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The Energy of the Excimer Luminescence of Naphthalene under a Variety of Geometrical Configurations

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A four-electron ASMO treatment of the interaction of two naphthalene molecules to yield excimers of D_{2h}, C_2, or S_4 is developed, and the energies of these excimers are calculated as a function of the angle, α, between corresponding bonds of the two molecules. It is shown that excimers are stable at two configurations, $\alpha=0°$ and $\alpha=75°$; that the excimer with $\alpha=0°$ does not emit because of the forbidden character of the transition, and that the excimer with $\alpha=75°$ emits and is considered to play a predominant role in the observed excimer fluorescence.

A large number of compounds exhibit, in a concentrated solution, a broad and structureless fluorescence about 6000 cm^{-1} to the red of the normal structured fluorescence. This broad fluorescence band is ascribed to the dimeric species produced by the photoassociation of one ground-state molecule and one excited-state molecule; the term "excimer fluorescence" has been used to describe this phenomenon. Although quite a lot of experimental information is available, theoretical interpretations of excimer fluorescence are scarce. Azumi and McGlynn(1) have suggested that the excimer state may be satisfactorily represented by a linear combination of molecular exciton states and charge resonance states. On the basis of this model, the energy of the excimer luminescence was calculated, by Azumi, Armstrong, and McGlynn,(2) for excimers of naphthalene, anthracene, pyrene, and perylene at the highest possible symmetry of excimer configuration (i. e., D_{2h}). Similar calculations have also been given by Murrell and Tanaka(3) and by Konijnenberg(4). The agreement between the calculated and the experimental excimer energies strongly supports the above-mentioned idea and the general scheme of the calculation. There are, however, some pitfalls in the calculations which have been presented in the past. The calculations given by these three sets of authors were all carried out for an excimer configuration which may not exist in reality. The excimer configuration for which the calculations were carried out is such that one of the molecules which constitute an excimer is exactly superposed, at some distance, over the other. In an excimer of such a high symmetry, the transition between the lowest excimer state and the dimeric ground state is dipole-forbidden. On the other hand, as has been illustrated by Birks, Dyson, and King,(5) the lifetime of the excimer fluorescence is quite short, indicating the allowed character of excimer luminescence. In some cases, an excimer luminescence of a long duration is observed; however, it has been clarified that this duration is due to triplet-triplet annihilation, and not to the inherent forbidden character of the excimer luminescence.(6-10) All these experimental evidences seem to reveal that excimer luminescence is essentially allowed, and that, consequently, the excimer has a symmetry lower than D_{2h}.

Various geometrical configurations of sandwich-type excimers (in which two molecular planes are parallel) were analyzed group-theoretically by Azumi and McGlynn.(11) It was shown that excimer luminescence should be forbidden not only for the D_{2h} configuration, but also for the C_{2h}, C'_{2h}, or S_2 configurations of the excimer. That is, if the corresponding bonds of the two molecules that constitute an excimer are aligned parallel, excimer luminescence is invariably forbidden. In order for excimer luminescence to be an allowed transition, as seems to be the case, there must be some angle between the corresponding bonds of the two molecules. These are schematically represented in Fig. 1 for the naphthalene excimer.

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* Postdoctoral fellow supported by the Japan Society for the Promotion of Science.

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

2) T. Azumi, A. T. Armstrong and S. P. McGlynn, ibid., **41**, 3839 (1964).

3) J. N. Murrell and J. Tanaka, *Mol. Phys.*, **7**, 363 (1964).

4) E. Konijnenberg, Thesis, University of Amsterdam (1963).

5) J. B. Birks, D. J. Dyson and T. A. King, *Proc. Roy. Soc.*, **A277**, 270 (1964).

6) T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **39**, 3553 (1963).

7) C. A. Parker and C. G. Hatchard, *Trans. Faraday Soc.*, **59**, 284 (1963).

8) C. Tanaka, J. Tanaka, E. Hutton and B. Stevens, *Nature*, **198**, 1192 (1962).

9) C. A. Parker, ibid., **200**, 331 (1963).

10) F. J. Smith and S. P. McGlynn, *J. Chem. Phys.*, **42**, 4308 (1965).

11) T. Azumi and S. P. McGlynn, ibid., **42**, 1675 (1965).

