BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 279—284 (1967)

A Simple Hückel Treatment of the Energy of Excimer Luminescence

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(Received May 20, 1966)

The energy of the excimer luminescence is interpreted in terms of a simple Hückel-type dimer orbitals, which are constructed by treating the excimer as one species. The present model of the excimer yields results quite similar to those of the complicated ASMO CI treatment as developed earlier; further, it is capable of explaining various characteristics of the excimer, including the 6000 cm^{-1} rule.

The observation that a number of aromatic compounds display, in a concentrated solution, a broad and structureless emission band about 6000 cm^{-1} to the red of the normal structured fluorescence has been interpreted in terms of an emission from an excimer,[1] a dimeric species which exists only in the excited states. The nature of the interaction forces between the two molecules in an excimer has been analyzed by Azumi and McGlynn,[2] and it has been shown that neither a molecular exciton concept[3] nor a charge resonance concept[4] can account for the observed energies of the excimer fluorescence. The ASMO CI calculations on the excimer have been carried out by Azumi, Armstrong, and McGlynn[5] for some D_{2h} excicmers produced by D_{2h} molecules. Similar calculations have also been given by Murrell and Tanaka[6] and by Konijnenberg[7]. In these calculations, the molecular exciton states of ^1L_a parentage are configurationally interacted with the charge resonance states. The ^1L_b states

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1) B. Stevens, *Nature*, **192**, 725 (1961).
2) T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **41**, 3131 (1964).
3) Th. Förster, *Pure Appl. Chem.*, **7**, 73 (1963).
4) J. Ferguson, *J. Chem. Phys.*, **28**, 765 (1958).
5) T. Azumi, A. T. Armstrong and S. P. McGlynn, *ibid.*, **41**, 3839 (1964).
6) J. N. Murrell and J. Tanaka, *Mol. Phys.*, **7**, 363 (1964).
7) E. Konijnenberg, thesis, University of Amsterdam, 1963.

were shown not to be important because of the small transition moments associated with them.[2] Such treatment has been considered successful. Namely, the calculations reproduce experimental excimer energies at an appropriate interplanar distance, and further, if the symmetry of the excimer is lowered, yield a satisfactory lifetime as well.[8] The calculations are of significance in understanding the nature of interaction forces between the two molecules of an excimer. However, there remain some points which are seemingly unsolved by this treatment.

Firstly, as has been pointed out by Birks,[9] the energy difference between the 0, 0 band of the monomer fluorescence and the peak of the excimer fluorescence is nearly constant, with the value of 6000 cm^{-1}, for a large number of aromatic compounds. Hardly no interpretations of this constancy (which will be called *the 6000 cm^{-1} rule* hereafter) have been made: For the majority of compounds which exhibit an excimer fluorescence, the monomer fluorescence is from the ^1L_b state, whereas the excimer fluorescence is from the molecular exciton states of ^1L_a parentage, modified by the mixing of the charge resonance states (see Fig. 1). It is difficult to see why the difference between the energy stabilization of the ^1L_a state by dimerization and the ^1L_a–^1L_b energy separation of the monomer, each of these quantity varying greatly from compound to compound, should be nearly constant over various compounds. The second pitfall of the above treatment is that the excimer energies converge, at an infinite separation of the two monomer molecules, on the ^1L_a state, which lies above the ^1L_b fluorescent state. This is unlikely, since the excimer fluorescence should naturally converge on the monomer fluorescence, which is the transition from the ^1L_b state, at an infinite separation of the two molecules. The third and the most serious shortcoming, if one dare say so, from a practical point of view, is the great difficulty involved in the computational procedures. The evaluation of interaction matrices in terms of molecular orbitals is quite complex. In addition to this, the numerical calculation of a number of intra and intermolecular interaction integrals over atomic orbitals requires a number of approximations; the repeated use of which might drastically affect the results. The entire calculational procedure is thus quite complex, even for the excimer of aromatic hydrocarbons. The treatment of excimers of molecules which contain heteroatoms is thus quite formidable indeed.

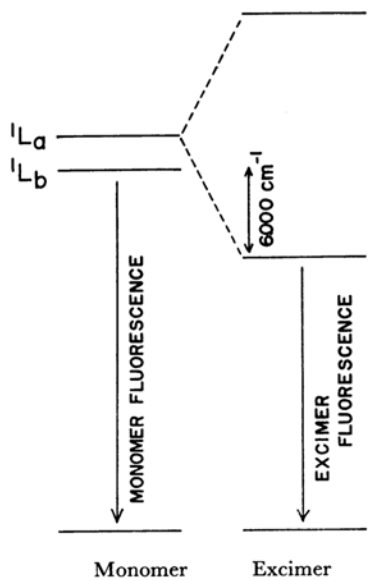

Fig. 1. Interpretation of excimer luminescence in terms of molecular exciton-charge resonance interaction treatment. The horizontal lines indicate the energies of electronic states.

