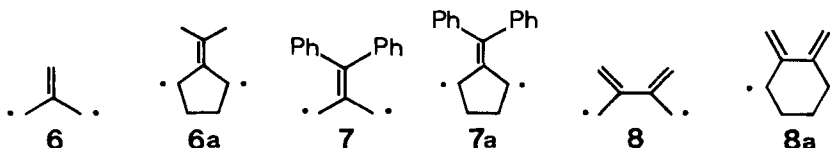
High-quality absorption, excitation, and emission spectra were obtained by Turro *et al.* for **7a**, whereas the determination of the spectrum of **6a** met with experimental difficulties⁵). Biradical **7a** exhibits a very weak ($f \approx 10^{-3}$) first absorption band at $2.08 \mu\text{m}^{-1}$ in near coincidence with the fluorescence peak. A series of strong bands ($f \approx 0.1$) was observed in the range of 3.0 to $3.8 \mu\text{m}^{-1}$. The authors have ensured that the entire optical spectra appear (upon irradiation of the azo precursor) and disappear (upon warming) in coincidence with the ESR spectrum of triplet **7a**. The experimental spectrum is in satisfactory agreement with the present calculation for **7** assuming that the entire spectrum arises from triplet-triplet transitions of (essentially) planar **7a**. The predicted transitions are not much affected by rotating the phenyl groups out of the molecular plane up to an angle of 45° . This simple interpretation of the optical spectra was, however, tentatively rejected by Turro *et al.* in favor of a 'two-species-postulate'; the optical spectra were thus attributed to a mixture of two species in thermal equilibrium, namely an (essentially) planar triplet state and a bisected singlet state of **7a** in which the diphenylmethylene moiety is orthogonal to the allyl moiety in the five-membered ring. The latter interpretation meets with a number of serious difficulties and the arguments originally put forward against the straightforward assignment of the spectra to triplet **7a** appear to fade away in the light of the results presented above.

On the other hand, the spectral data reported [39] for **6a** are obviously less reliable (fluorescence emission below $1.9 \mu\text{m}^{-1}$, extremely weak absorption, $\epsilon \approx 10$, above $2.3 \mu\text{m}^{-1}$ and weak absorptions, $\epsilon \approx 10^2 \text{ dm}^3 \text{ mol cm}^{-1}$, above $3.1 \mu\text{m}^{-1}$). In this case we agree with the authors that the discrepancy with the theoretical predictions for **6** is serious (the present PPP calculation is in qualitative agreement with the earlier *ab initio* predictions [28]). The 'two-species postulate' [39], implicating a thermal equilibrium between the triplet and singlet state of **6a** at 77 K, has

⁴) The necessary experiments are planned in collaboration with the two research groups.

⁵) Earlier attempts in this laboratory to obtain the optical spectra of parent **6** by low-temperature photolysis of 4-methylene pyrazoline have failed entirely.

become untenable since the recent revision of the singlet-triplet energy gap from ≤ 3.5 kcal/mol [40] to ≥ 13.3 kcal/mol [41] by the *Berson* group. We would, therefore, suggest that the extremely weak features (absorption and emission) observed in the visible region may be due to adventitious photoproducts other than **6a**. Clearly, more work will be needed to establish the optical spectra of trimethylene-methane.



Roth et al. [42] have reported a low-temperature absorption spectrum for 2,3-dimethylene-1,4-cyclohexadiyl (**8a**). The same spectrum was obtained from two different precursors and the species was also observed by room-temperature flash photolysis. The agreement of the observed spectrum (absorption onset near $1.9 \mu\text{m}^{-1}$, medium-intensity band, $\epsilon \approx 10^3$, at $2.3 \mu\text{m}^{-1}$ and strong end absorption, $\epsilon \geq 10^4$, above $4.0 \mu\text{m}^{-1}$) with our calculation for planar triplet 2,2'-bisallyl **8** (*Table 3*) is rather poor. However, both the experimental results by *Roth & Scholz* [43] and the theoretical predictions by *Döhnert & Koutecky* [29] and *Kollmar* [44] agree that in this case the lowest singlet state of **8** is nearly degenerate with the triplet state. Therefore, the possibility remains that the diffuse band at $2.3 \mu\text{m}^{-1}$ is due to singlet **8a** and that the very weak triplet-triplet transitions predicted below $1.5 \mu\text{m}^{-1}$ have escaped detection. It would be of interest to study the temperature dependence of the ESR and optical spectra of **8a**.

Finally, the qualitative results obtained by the flash-photolysis technique for the triplet absorption spectra of the [4n]annulenes **22** (tetraalkyl derivative [45]), **23** [46], and cycl[3.3]azine [47] are in agreement with the present calculations. Since we have retained the standard parameter set used for PPP-SCI calculations of closed-shell hydrocarbons, it is likely that heterocycles can be treated by the same method using standard parameters for the heteroatoms.

Appendix. – The pairing theorem, originally derived for *Hückel* molecular orbitals of alternant hydrocarbons (AH's) [30], is known [2] [24] [31] to hold within the PPP formalism. The lowest triplet configuration $\chi(k \rightarrow m)$ is therefore degenerate with its pair $\chi(n \rightarrow s)$. In AH biradicals, where the singly occupied orbitals ψ_m and ψ_n are (nearly) degenerate, there will be two degenerate pairs of nearly the same energy, namely $\chi(k \rightarrow m)$, $\chi(n \rightarrow s)$ and $\chi(k \rightarrow n)$, $\chi(m \rightarrow s)$, cf. the *Figure*. The interaction element between paired configurations (*Table 1*) is equal to an exchange integral $\langle km | ns \rangle = K_{km}$, and $\langle kn | ms \rangle = K_{k-m}$, if $\psi_n = \psi_{-m}$ and $\psi_s = \psi_{-k}$ and therefore positive as proven by *Roothaan* [48]. First-order CI between the paired configurations will thus stabilize the odd combination and destabilize the even combination of paired configurations. Therefore, the lowest excited triplet state will be of odd parity; in AH biradicals there will be two very close-lying lowest odd states after first-order CI. In most of the cases treated (*Table 3*) these belong to a different symmetry representation and do not interact any further. Since the lowest triplet configuration χ_0 is also of odd parity [31], the first two (or more) transitions will be forbidden by the parity rule.

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