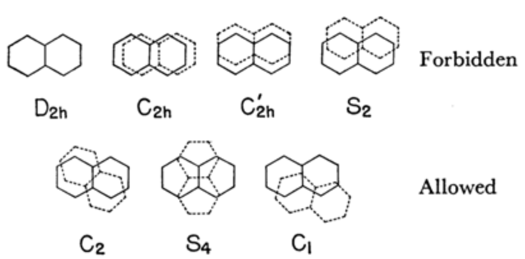

Fig. 1

This conclusion, arrived at group-theoretically, might, however, be hard to accept. First of all, it is against the intuition of chemists that a symmetrical configuration should be favored over an asymmetrical one. In addition, since in most aromatic crystals the two nearest molecules are aligned in the way of C_{2h} or S_2, there has been a suggestion that the excimer should have a similar configuration. It is, in this respect, desirable that some experimental or other kind of theoretical support of the above conclusion be obtained. Polarization measurements, conjoined with group theoretical analysis, would be most fruitful. Unfortunately, however, the polarization measurement of the excimer luminescence in a liquid solution is not possible because excimer formation is diffusion-controlled.[12] As a result, there has not been any experimental information thus far regarding the geometry of the excimer. Another way to approach this goal is to calculate the energy of the excimer luminescence for a variety of the geometrical configurations which give allowed dipole transitions and to see if there is any stable configuration among them. It is this which is effected in this paper.

In this paper, the effect of the angle, α, between the corresponding bonds of the two molecules is analyzed. Namely, excimers of D_{2h} $(\alpha=0°)$, C_2 $(0°<\alpha<90°)$, and S_4 $(\alpha=90°)$ are considered, and the energy of the excimer luminescence is calculated as a function of the angle, α. (See Fig. 2.) Interest is focussed on the variation in energy with respect to the angle, α; in this respect, the separation of the two molecular planes is arbitrarily taken to be 3 Å.

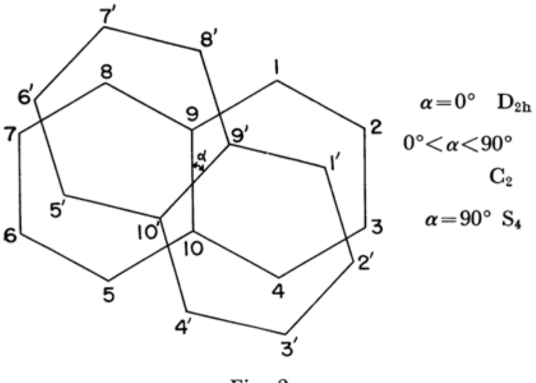

Fig. 2

Zeroth-order Dimeric Wave Functions

The general scheme of calculation is essentially identical with those given by Azumi, Armstrong, and McGlynn,[2] since the methods employed by these authors proved satisfactory. The highest-occupied and the lowest-vacant molecular orbitals of one ground state molecule (say, Molecule A) are designated, respectively, as ϕ_1 and ϕ_2, and the corresponding orbitals of the other molecule (say, Molecule B), as θ_1 and θ_2. ϕ_1 and ϕ_2 are orthogonal, as are also θ_1 and θ_2. It is assumed that orthogonality exists between ϕ_1 and θ_2 and between θ_1 and ϕ_2; the overlap between these orbitals is not exactly zero in our overlap approximation (see below), but it is surely very small and may well be neglected. The overlap integrals between ϕ_1 and θ_1 and between ϕ_2 and θ_2 are designated, respectively, as S_1 and S_2; namely, in the bracket notation:

$$S_1=(\phi_1\mid\theta_1) \tag{1}$$

$$S_2=(\phi_2\mid\theta_2) \tag{2}$$

The zeroth-order dimeric wave functions of interest are, then, expressed in terms of these four molecular orbitals. The wave function for the dimeric ground state is:

$$\psi_G=(1-2S_1{}^2+S_1{}^4)^{-1/2}\mid\phi_1\overline{\phi}_1\theta_1\overline{\theta}_1\mid \tag{3}$$

where:

$$\mid abcd\mid=(4!)^{-1/2}\sum_p(-1)^p\mathbf{P}a(1)b(2)c(3)d(4) \tag{4}$$

The excitation of one electron to a higher orbital produces two molecular exciton states, ψ_A and ψ_B, and two charge resonance states, ψ_C and ψ_D.