The extended Hückel treatment has recently been applied to obtain the energy of the excimer luminescence;[10,11] however, this treatment does not pave the way to a solution of the above difficulties either.

In the present paper, Hückel-type π molecular orbitals are constructed by treating the whole excimer as one species. The interaction between the two monomer molecules is represented by the intermolecular resonance integrals and the overlap integrals. The method admittedly lacks exactness; yet, a number of important characteristics of the excimer, involving the three points discussed above, may be interpreted within the framework of this model. Moreover, the simplicity of the model affords wide applicability to excimers of almost any kinds of molecules.

Dimer Orbitals for Aromatic Hydrocarbons

The excimers of aromatic hydrocarbons will be treated first; an application to heterocyclic molecules can then be easily made, and will be treated in a later part of the present paper. The treatment will, further, be limited to an excimer in which one molecule is exactly superposed, at some distance, over the other. In excimers of such a geometrical configuration, the excimer luminescence is dipole-forbidden[12]; however, we shall tolerate this point for a while, and consider only

8) T. Azumi and H. Azumi, This Bulletin, **39**, 2317 (1966).
9) J. B. Birks, M. D. Lumb and I. H. Munro, *Proc. Roy. Soc.*, **A280**, 289 (1964).
10) D. B. Chesnut, C. J. Fritchie and H. E. Simmons, *J. Chem. Phys.*, **42**, 1127 (1965).
11) R. Polak and J. Paldus, *Theoret. Chim. Acta (Berl.)*, **4**, 37 (1966).
12) T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **42**, 1675 (1965).

the excitation energies. The Hückel-type molecular orbitals are constructed by treating the entire dimer as one species; such orbitals will be called "dimer orbitals."

Let the number of π electrons in one molecule be $2n$. The dimer orbitals will be designated, in the order of increasing energy, $\Psi_1, \Psi_2, \cdots \Psi_{4n}, \Psi_{2n}$ being the highest occupied orbital of the dimeric ground state; on the other hand, molecular orbitals of the monomer are designated as $\Phi_1, \Phi_2, \cdots \Phi_{2n}$. It is immediately clear that the Ψ_{2i-1} and Ψ_{2i} of the dimer are of Φ_i parentage. Let the carbon atoms (and the carbon $2p\pi$ atomic orbitals) in one molecule be designated by $r, t, \cdots$, and the corresponding atoms (and the atomic orbitals) in the other molecules by $r', t', \cdots$ The dimer orbitals are then constructed in the following way. *Intramolecular* matrix elements are obtained in the usual way; namely,

$$\left.\begin{aligned} H_{rs} &= \alpha\delta_{rs} + \beta M_{rs} \\ S_{rs} &= \delta_{rs} + SM_{rs} \end{aligned}\right\} \quad (1)$$

where δ_{rs} is the Kronecker delta, where M_{rs} is the element of the topological matrix,[13] and where

$$\left.\begin{aligned} M_{rs} &= 1 \text{ when } r \text{ and } s \text{ are adjacent} \\ &= 0 \text{ otherwise} \end{aligned}\right\} \quad (2)$$

For *intermolecular* integrals, it is assumed that:

$$\left.\begin{aligned} H_{rs'} &= \beta'\delta_{rs} \\ S_{rs'} &= S'\delta_{rs} \end{aligned}\right\} \quad (3)$$

where the coordinate of the second molecule is chosen so that:

$$\beta' < 0 \quad \text{and} \quad S' > 0, \quad (4)$$

in conformity with the intramolecular integrals, β and S.

