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Semiempirical Theory of Excimer Luminescence*

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A semiempirical theory based on limited configuration interaction has been developed for the excimer luminescence of alternant hydrocarbons. The theory adequately accounts for (1) the energy of excimer luminescence (fluorescence and phosphorescence), (2) the linear relationship between the energies of the excimer fluorescence and the p band of the monomer, and (3) the near constancy of the energy difference between the monomer and excimer fluorescence.

I. INTRODUCTION

The transannular interaction between two closely lying and parallel aromatic molecules in excimers¹ and paracyclophanes is a subject of considerable interest and importance. The theoretical work on the electronic states of excimers and paracyclophanes developed along two lines. One is a semiempirical LCAO MO approximation in which all the π electrons of the two interacting systems are considered, and the other is based on the configuration interaction between the molecular exciton states and the charge resonance states. A treatment of the first kind has been carried out for [2.2] paracyclophane (which is essentially a dimer whose moieties are *para*-xylene molecules) with comparative success,² while the configuration-interaction method yielded energies which are in fair agreement with experiment for [2.2] paracyclophane³ and excimers of several aromatic hydrocarbons.⁴⁻⁶ Although most experiments to date have not been decisive in revealing the nature of the intermolecular interactions in these molecules, there are several recent experimental results which suggest that the configuration-interaction method yields a poor description of the electronic absorption spectra of anthracene dimers.⁷

In this paper we present a semiempirical theory of excimer luminescence, with particular emphasis focused on the relationship between the ordering and energies of excimer electronic states relative to those of monomer electronic states. The theory makes use of a supermolecule approximation in which all the π electrons of the two interacting aromatic molecules are treated using Hückel orbitals for dimers. Full account is taken

of electron interaction by using a complete Hamiltonian. The configuration interaction among various states is considered using the formalism developed by Dewar and Longuet-Higgins⁸ and by Pople⁹ for electronic spectra of alternant hydrocarbons.

It will be shown that the theory adequately accounts for (1) the energy of excimer luminescence (fluorescence and phosphorescence), (2) the experimentally observed linear relationship between the energies of excimer fluorescence and the p band of the monomer, and (3) the near constancy of the energy difference between the monomer and excimer fluorescence in various aromatic hydrocarbons.

II. THEORY

We consider an excimer in which the two molecules lie parallel to each other in a perfect sandwich structure.

Let the number of π electrons in one molecule be $2m$ and the molecular orbitals these electrons occupy in the ground state be 1, 2, 3, \dots , m , with m representing the highest filled orbital. Using a supermolecule approximation we designate the Hückel-type dimer orbitals as $\phi_1, \phi_2, \dots, \phi_{2m}$, so that ϕ_{2m} represents the highest filled orbital. This description of dimer orbitals, which has previously been introduced by Azumi and Azumi,¹⁰ is convenient since orbitals ϕ_{2k-1} and ϕ_{2k} in the dimer are readily seen to belong to k parentage in the monomer. The atomic orbitals (or the carbon atoms) in one molecule (say, A) will be designated using symbols r_A, t_A, \dots , while the corresponding orbitals in the other molecule (say, B) are written as r_B, t_B, \dots .

In addition to the orthogonality between the highest filled (m or m') and the lowest vacant molecular orbital [$m+1$ or $(m+1)'$] of the same molecule, it is assumed that orthogonality exists between m and $(m+1)'$ and between $m+1$ and m' . The intermolecular overlap integrals between m and m' or between $m+1$ and $(m+1)'$ can be written as

$$\langle r_A | t_B \rangle = \delta_{rt} S', \quad (1)$$

⁸ M. J. S. Dewar and H. C. Longuet-Higgins, Proc. Phys. Soc. (London) **A67**, 795 (1954).

⁹ J. A. Pople, Proc. Phys. Soc. (London) **A68**, 81 (1955).

¹⁰ T. Azumi and H. Azumi, Bull. Chem. Soc. Japan **40**, 279 (1967).

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¹ The term excimer is used to denote an excited dimeric species which is stable only in the excited state.

² J. Koutecký and J. Paldus, Collection Czech. Chem. Commun. **27**, 599 (1962).

³ M. T. Vala, I. H. Hiller, S. A. Rice, and J. Jortner, J. Chem. Phys. **44**, 23 (1966).

⁴ T. Azumi, A. T. Armstrong, and S. P. McGlynn, J. Chem. Phys. **41**, 3839 (1964).

⁵ J. N. Murrell and J. Tanaka, Mol. Phys. **4**, 363 (1964).

⁶ E. Konijnenberg, Doctoral thesis, Free University of Amsterdam, Holland, 1963.

⁷ E. A. Chandross and J. Ferguson, J. Chem. Phys. **45**, 397 (1966).