The C_2 Excimer.—When an excimer is of the C_2 symmetry, it may easily be shown group-theoretically that all of the four wave functions form bases for the irreducible representation of B. The normalized wave functions are:

$$\psi_A=\{2(1-S_1{}^2)\}^{-1/2}\{\mid\phi_1\overline{\phi}_1\theta_1\overline{\theta}_2\mid+\mid\phi_1\overline{\phi}_1\theta_2\overline{\theta}_1\mid\} \tag{5}$$

$$\psi_B=\{2(1-S_1{}^2)\}^{-1/2}\{\mid\phi_1\overline{\phi}_2\theta_1\overline{\theta}_1\mid+\mid\phi_2\overline{\phi}_1\theta_1\overline{\theta}_1\mid\} \tag{6}$$

$$\psi_C=\{2(1-S_1{}^2)\}^{-1/2}\{\mid\phi_1\overline{\theta}_2\theta_1\overline{\theta}_1\mid+\mid\theta_2\overline{\phi}_1\theta_1\overline{\theta}_1\mid\} \tag{7}$$

$$\psi_D=\{2(1-S_1{}^2)\}^{-1/2}\{\mid\phi_1\overline{\phi}_1\phi_2\overline{\theta}_1\mid+\mid\phi_1\overline{\phi}_1\theta_1\overline{\phi}_2\mid\} \tag{8}$$

The D_{2h} Excimer.—When an excimer is of the D_{2h} symmetry, namely, when $\alpha=0°$, the two

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[12] J. B. Birks, D. J. Dyson and I. H. Munro, *Proc. Roy. Soc.*, **A275**, 575 (1963).

wave functions ψ_{I} and ψ_{II} fall into the B_{3g} representation, and the two wave functions ψ_{III} and ψ_{IV} into the B_{2u} representation. These are, in terms of Eqs. 5—8;

$$\psi_{\mathrm{I}} = \{2(1 + S_1S_2)\}^{-1/2}(\psi_{\mathrm{A}} - \psi_{\mathrm{B}}) \tag{9}$$

$$\psi_{\mathrm{II}} = \{2(1 + S_1S_2)\}^{-1/2}(\psi_{\mathrm{C}} - \psi_{\mathrm{D}}) \tag{10}$$

$$\psi_{\mathrm{III}} = \{2(1 - S_1S_2)\}^{-1/2}(\psi_{\mathrm{A}} + \psi_{\mathrm{B}}) \tag{11}$$

$$\psi_{\mathrm{IV}} = \{2(1 - S_1S_2)\}^{-1/2}(\psi_{\mathrm{C}} + \psi_{\mathrm{D}}) \tag{12}$$

The $\mathbf{S_4}$ Excimer.—When an excimer is of the S_4 symmetry, namely, when $\alpha=90°$, the two wave functions $\psi_{\mathrm{A}}\pm i\psi_{\mathrm{B}}$ fall into the degenerate E representation, and are also $\psi_{\mathrm{C}}\pm i\psi_{\mathrm{D}}$. When the configuration interaction between these two E states is considered, only one wave function from each E state may be taken. These are:

$$\psi_{\alpha} = 2^{-1/2}(\psi_{\mathrm{A}} + i\psi_{\mathrm{B}}) \tag{13}$$

$$\psi_{\beta} = 2^{-1/2}(\psi_{\mathrm{C}} + i\psi_{\mathrm{D}}) \tag{14}$$

Hamiltonian Matrix Elements

The Hamiltonian of the system is expressed in atomic units as:

$$H = \sum H_c(\nu) + \sum_{\nu<\mu} 1/r_{\nu\mu} \tag{15}$$

where $1/r_{\nu\mu}$ is the electrostatic repulsion between π electrons, ν and μ, and where $H_{\mathrm{C}}(\nu)$ represents the effect of the core on the ν electron. In expressing integrals over molecular orbitals, the following notational simplification is made: ϕ_1 and ϕ_2 are designated as 1 and 2 respectively, and θ_1 and θ_2, as 1′ and 2′ respectively. Further,

$$(ij \mid kl) = \iint i(\nu)j(\nu)(1/r_{\nu\mu})k(\mu)l(\mu)\mathrm{d}\tau_\nu\mathrm{d}\tau_\mu \tag{16}$$

$$H^c_{ij} = \int i(\nu)H_c(\nu)j(\nu)\mathrm{d}\tau_\nu \tag{17}$$

The energy of the ground state, E_0, is then expressed as:

$$\begin{aligned} E_0 = {} & (1-2S_1^2+S_1^4)^{-1}[2(11 \mid 11) \\ & + (4-2S_1^2)(11 \mid 1'1') - 8S_1(11 \mid 11') \\ & + (-2+6S_1^2)(11' \mid 11') + (4-4S_1^2)H^c_{11} \\ & + (-4S_1+4S_1^3)H^c_{11'}] \end{aligned} \tag{18}$$

The other matrix elements are obtained similarly.