The energy of the Φ_i orbital of the monomer is, as is well known:

$$E(\phi_i) = \alpha - m_i\gamma/(1-m_iS) \quad (5)$$

where:

$$\gamma = \beta - \alpha S \quad (6)$$

and where $-m_i$ is the ith eigenvalue of the topological matrix.[13] The energy of the Ψ_{2i} and Ψ_{2i-1} orbitals of the dimer are easily obtained, and

$$\left.\begin{aligned} E(\Psi_{2i}) &= \alpha - \beta' - [(\gamma + \beta'S)m_i \\ &\quad + (\alpha-\beta')S']/(1 - S' - m_iS) \\ E(\Psi_{2i-1}) &= \alpha + \beta' - [(\gamma - \beta'S)m_i \\ &\quad + (\alpha + \beta')S']/(1 + S' - m_iS) \end{aligned}\right\} \quad (7)$$

By means of the monomer and dimer orbitals thus constructed, the excitation energies may be obtained in a way similar to the Göpert-Mayer-Sklar method[14]; however, to do so requires the evaluation of a number of integrals and is in discord with the aim of the present paper. Therefore, we take the simplest attitude possible; namely, the fluorescence is always associated with the transition between the lowest vacant orbitals and the highest occupied orbitals, and the fluorescence energies are equated to the differences between the two orbital energies. This is schematically represented in Fig. 2.

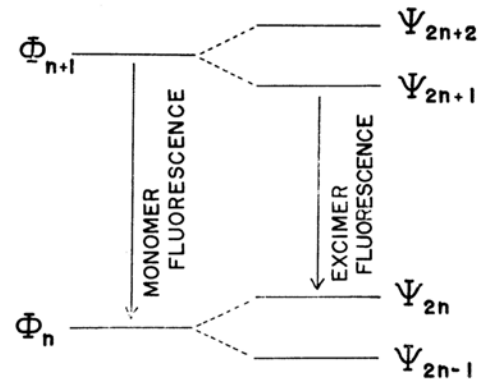

Fig. 2. Interpretation of excimer luminescence in terms of a simple Hückel treatment. The horizontal lines indicate the energies of molecular orbitals.

It will be seen below that some of the characteristics of the excimer may be well explained within the framework of the present model.

The Stability of the Excimer as Compared with the Two Separate Molecules

The present model should first be consistent with the fact that the excimer exists only in the excited state; namely, the stabilization by dimerization occurs only in the excited state, and not in the ground state. Let the energies of the monomer ground state and of the excited state be designated as E(A) and E(A*), and let those of the dimer ground state and the excited state (excimer state) be E(AA) and E(AA*) respectively. Then, in our approximation:

$$\left.\begin{aligned} \mathrm{E(A)} &= 2\sum_{i=1}^{n} E(\Phi_i) \\ \mathrm{E(A^*)} &= 2\sum_{i=1}^{n-1} E(\Phi_i) + E(\Phi_n) + E(\Phi_{n+1}) \\ \mathrm{E(AA)} &= 2\sum_{i=1}^{2n} E(\Psi_i) \\ \mathrm{E(AA^*)} &= 2\sum_{i=1}^{2n-1} E(\Psi_i) + E(\Psi_{2n}) + E(\Psi_{2n+1}) \end{aligned}\right\} \quad (8)$$

13) K. Ruedenberg, *ibid.*, **34**, 1861 (1961).

14) M. Göpert-Meyer and A. L. Sklar, *ibid.*, **6**, 645 (1938).

It is shown by Eqs. (5) and (7) that:

$$\mathrm{E(AA)} - 2\mathrm{E(A)} = 4\sum_{i=1}^{n} S'(1-m_iS)^{-2}[-\alpha(1-m_iS) - \beta'(Sm_i-S')] \quad (9)$$

This quantity is clearly positive. Hence, the dimer ground-state molecule is unstable compared with the two separate ground-state molecules. In attempting to compare the energies of excited states, it is most illustrative to put:

$$S' = 0 \quad (10)$$

Then:

$$\mathrm{E(AA^*)} - \mathrm{E(A)} - \mathrm{E(A^*)} = \beta'[(1-m_nS)^{-1}+(1-m_{n+1}S)^{-1}] \quad (11)$$

This quantity is negative. Hence, the excimer is more stable than two separate molecules, one of which is excited. The inclusion of S' makes the above equation more complicated; however, a leading term is expressed as in Eq. (11), and the above conclusion remains valid.

The 6000 cm^{-1} Rule

The difference between the fluorescence energies of the monomer and the excimer is, under the approximation of $S'=0$:

$$\Delta\tilde{\nu} = (-\beta')[(1-m_{n+1}S)^{-1}+(1-m_nS)^{-1}] \quad (12)$$

The m_{n+1} value (which is equal to the $-m_n$ value for alternant hydrocarbons) may vary from $\sim$0.3 to $\sim$0.6 (specifically, 0.618 for naphthalene and 0.445 for pyrene), but, because of the $S\sim$0.25 factor, the above quantity remains nearly constant. In this sense one may as well neglect the intramolecular overlap integral, S, and set:

$$\Delta\tilde{\nu} = 2(-\beta') \quad (13)$$

Hence, the energy difference between the monomer fluorescence and the excimer fluorescence may be interpreted as being twice the intermolecular resonance integral, β'. Therefore, it may be concluded that the monomer-excimer fluorescence separation is constant in all compounds provided the intermolecular distance is constant. The 6000 cm^{-1} rule[9] implies, then, that the intermolecular distance is nearly constant and that β' is approximately -3000 cm^{-1}.