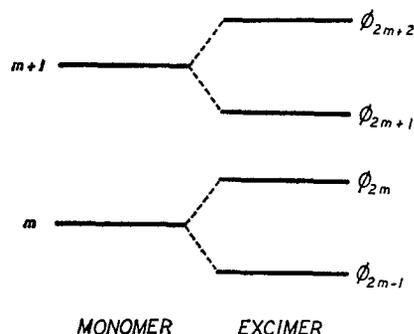


Fig. 1. Relationship between the monomer and excimer orbitals.

where δ_{ri} represents the Kronecker delta. If we define the complete electronic Hamiltonian in a usual way, i.e.,

$$H = \sum_i H_i^{\text{core}} + \frac{1}{2} \sum_{i,j} (r_{ij})^{-1}, \quad (2)$$

then the intermolecular resonance integral β' takes the form

$$\langle \tau_A(i) | H_i^{\text{core}} | t_B(i) \rangle = \delta_{ri} \beta'. \quad (3)$$

The coordinates of the two molecules in the excimer are chosen so that $S' > 0$ and $\beta' < 0$ in conformity with the corresponding intramolecular integrals. The energies and the normalized wavefunctions of the dimer orbitals are related to those of the monomer as follows:

$$\begin{aligned} E_{2(m+n)} &= E_{m+n} - \beta', \\ E_{2(m+n)-1} &= E_{m+n} + \beta', \end{aligned} \quad (4)$$

$$\begin{aligned} \phi_{2(m+n)} &= \sqrt{2}^{-1} [(m+n) - (m+n)'], \\ \phi_{2(m+n)-1} &= \sqrt{2}^{-1} [(m+n) + (m+n)'], \end{aligned} \quad (5)$$

where $n=0, 1, 2, 3, \dots$. The dimer orbitals are therefore split by an energy $2\beta'$. The orbital-energy diagram for monomer and excimer is shown in Fig. 1.

The configurational wavefunctions for the excited states of the dimer can be constructed from these dimer orbitals. Thus, for the four low-lying excited singlet states, we write

$$\begin{aligned} \chi_1 &= \phi_{2m} \phi_{2m+1}, & A \\ \chi_2 &= \phi_{2m} \phi_{2m+2}, & S \\ \chi_3 &= \phi_{2m-1} \phi_{2m+1}, & \\ \chi_4 &= \phi_{2m-1} \phi_{2m+2}, & A \end{aligned} \quad (6)$$

in which $\phi_k \phi_l$ represents a configuration in which an electron is promoted from an occupied orbital ϕ_k to an unoccupied orbital ϕ_l . These configurations, which are the sum of two Slater determinants, are either symmetric (*S*) or antisymmetric (*A*) with respect to reflection in a plane that lies midway between, and parallel to, two monomers. The configurations χ_2 and χ_3 are degenerate in the Hückel approximation. Other possible configurational wavefunctions, such as those involving orbitals of either $m-1$ or $m+2$ parentage

(in the monomer), are not taken into account in this paper since they are not regarded as important for the discussion of the energetics of excimer emission.

The configurational excitation energy, $\langle \chi_i | H | \chi_i \rangle - \langle \chi_0 | H | \chi_0 \rangle$ between the ground state χ_0 and the excited singlet state χ_i , is not equal to the difference in orbital energies if electron interaction is included. The excitation energies for the singlet states can be found from the matrix elements of the total Hamiltonian. These are obtained by the usual method¹¹ and can be reduced, with the aid of the orthogonality property of molecular orbitals, to integrals over one or two electrons. The results are

$$\begin{aligned} \chi_1: \quad E_{2m+1} - E_{2m} - \langle 2m, 2m | 2m+1, 2m+1 \rangle \\ + 2 \langle 2m, 2m+1 | 2m, 2m+1 \rangle, \end{aligned} \quad (7)$$

$$\begin{aligned} \chi_2: \quad E_{2m+2} - E_{2m} - \langle 2m, 2m | 2m+2, 2m+2 \rangle \\ + 2 \langle 2m, 2m+2 | 2m, 2m+2 \rangle, \end{aligned} \quad (8)$$

$$\begin{aligned} \chi_3: \quad E_{2m+1} - E_{2m-1} - \langle 2m-1, 2m-1 | 2m+1, 2m+1 \rangle \\ + 2 \langle 2m-1, 2m+1 | 2m-1, 2m+1 \rangle, \end{aligned} \quad (9)$$

$$\begin{aligned} \chi_4: \quad E_{2m+2} - E_{2m-1} - \langle 2m-1, 2m-1 | 2m+2, 2m+2 \rangle \\ + 2 \langle 2m-1, 2m+2 | 2m-1, 2m+2 \rangle. \end{aligned} \quad (10)$$

In these equations E_{2m+n} represents the energy of the $(2m+n)$ th dimer orbital, and the two electron integrals are defined by

$$\langle ij | kl \rangle = \iint \phi_i(\mu) \phi_k(\nu) (r_{\mu\nu})^{-1} \phi_j(\mu) \phi_l(\nu) d\tau_\mu d\tau_\nu. \quad (11)$$