The $\mathbf{C_2}$ Excimer.—The hamiltonian matrix elements are:

$$\begin{aligned} & H_{\mathrm{AA}} = H_{\mathrm{BB}} \\ & =(1-S_1^2)^{-1}[(11 \mid 11)+(11 \mid 22)+2(11 \mid 1'1') \\ & \quad +(2-S_1^2)(11 \mid 2'2')+(12 \mid 12) \\ & \quad -2S_1(11 \mid 11')-2S_1(11' \mid 22)-(11' \mid 11') \\ & \quad -2S_1(12 \mid 1'2)+(-1+2S_1^2)(12' \mid 12') \\ & \quad +(3-S_1^2)H^c_{11}+(1-S_1^2)H^c_{22}-2S_1H^c_{11'}] \end{aligned} \tag{19}$$

$$\begin{aligned} & H_{\mathrm{CC}} = H_{\mathrm{DD}} \\ & =(1-S_1^2)^{-1}[(11 \mid 11)+(2-S_1^2)(11 \mid 22) \\ & \quad +2(11 \mid 1'1')+(11 \mid 2'2') \\ & \quad +(-1+2S_1^2)(12 \mid 12)-2S_1(11 \mid 11') \\ & \quad -2S_1(11' \mid 22)-(11' \mid 11')-2S_1(12 \mid 1'2) \\ & \quad +(12' \mid 12')+(3-S_1^2)H^c_{11}+(1-S_1^2)H^c_{22} \\ & \quad -2S_1H^c_{11'}] \end{aligned} \tag{20}$$

$$\begin{aligned} & H_{\mathrm{AB}} \\ & =(1-S_1^2)^{-1}[-S_1S_2(11 \mid 1'1') \\ & \quad +(2-S_1^2)(12 \mid 1'2')-2S_2(11 \mid 11') \\ & \quad -2S_1(11 \mid 22')+3S_1S_2(11' \mid 11') \\ & \quad +(-1+3S_1^2)(11' \mid 22')-2S_1(12 \mid 12') \\ & \quad +S_1^2(12' \mid 1'2)-2S_1S_2H^c_{11}+(3S_1^2S_2-S_2)H^c_{11'} \\ & \quad +(-S_1+S_1^3)H^c_{22'}] \end{aligned} \tag{21}$$

$$\begin{aligned} & H_{\mathrm{AC}} = H_{\mathrm{BD}} \\ & =(1-S_1^2)^{-1}[-S_1(11 \mid 22)-S_1(11 \mid 1'1') \\ & \quad -S_1(11 \mid 2'2')-S_1(12 \mid 12)-2(11 \mid 11') \\ & \quad +(3S_1^2-1)(11' \mid 22)+3S_1(11' \mid 11') \\ & \quad +2(12 \mid 1'2)-S_1(12' \mid 12')-2S_1H^c_{11} \\ & \quad +(-S_1+S_1^3)H^c_{22}+(-1+3S_1^2)H^c_{11'}] \end{aligned} \tag{22}$$

$$\begin{aligned} & H_{\mathrm{AD}} = H_{\mathrm{BC}} \\ & =(1-S_1^2)^{-1}[S_2(11 \mid 11)+2S_2(11 \mid 1'1') \\ & \quad -S_1(12 \mid 1'2')-2S_1S_2(11 \mid 11') \\ & \quad +(3-S_1^2)(11 \mid 22')-S_2(11' \mid 11') \\ & \quad -2S_1(11' \mid 22')+2S_1^2(12 \mid 12') \\ & \quad -S_1(12' \mid 1'2)+(3S_2-S_1^2S_2)H^c_{11} \\ & \quad -2S_1S_2H^c_{11}+(1-S_1^2)H^c_{22'}] \end{aligned} \tag{23}$$

$$\begin{aligned} & H_{\mathrm{CD}} \\ & =(1-S_1^2)^{-1}[-S_1S_2(11 \mid 1'1')+S_1^2(12 \mid 1'2') \\ & \quad -2S_2(11 \mid 11')-2S_1(11 \mid 22') \\ & \quad +3S_1S_2(11' \mid 11')+(-1+3S_1^2)(11' \mid 22') \\ & \quad -2S_1(12 \mid 12')+(2-S_1^2)(12' \mid 1'2) \\ & \quad -2S_1S_2H^c_{11}+(-S_2+3S_1^2S_2)H^c_{11'} \\ & \quad +(-S_1+S_1^3)H^c_{22'}] \end{aligned} \tag{24}$$