The neglect of the overlap integrals, S', in this section leads to a great simplification. This may seem rather peculiar, for if S' be zero there would be no intermolecular interaction. The only justification for equating S' to zero is that the intermolecular resonance integral, β', is determined, as will be shown below, so as to take the overlap integrals into account.

The Excimer Energies *vs.* The Intermolecular Distances

The next task is to evaluate the excimer energies as a function of the intermolecular distance. Since the monomer fluorescence energy can always be obtained experimentally, it is sufficient to calculate the monomer-excimer separation, $\Delta\tilde{\nu}$. We will henceforth assume the zero overlap approximation. The evaluation of $\Delta\tilde{\nu}$ *via* Eq. (13) requires the estimation of β' only. It is here assumed that

$$\beta/S = \beta'/S' \quad (14)$$

holds true at any intermolecular distance; no further effort will be devoted to estimating the validity of this assumption. Then:

$$\Delta\tilde{\nu} = -2\beta S'/S \quad (15)$$

where $S=0.25$, and S' may be calculated by the formula[15]:

$$S' = (1/240)\exp(-\rho/2)[\rho^4+4\rho^3-12\rho^2-120\rho-240] \quad (16)$$

where $\rho=3.18R$, R being the intermolecular distance.*2 β is determined, for the individual molecule, so that the monomer excitation energy, $-(m_{n+1}-m_n)\beta$, gives the observed fluorescence energy.

The results of the calculation are shown in Fig. 3 for naphthalene and in Fig. 4 for pyrene. Figures 3 and 4 also show the results of the ASMO CI

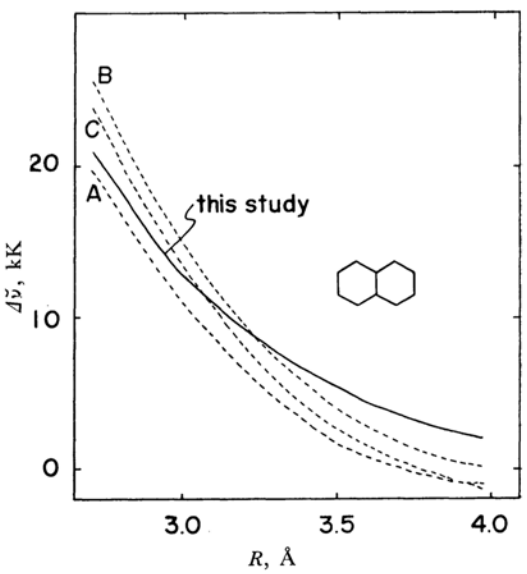

Fig. 3. Calculated monomer-excimer fluorescence separation of naphthalene as a function of interplanar distance.

15) R. G. Parr and B. L. Crawford, *ibid.*, **16**, 1049 (1948).

*2 If the phase of S' is chosen in this way, S' is positive for $R>0.9$ Å; this is in conformity with Eq. (4).

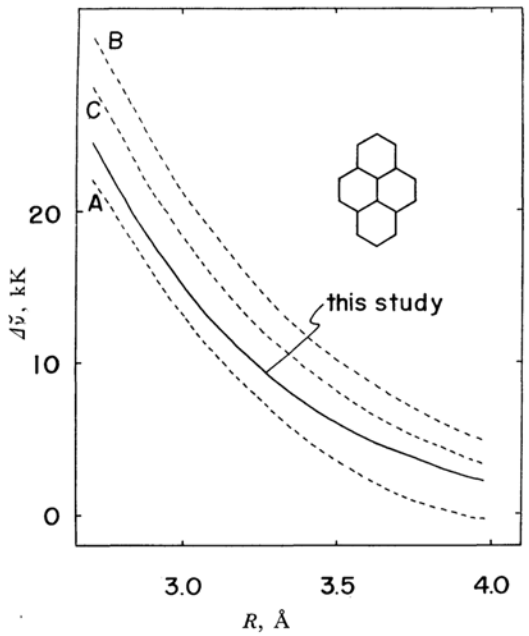

Fig. 4. Calculated monomer-excimer fluorescence separation of pyrene as a function of interplanar distance.

calculations given by Azumi, Armstrong, and McGlynn.[5] In the latter calculations, three sets of results, marked A, B, and C in Figs. 3 and 4, are given; these results are based on three slightly different methods of evaluating the diagonal matrix elements in configuration interaction. (For further details see Ref. 5).