All the two electron integrals over the dimer orbitals can be reduced to integrals over the monomer orbitals. The matrix elements between two configurations of different symmetry are zero, while those between two different configurations of the same symmetry have the following values:

$$\begin{aligned} \langle \chi_1 | H | \chi_4 \rangle &= 2 \langle 2m, 2m+1 | 2m-1, 2m+2 \rangle \\ &\quad - \langle 2m, 2m-1 | 2m+1, 2m+2 \rangle, \end{aligned} \quad (12)$$

$$\begin{aligned} \langle \chi_2 | H | \chi_3 \rangle &= 2 \langle 2m, 2m+2 | 2m-1, 2m+1 \rangle \\ &\quad - \langle 2m, 2m-1 | 2m+2, 2m+1 \rangle. \end{aligned} \quad (13)$$

The degeneracy between the configurations χ_2 and χ_3 , which appears in the Hückel approximation, is retained even after the electron interaction is included. This is because the two-electron integrals appearing in Eq. (8) are equivalent to those in Eq. (9) due to the pairing property of the dimer orbital. An interaction element of the type (13) can, however, remove this degeneracy and split the singlets into two levels which we designate as δ and γ .

¹¹ E. U. Condon and H. G. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, England, 1935).

The wavefunctions for the four low-lying excited singlet states of the dimer can be written as

$$\begin{aligned}\sigma &: [1/(1+\lambda^2)^{1/2}](\chi_1+\lambda\chi_4), \\ \rho &: [1/(1+\lambda'^2)^{1/2}](\chi_1+\lambda'\chi_4), \\ \gamma &: \sqrt{2}^{-1}(\chi_2+\chi_3), \\ \delta &: \sqrt{2}^{-1}(\chi_2-\chi_3),\end{aligned}\quad (14)$$

where λ and λ' are the configurational mixing coefficients in the lower and higher excited states, respectively. The value of λ and λ' in Eq. (14) depends on the interaction element (12) as well as on the magnitude of β' by

$$2\beta' \pm [4\beta'^2 + \langle \chi_1 | H | \chi_4 \rangle^2]^{1/2} / \langle \chi_1 | H | \chi_4 \rangle, \quad (15)$$

in which the lower negative sign defines λ , and the upper positive sign defines λ' .

The effect of configuration interaction on the excited singlet states of dimer is illustrated in Fig. 2.

If the intermolecular differential overlaps are neglected, the excitation energies of various dimeric states take the form (see Appendix)

$$\begin{aligned}E(\sigma) &= \Delta E - 2 \left(\frac{1-\lambda^2}{1+\lambda^2} \right) \beta' + \left(1 + \frac{2\lambda}{1+\lambda^2} \right) \\ &\times [\langle m, m+1 | m, m+1 \rangle - \frac{1}{2} \langle m, m | m+1, m+1 \rangle] \\ &- \frac{1}{2} \left(1 - \frac{2\lambda}{1+\lambda^2} \right) \langle m, m | (m+1)', (m+1)' \rangle \\ &- \left(1 + \frac{2\lambda}{1+\lambda^2} \right) \langle m, m+1 | m', (m+1)' \rangle,\end{aligned}\quad (16)$$

$$\begin{aligned}E(\gamma) &= \Delta E - \langle m, m | m+1, m+1 \rangle \\ &+ 2 \langle m, m+1 | m, m+1 \rangle + 2 \langle m, m+1 | m', (m+1)' \rangle,\end{aligned}\quad (17)$$

$$E(\delta) = \Delta E - \langle m, m | (m+1)', (m+1)' \rangle. \quad (18)$$

In the above equations it is seen that ΔE is the difference between the two eigenvalues corresponding to the orbitals m and $m+1$ of the monomer. The energy of

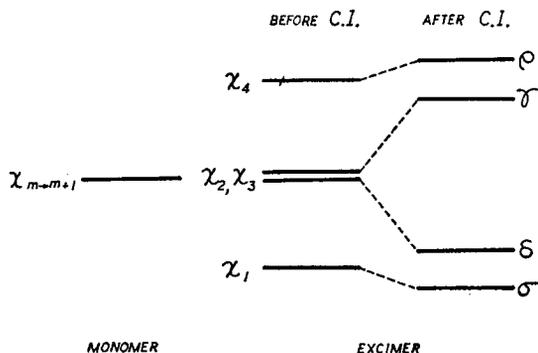


FIG. 2. Effect of configuration interaction on the energy levels of excimer.