Overlap matrix elements are:

$$S_{\mathrm{AB}} = S_{\mathrm{CD}} = - S_1S_2 \tag{25}$$

$$S_{\mathrm{AC}} = S_{\mathrm{BD}} = - S_1 \tag{26}$$

$$S_{\mathrm{AD}} = S_{\mathrm{BC}} = S_2 \tag{27}$$

The $\mathbf{D_{2h}}$ Excimer.—Hamiltonian and overlap matrix elements are expressed as follows. For B_{3g} states:

$$H_{\mathrm{I\,I}} = (1 + S_1S_2)^{-1}(H_{\mathrm{AA}} - H_{\mathrm{AB}}) \tag{28}$$

$$H_{\mathrm{II\,II}} = (1 + S_1S_2)^{-1}(H_{\mathrm{CC}} - H_{\mathrm{CD}}) \tag{29}$$

$$H_{\mathrm{I\,II}} = (1 + S_1S_2)^{-1}(H_{\mathrm{AC}} - H_{\mathrm{AD}}) \tag{30}$$

$$S_{\mathrm{I\,II}} = - (1 + S_1S_2)^{-1}(S_1 + S_2) \tag{31}$$

For B_{2u} states:

$$H_{\mathrm{III\,III}} = (1 - S_1S_2)^{-1}(H_{\mathrm{AA}} + H_{\mathrm{AB}}) \quad (32)$$

$$H_{\mathrm{IV\,IV}} = (1 - S_1S_2)^{-1}(H_{\mathrm{CC}} + H_{\mathrm{CD}}) \quad (33)$$

$$H_{\mathrm{III\,IV}} = (1 - S_1S_2)^{-1}(H_{\mathrm{AC}} + H_{\mathrm{AD}}) \quad (34)$$

$$S_{\mathrm{III\,IV}} = -(1 - S_1S_2)^{-1}(S_1 - S_2) \quad (35)$$

The S_4 Excimer.—The Hamiltonian and overlap matrix elements are:

$$H_{\alpha\alpha} = H_{\mathrm{AA}} \quad (36)$$

$$H_{\beta\beta} = H_{\mathrm{CC}} \quad (37)$$

$$H_{\alpha\beta} = H_{\mathrm{AC}} \quad (38)$$

$$S_{\alpha\beta} = -S_1 \quad (39)$$

MO Integrals in Terms of AO Integrals

As bases molecular orbitals, ϕ_1, ϕ_2, θ_1, and θ_2, simple Hückel molecular orbitals are used. The differential overlap within any one molecule is neglected, since this approximation has been proved to be rather successful. No simplification is made for an intermolecular overlap integral (i. e., the overlap between two atomic orbitals which belong to different molecules.).

Hereafter, r, s, t, and u refer to atomic orbitals. The numbering r, s, t, or u, which designates the atom position within a molecule, is common to both Molecule A and Molecule B, and corresponding atoms on different molecules have the same number. Only when it is necessary specifically to indicate that the r atom is in Molecule A (or Molecule B) is the atomic orbital designated as r_{A} (or r_{B}) instead of just r.

The integrals over molecular orbitals are expressed in terms of integrals over atomic orbitals in the following way:

Overlap Integrals.—S_1 and S_2 are expressed as:

$$S_1 = \sum_r\sum_t C_{r1}C_{t1}(r_{\mathrm{A}} \mid t_{\mathrm{B}}) \quad (40)$$

$$S_2 = \sum_r\sum_t C_{r2}C_{t2}(r_{\mathrm{A}} \mid t_{\mathrm{B}}) \quad (41)$$

Electron Repulsion Integrals.—Mulliken's approximation[13] is applied consistently; it is set as:

$$r(\nu)t(\nu) = (1/2)(r \mid t)[r(\nu)r(\nu) + t(\nu)t(\nu)] \quad (42)$$

The electron repulsion integral is, then, expressed as:

$$(ij \mid kl) = (1/4)\sum_r\sum_s\sum_t\sum_u C_{ri}C_{sj}C_{tk}C_{ul}\,(r \mid s)(t \mid u)[\gamma_{rt} + \gamma_{ru} + \gamma_{st} + \gamma_{su}] \quad (43)$$

where:

$$\gamma_{rt} = (rr \mid tt)$$

is the atomic Coulomb repulsion integral.