As may be seen in Figs. 3 and 4, the simple Hückel approach as used in this paper gives results which are quite similar to the complicated ASMO CI calculations. In fact, the differences between the results of the present treatment and those based on one of the three methods in the ASMO CI treatments are even smaller than the differences caused by the slight variation in the estimation of matrix elements in the latter treatments. At a large intermolecular distance, however, a deviation between the two sets of the treatments is observed. In the present treatment, the excimer fluorescence converges, at an infinite separation of the two molecules, on the monomer fluorescence, whereas in the ASMO CI methods, as has been described earlier, it converges on a fluorescence which lies at a shorter wavelength than the monomer fluorescence (*vide supra*). The latter situation seems unlikely; the present model appears to be qualitatively more satisfactory in this regard.

The Application to Heterocyclic Molecules

Having seen that the simple Hückel approach is as satisfactory as the ASMO CI treatment, we shall now apply the present method to heterocyclic molecules. Acridine will be taken as an example. The excimer fluorescence has not been observed for acridine; however, it is observed for one of its derivatives, acriflavine.[16] It is appropriate to assume that the excimer of acridine is of the C_{2h} symmetry; namely, the two molecular planes are parallel, and the nitrogen atom of one molecule is placed above the carbon atom of the opposite position of the other molecule. The matrix elements involving nitrogen are determined by means of the parameters, δ_N and ρ_{CN}. Namely, for *intramolecular* matrix elements:

$$\alpha_N = \alpha_C + \delta_N\beta_{CC} \tag{17}$$

and:

$$\beta_{CN} = \beta_{CC}\rho_{CN} \tag{18}$$

For an intermolecular resonance integral, it is assumed that:

$$\beta'_{CN} = \beta'_{CC}\rho_{CN} \tag{19}$$

where β'_{CC} is given by Eq. (14). Calculations were carried out by using the parameter values given by Streitwieser[17]:

$$\delta_N = 0.5 \quad \text{and} \quad \rho_{CN} = 0.8 \tag{20}$$

The results are shown in Fig. 5. It may be seen that the results are quite similar to those on the hydrocarbon excimers. Since the present paper aims merely to illustrate the application to heterocyclic molecules, no effort shall be devoted to choosing the most appropriate parameter values. It is, however, believed that the deviation in results with the different choices of parameter values may be smaller than the deviation in the results associated

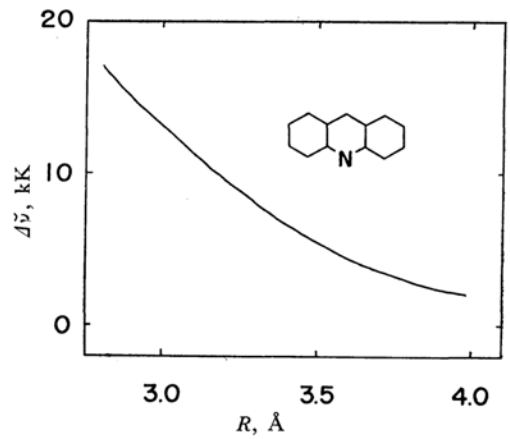

Fig. 5. Calculated monomer-excimer fluorescence separation of acridine as a function of interplanar distance.

16) M. Sato, T. Azumi and H. Azumi, This Bulletin, **39**, 857 (1966).
17) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, New York (1961).

with the various approximations one has to introduce in "exact" calculations.

Concluding Remarks

It has been shown that the simple Hückel approach used in this paper gives results quite similar to those of complicated ASMO CI calculations. The present treatment is further capable of explaining the various properties of the excimer, some of which have hitherto been inexplicable. It is by no means implied, however, that the present theory of the excimer surpasses the previously-developed molecular exciton-charge resonance interaction theory. The present treatment surely lacks exactness, yet it is of significance because of its simplicity. It is rather of importance that the ASMO CI treatments developed earlier yield, at the present stage, only as rough results as the simple Hückel treatment. This implies that a further refinement of the former treatment is in order.

The authors wish to express their appreciation to Dr. Yoshito Amako for valuable discussions.