the dimeric state ρ is given by an expression similar to Eq. (16) except that the λ in the equation is replaced by λ' . Since the excitation energy for the singlet p band (in Clar's notation), corresponding to the transition from m to $m+1$, of the monomer is given by⁹

$$E(p) = \Delta E - \langle m, m | m+1, m+1 \rangle + 2 \langle m, m+1 | m, m+1 \rangle, \quad (19)$$

the difference between the transition energy of the p band of monomer and the excitation energies of the dimer can be written as

$$\begin{aligned}E(p) - E(\sigma) &= 2 \left(\frac{1-\lambda^2}{1+\lambda^2} \right) \beta' + \left(1 - \frac{2\lambda}{1+\lambda^2} \right) \\ &\times [\langle m, m+1 | m, m+1 \rangle - \frac{1}{2} \langle m, m | m+1, m+1 \rangle \\ &+ \frac{1}{2} \langle m, m | (m+1)', (m+1)' \rangle] \\ &+ \left(1 + \frac{2\lambda}{1+\lambda^2} \right) \langle m, m+1 | m', (m+1)' \rangle,\end{aligned}\quad (20)$$

$$E(p) - E(\gamma) = -2 \langle m, m+1 | m', (m+1)' \rangle, \quad (21)$$

$$\begin{aligned}E(p) - E(\delta) &= 2 \langle m, m+1 | m, m+1 \rangle \\ &- \langle m, m | m+1, m+1 \rangle + \langle m, m | (m+1)', (m+1)' \rangle.\end{aligned}\quad (22)$$

It is to be noted that for infinite separation of the monomer $\lambda=1$ and the intermolecular Coulomb repulsion integrals vanish. The energies of σ and γ states therefore converge, at an infinite separation of the two monomer molecules, to the energy of the monomer p band. The energy of the δ state, on the other hand, converges to ΔE at infinite monomer separation as seen from Eqs. (22) and (19). The latter result is believed to be fortuitous.

The excitation energies of the triplet states of the dimer can be readily obtained from the energies of the corresponding singlet states and the energy difference between the singlet and triplet dimeric states of the same configuration. The singlet-triplet splittings in the excimer states under considerations are given by

$$\begin{aligned}E({}^1\sigma) - E({}^3\sigma) &= \left(1 + \frac{2\lambda}{1+\lambda^2} \right) [\langle m, m+1 | m, m+1 \rangle \\ &- \langle m, m+1 | m', (m+1)' \rangle],\end{aligned}\quad (23)$$

$$\begin{aligned}E({}^1\gamma) - E({}^3\gamma) &= 2 \langle m, m+1 | m, m+1 \rangle \\ &+ 2 \langle m, m+1 | m', (m+1)' \rangle,\end{aligned}\quad (24)$$

$$E({}^1\delta) - E({}^3\delta) = 0. \quad (25)$$

Once again, the expression for the ρ state is the same as for the σ state except that λ is replaced by λ' . At infinite separation of the monomers, for which $\lambda=1$ and the intermolecular integral is zero, the singlet-triplet splitting in the excimer becomes equal to $2 \langle m, m+1 | m, m+1 \rangle$, which is the singlet-triplet

TABLE I. Matrix elements $\langle \chi_1 | H | \chi_4 \rangle$ in electron volts.

D (Å)	Naphthalene	Anthracene	Perylene
2.5	-0.1819	-0.1111	-0.0670
3.0	-0.2990	-0.1822	-0.1212
3.5	-0.4220	-0.2657	-0.1817
4.0	-0.5271	-0.3503	-0.2419
5.0	-0.7208	-0.5063	-0.3538
6.0	-0.8762	-0.6384	-0.4516

splitting in the monomer p states according to a two-electron treatment. Therefore Eqs. (23) and (24) extrapolate to a correct energy limit. The degeneracy between the ${}^1\delta$ and ${}^3\delta$ states, which Eq. (25) predicts, is undoubtedly a fortuitous result which would not hold in a more refined calculation. It should be pointed out that a similar degeneracy is predicted between the ${}^1\alpha$ (in Clar's notation) and the ${}^3\alpha$ states in the Pariser-Paar-Pople treatments of the electronic spectra of alternant hydrocarbons.

III. COMPARISON WITH THE EXPERIMENTAL DATA

A. Energy of Excimer Fluorescence

The values of the intramolecular and intermolecular integrals appearing in Eqs. (20)–(22) depend on the choice of the effective nuclear charge Z . The value $Z=3.18$ has been found to yield the best calculated values for intramolecular quantities. Azumi, Armstrong, and McGlynn⁴ have found that the same value of Z may also be considered appropriate for the evaluation of intermolecular quantities provided that the monomer separations in the excimers are 3–4 Å, the order of separation in the unexcited crystal. Since the interplanar separation of 3–4 Å seems to be realistic, we use the numerical results of McGlynn *et al.*⁴ for various molecular integrals. These integrals are based on the Hückel molecular orbitals of the monomer. The use of Hückel molecular orbitals is justified since it is known that these orbitals are not very different from the self-consistent-field molecular orbitals in the case of alternant hydrocarbons.

Since it is not possible, *a priori*, to decide whether the emitting state is σ or δ , we consider theoretical

TABLE II. Values of β' (electron volts) and D (angstroms) at which calculated $E(p) - E(\sigma)$ agree with the observed energy gap between the monomer p band and excimer fluorescence.

	D	$-\beta'$	$E(p) - E(\sigma)$	ΔE_{obs}
Naphthalene	3.0	0.50	1.20	1.22
Anthracene	3.5	0.40	0.94	0.94 ^a
Perylene	4.0	0.30	0.81	0.71

^a Value for 9-methylanthracene.

energies of both the σ and δ excimer states for comparison with the energy of excimer fluorescence.

The energy gap between the p state of the monomer and the σ state of the dimer is given by Eq. (20). The values of λ can be obtained from Eq. (15) using the values of $\langle \chi_1 | H | \chi_4 \rangle$ and β' . Both the matrix elements and the intermolecular resonance integral depend on the interplanar separation in the excimer. Table I gives the value of $\langle \chi_1 | H | \chi_4 \rangle$ for naphthalene, anthracene, and perylene at several interplanar separations D . Since no unique and simple relationship is known between β' and D , we choose the arbitrary value of β' to give the best agreement with the observed energies. The values of β' (in electron volts) and the interplanar separation (in angstroms) at which the calculated value of $E(p) - E(\sigma)$ gives reasonably good agreement with the observed energy gap between the monomer p band and the excimer fluorescence are listed in Table II. The results indicate that for values of interplanar distances between 3 and 4 Å and the values of intermolecular resonance integral between 0.3 and 0.5 eV, the energy of the dimeric σ state can

TABLE III. Calculated values of $E(p) - E(\delta)$ at various interplanar separations.

D	Naphthalene (observed, +1.22)	Anthracene (observed, +0.94)	Perylene (observed, +0.71)
2.5	+0.34	+0.55	+0.70
3.0	-0.14	+0.16	+0.41
3.5	-0.52	-0.16	+0.13
4.0	-0.83	-0.43	-0.08

satisfactorily account for the energy of excimer fluorescence. It happens that these values of the intermolecular resonance integrals are very close to what has been estimated¹² for paracyclophanes in which the interplanar separation is roughly 3.1 Å.

Table III lists the energy difference $E(p) - E(\delta)$ calculated from Eq. (22) for different interplanar distances. As is clear from the table, the calculated values do not yield the observed energy difference between the monomer p band and the excimer fluorescence unless interplanar separation of considerably less than 2.5 Å is assumed. We consider that D values less than 2.5 Å are much too small to be physically reasonable.

These results therefore indicate that the lowest excited singlet state of the excimer is the σ state. This conclusion will be further tested in the subsequent section. A serious attempt to obtain more reasonable values of D and β' which reproduce the energy of excimer fluorescence is not considered to be of value when the semiquantitative nature of the calculation is remembered.

¹² J. Koutecký and J. Paldus, *Tetrahedron* **19**, 201 (1963).

B. Approximate Proportionality between the Transition Energies of Excimer Fluorescence and the p Band of the Monomer

We have very recently noted that energy of excimer fluorescence (measured at the peak of emission) is approximately proportional to the energy of the monomer p band for all polycyclic hydrocarbons for which excimer fluorescence has been observed (Table IV and Fig. 3). It is very desirable to examine this linear relationship as a further test of the validity of the present theory.

The transition energies of excimer fluorescence $E(\sigma)$ are related to those of the monomer p band $E(p)$ by Eq. (20). The equation may be written as

$$E(\sigma) = (1-K)E(p) + K[\Delta E - \langle m, m | (m+1)', (m+1)' \rangle - 2 \left(\frac{1-\lambda^2}{1+\lambda^2} \right) \beta' - \left(1 + \frac{2\lambda}{1+\lambda^2} \right) \langle m, m+1 | m', (m+1)' \rangle], \quad (26)$$

in which ΔE represents the energy difference between the lowest vacant and highest filled orbitals of the monomer and K is given by $\frac{1}{2} \{ 1 - [2\lambda / (1+\lambda^2)] \}$. The numerical values of the intermolecular Coulombic repulsion integrals appearing in Eq. (26) were evaluated for naphthalene, anthracene, and perylene by Azumi, Armstrong, and McGlynn,¹⁰ while the values of ΔE can be determined from the observed transition energy

TABLE IV. Energies of p -band and excimer fluorescence.

Compound ^a		p band ^b (eV)	Excimer fluorescence ^c (eV)
p -Xylene	(14)	5.79 ^d	4.19 ^e
Naphthalene	(13)	4.35	3.13
Acenaphthene	(12)	4.28 ^f	3.06
Phenanthrene	(11)	4.09	2.88
1:2-Benzopyrene	(10)	3.74	2.67 ^e
Pyrene	(9)	3.72	2.59
1:2,3:4-Dibenzanthracene	(8)	3.55	2.55
1:2-Benzanthracene	(7)	3.45	2.44
1:2,4:5-Dibenzopyrene	(6)	3.28	2.54 ^e
3:4-Benzopyrene	(5)	3.22	2.41
9-Methylanthracene	(4)	3.21	2.27
1:12-Benzperylene	(3)	3.20	2.46
Anthanthrene	(2)	2.86	2.14 ^e
Perylene	(1)	2.86	2.14

^a Number in parenthesis refers to Fig. 3.

^b E. Clar, *Polycyclic Hydrocarbons* (Academic Press Inc., New York, 1964). Refers to the 0, 0 band.

^c T. Azumi and S. P. McGlynn, *J. Chem. Phys.* **41**, 3131 (1964).

^d P. E. Stevenson, *J. Chem. Educ.* **41**, 234 (1964).

^e Estimated from the data in [2.2] paracyclophane (see Sec. III.D in the text).

^f R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds* (John Wiley & Sons, Inc., New York, 1951).

^g J. B. Birks and L. G. Christophorou, *Proc. Roy. Soc. (London)* **A277**, 571 (1964).

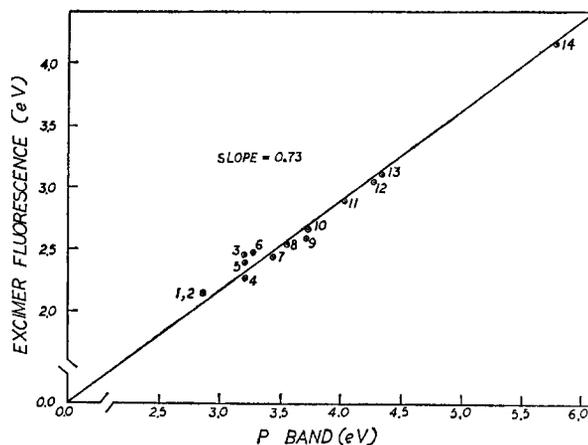


FIG. 3. Plot of the energy of the p band against the energy of excimer fluorescence.

of the p band and the values of the intramolecular Coulombic repulsion integrals through the use of Eq. (19). The intermolecular resonance integral β' is difficult to estimate, but it may be considered to be in the range of 0.3–0.5 eV for an interplanar separation of 3–4 Å. Using the value of λ computed from the experimental slope $(1-K)$, the sum of the second, third, and the fourth terms appearing on the right-hand side of Eq. (26) can be determined for an appropriate interplanar separation. The results, which are shown in Table V for naphthalene, anthracene, and perylene, indicate that the sum is generally very small compared with the first term in Eq. (26) for $K=0.27$. Thus, for molecules with a relatively large p -band transition energy, Eq. (26) takes the simple form

$$E(\sigma) \cong (1-K)E(p) \quad (27)$$

and it predicts a linear relationship between the transition energy of excimer fluorescence and that of the p absorption band of monomer. The observed linear relation with near-zero intercept indicates that the emitting excimer state is σ state in all polycyclic hydrocarbons from which excimer fluorescence has been observed. This conclusion is strengthened by the finding that the estimated energy of the dimeric state of p parentage in [2.2] paracyclophane also gives good fit to the linear plot of Fig. 3 (*vide infra*).

C. Energy Gap between Monomer and Excimer Fluorescence

As pointed out by Birks *et al.*,¹³ frequency difference between the 0, 0 band of the monomer fluorescence and the peak of the excimer fluorescence is nearly constant and equal to $\sim 6000 \text{ cm}^{-1}$ (0.7–0.8 eV) for all aromatic hydrocarbons. The near constancy of this energy gap over various molecules is indeed surprising when it is remembered that the emitting state of the monomer is of p type in some molecules while it is of

¹³ J. B. Birks, M. D. Lumb, and I. H. Munro, *Proc. Roy. Soc. (London)* **A280**, 289 (1964).

TABLE V. Values (in electron volts) of the last three terms appearing in Eq. (26).

	D (Å)	$K[\Delta E - \langle m, m (m+1)'(m+1)' \rangle]$	$-2\left(\frac{1-\lambda^2}{1+\lambda^2}\right)\beta'$	$-\left(1+\frac{2\lambda}{1+\lambda^2}\right)\langle m, m+1 m', (m+1)' \rangle$	Sum
Naphthalene	3.0	1.21	-0.90	-0.33	-0.02
Anthracene	3.5	0.93	-0.72	-0.26	-0.05
Perylene	4.0	0.79	-0.54	-0.29	-0.04

α type in others. Very recently, Azumi and Azumi¹⁰ have attempted to account for this energy gap by the use of a model based on simple Hückel-type dimer orbitals. The validity of their conclusions is, however, very doubtful since, in addition to the well-known inability of simple Hückel theory to account for the electronic spectra of benzenoid hydrocarbons, their treatment uses an unjustifiable assumption that the fluorescence of the monomer is always associated with the transition between the lowest vacant and highest filled orbitals. As there appears to be no good theoretical reason to expect the constancy of the energy gap between the monomer and excimer fluorescence, we believe that the 6000-cm⁻¹ gap arises accidentally because of the linear relation between the energy of the excimer fluorescence and the p band of the monomer. This supposition is supported by the observation that the energy gap between the lowest excited singlet state (α or p) and 0.73 times the energy of the p band is, with very few exceptions, 0.6–0.9 eV for over 40 benzenoid hydrocarbons.

D. Energy of Excimer Phosphorescence

Comparison of Eqs. (23)–(25), together with the results in the previous sections, indicates that the lowest triplet state of the dimer is certainly of the σ type.

The relation between the singlet–triplet splitting in σ states of the dimer and the energy gap between the singlet and triplet p states of the monomer is, from Eq. (23),

$$E(^1\sigma) - E(^3\sigma) = \frac{1}{2} \{ 1 + [2\lambda / (1 + \lambda^2)] \} \times \{ [E(^1p) - E(^3p)] - 2\langle m, m+1 | m', (m+1)' \rangle \}. \quad (28)$$

If the intermolecular Coulombic repulsion integrals are taken to be of the order of 0.2 eV at interplanar separation of about 3.0–3.5 Å, the equation yields, for $\lambda = 0.23$ (from observed $K = 0.27$),

$$E(^1\sigma) - E(^3\sigma) = 0.73 \{ [E(^1p) - E(^3p)] - 0.4 \}; \quad (29)$$

Eq. (29) allows calculation of the energy difference between the excimer fluorescence and phosphorescence from the observed singlet–triplet splitting of monomer p electronic bands. Unfortunately, a rigorous test of the validity of the equation cannot be made since the experimental information regarding the excimer triplet state is very scanty. In fact, excimer phosphorescence

has so far been reported only for certain halogenated benzenes.^{14,15} Some cursory test of the Eq. (29) is nevertheless possible through the study of absorption and luminescence spectra of [2.2] paracyclophane. The fluorescence of [2.2] paracyclophane, with peak intensity at about 360 m μ , is understood to arise from the lowest excited singlet state of α parentage. The energy of “hypothetical” fluorescence from the lowest energy dimeric state of p parentage may be obtained by adding, to the observed fluorescence peak, the energy difference between the lowest excited singlet states of α and p parentage. The theoretical considerations of the electronic states of [2.2] paracyclophane indicate that absorption bands of this molecule at about 260 and 310 m μ correspond to transitions to the dimeric states of p and α parentage, respectively.³ The hypothetical fluorescence from the lowest energy excimer state of p parentage can therefore be expected to occur at about 4.2 eV. The energy difference between this fluorescence from the dimeric state of p parentage and the observed phosphorescence (peak at 480 m μ)¹⁶ is 1.6 eV. This value is in reasonable agreement with the value of 1.4 eV predicted from Eq. (29) using the observed singlet–triplet splitting (2.3 eV)¹⁷ of the p electronic states of p -xylene.

IV. CONCLUSION

The present semiempirical theory adequately accounts for the more prominent features of the excimer luminescence of polycyclic hydrocarbons. In addition to yielding energies which are in good agreement with experiments, the model shows that the lowest energy excimer state is of p state parentage for both the singlet and triplet manifold. The linear relation between the energies of excimer fluorescence and monomer p band, which is believed to be responsible for the near constancy of the energy gap between the monomer and excimer fluorescence, is also adequately accounted for by the theory.

The chief advantages of the theory lie in its simplicity and in its ability to rationalize general features of

¹⁴ G. Castro and R. M. Hochstrasser, J. Chem. Phys. **45**, 4352 (1966).

¹⁵ E. C. Lim and S. K. Chakrabarti, Mol. Phys. **13**, 293 (1967).

¹⁶ S. K. Chakrabarti and E. C. Lim (unpublished results).

¹⁷ L. Blackwell, Y. Kanda, and H. Sponer, J. Chem. Phys. **32**, 1465 (1960).

excimer luminescence in various polycyclic hydrocarbons.

It should be pointed out that fluorescence is dipole forbidden for an excimer with a perfect sandwich structure. A slight distortion from this configuration may, however, induce dipole-allowed character to fluorescence without greatly affecting its energy. This possibility is being examined at the present time.

APPENDIX

We shall first consider the σ state of the excimer for which the wavefunction is given by

$$\sigma: [1/(1+\lambda^2)^{-1/2}](\chi_1 + \lambda\chi_4), \quad (\text{A1})$$

where

$$\begin{aligned} \chi_1 &= \sqrt{2}^{-1} [| \phi_{2m} \bar{\phi}_{2m+1} | + | \bar{\phi}_{2m} \phi_{2m+1} |], \\ \chi_4 &= \sqrt{2}^{-1} [| \phi_{2m-1} \bar{\phi}_{2m+2} | + | \bar{\phi}_{2m-1} \phi_{2m+2} |], \end{aligned}$$

and λ is the mixing coefficient. When the interaction with the closed shell of filled orbitals $\phi_1\phi_2\cdots\phi_{2m-3}\phi_{2m-2}$ is neglected, the energy of the σ state relative to the energy of the ground state of the dimer is given by

$$E(\sigma) = (1+\lambda^2)^{-1} [\langle \chi_1 | H | \chi_1 \rangle + \lambda^2 \langle \chi_4 | H | \chi_4 \rangle + 2\lambda \langle \chi_1 | H | \chi_4 \rangle] - E(\chi_0), \quad (\text{A2})$$

where $E(\chi_0)$ is the energy of the ground state of dimer. Rewriting Eq. (A2) as

$$\begin{aligned} E(\sigma) &= \frac{1}{1+\lambda^2} [\langle \chi_1 | H | \chi_1 \rangle - E(\chi_0)] \\ &+ \frac{\lambda^2}{1+\lambda^2} [\langle \chi_4 | H | \chi_4 \rangle - E(\chi_0)] + \frac{2\lambda}{1+\lambda^2} \langle \chi_1 | H | \chi_4 \rangle, \end{aligned}$$

and then making use of Eqs. (7) and (11) of the text one obtains

$$\begin{aligned} E(\sigma) &= \frac{1}{1+\lambda^2} [\Delta E - 2\beta' - \langle 2m, 2m | 2m+1, 2m+1 \rangle \\ &+ 2 \langle 2m, 2m+1 | 2m, 2m+1 \rangle] \\ &+ \frac{\lambda^2}{1+\lambda^2} [\Delta E + 2\beta' - \langle 2m-1, 2m-1 | 2m+2, 2m+2 \rangle \\ &+ 2 \langle 2m-1, 2m+2 | 2m-1, 2m+2 \rangle] \\ &+ \frac{2\lambda}{1+\lambda^2} [2 \langle 2m, 2m+1 | 2m-1, 2m+2 \rangle \\ &- \langle 2m, 2m-1 | 2m+1, 2m+2 \rangle]. \quad (\text{A3}) \end{aligned}$$

In Eq. (A3) ΔE is the difference between two eigenvalues and corresponding to the orbitals m and $m+1$ of monomer, and the molecular integrals are as defined by Eq. (11) of the text. Using the pairing property of the dimer orbitals, and reducing the dimer orbitals to the monomer orbitals in accordance with Eq. (5), one can write Eq. (A3) as

$$\begin{aligned} E(\sigma) &= \Delta E - 2 \left(\frac{1-\lambda^2}{1+\lambda^2} \right) \beta' + \left(1 + \frac{2\lambda}{1+\lambda^2} \right) \\ &\times [\langle m, m+1 | m, m+1 \rangle - \frac{1}{2} \langle m, m | m+1, m+1 \rangle] \\ &- \frac{1}{2} \left(1 - \frac{2\lambda}{1+\lambda^2} \right) \langle m, m | (m+1)', (m+1)' \rangle \\ &- \left(1 + \frac{2\lambda}{1+\lambda^2} \right) \langle m, m+1 | m', (m+1)' \rangle, \quad (\text{A4}) \end{aligned}$$

in which the intermolecular differential overlap is neglected. The expression for the energy of the ρ state relative to the energy of the ground state of the dimer is similar to Eq. (A4) except that λ in the equation is replaced by λ' .

We shall consider next the γ and δ states of excimer for which the wavefunctions are given by

$$\begin{aligned} \gamma &: \sqrt{2}^{-1} (\chi_2 + \chi_3), \\ \delta &: \sqrt{2}^{-1} (\chi_2 - \chi_3), \quad (\text{A5}) \end{aligned}$$

where

$$\begin{aligned} \chi_2 &= \sqrt{2}^{-1} [| \phi_{2m} \bar{\phi}_{2m+2} | + | \bar{\phi}_{2m} \phi_{2m+2} |], \\ \chi_3 &= \sqrt{2}^{-1} [| \phi_{2m-1} \bar{\phi}_{2m+1} | + | \bar{\phi}_{2m-1} \phi_{2m+1} |]. \end{aligned}$$

The energy of the γ and δ states relative to the energy of the ground state of dimer is as follows:

$$\begin{aligned} \frac{1}{2} [\langle \chi_2 | H | \chi_2 \rangle - E(\chi_0)] &+ \frac{1}{2} [\langle \chi_3 | H | \chi_3 \rangle - E(\chi_0)] \\ &\pm \langle \chi_2 | H | \chi_3 \rangle. \quad (\text{A6}) \end{aligned}$$

In (A6) the upper positive and lower negative signs define $E(\gamma)$ and $E(\delta)$, respectively. Making use of Eqs. (8), (9), and (12) of the text, and proceeding as before, we obtain

$$\begin{aligned} E(\gamma) &= \Delta E - \langle m, m | m+1, m+1 \rangle \\ &+ 2 \langle m, m+1 | m, m+1 \rangle + 2 \langle m, m+1 | m', (m+1)' \rangle, \quad (\text{A7}) \end{aligned}$$

$$E(\delta) = \Delta E - \langle m, m | (m+1)', (m+1)' \rangle. \quad (\text{A8})$$