Core Integrals.—The core integral over molecular orbitals, i and j, is expressed as[2]:

$$H^c_{ij} = \sum_r\sum_t C_{ri}C_{tj}(r \mid t)[-A_c - (1/2)\sum_{q\neq t}\{(q:rr) + (q:tt)\}] - 2(11 \mid ij) - 2(1'1' \mid ij) \quad (44)$$

where summation over q should be carried out over all the carbon atoms in both Molecule A and Molecule B. A_c is the experimental electron affinity of the carbon atom in its valence state, and has the value[14] of:

$$A_c = 0.69\ \mathrm{eV}.$$

and $(q : rr)$ is the Coulomb penetration integral.[15]

The Evaluation of AO Integrals

As basis functions for atomic orbitals, carbon 2p Slater orbitals are used. The appropriate choice of orbital exponent, Z, is a difficult task, but, in this paper, Z=3.18 is taken, since satisfactory results were obtained by Azumi, Armstrong, and McGlynn[2] with this Z value.

The integrals over atomic orbitals were evaluated in the following way:

Overlap Integrals.—As has been mentioned above, the differential overlap within any one molecule is neglected; namely, for the *intramolecular* overlap integral:

$$(r_{\mathrm{A}} \mid t_{\mathrm{A}}) = \delta_{rt} \quad (45)$$

The *intermolecular* overlap integral was evaluated by the formulas presented by Parr and Crawford[15];

$$(r_{\mathrm{A}} \mid t_{\mathrm{B}}) = S_\pi \cos^2\theta + S_\sigma \sin^2\theta \quad (46)$$

where

$$S_\pi = 240^{-1}\exp(-\rho/2)[240 + 120\rho + 12\rho^2 - 4\rho^3 - \rho^4] \quad (47)$$

$$S_\sigma = 120^{-1}\exp(-\rho/2)[120 + 60\rho + 12\rho^2 + \rho^3] \quad (48)$$

where:

$$\rho \equiv ZR \quad (49)$$

and where R is the distance, in atomic units, between two atoms, r_{A} and t_{B}. Furthermore, (see Fig. 3):

$$\cos\theta = v/R,\ \sin\theta = h/R \quad (50)$$

Coulomb Repulsion Integrals.—The *intramolecular* Coulomb repulsion integral, $\gamma_{r_{\mathrm{A}}t_{\mathrm{A}}}$, was taken from the table presented by Pariser.[16] These values were calculated from the Slater orbitals, with the exception of the one-center integral and the nearest neighbor two-center integrals; the latter values were obtained semi-empirically from the benzene spectrum.

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13) R. S. Mulliken, *J. Chim. Phys.*, **46**, 497 (1949).

14) R. S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934).

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

16) R. Pariser, ibid., **24**, 324 (1956).

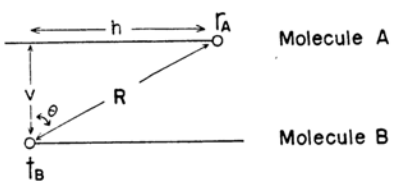

Fig. 3

Intermolecular Coulomb repulsion integrals were calculated, by the multiple expansion method proposed by Parr,(17) in atomic units(18);

$$\gamma_{r_A t_B} = R^{-1}[1 + (q/2R^2)(3\cos^2\theta - 1) + (3q^2/16R^4)(3 - 30\cos^2\theta + 35\cos^4\theta)] \quad (51)$$

where:

$$q = 24/Z^2 \quad (52)$$

Coulomb Penetration Integrals.—Since the penetration integral decreases very rapidly with the distance, some of the integrals may well be neglected, as is shown below.

The *intramolecular* Coulomb penetration integral, $(q_A : r_A r_A)$, is non-zero only when $q=r$ or q and r are adjacent. The integrals in these cases are evaluated by the formula given by Parr and Crawford(15):

$$(q_A : r_A r_A) = (Z/3840)\exp(-\rho)[(4/7)\rho^5 + (67/7)\rho^4 + 86\rho^3 + 461\rho^2 + 1125(\rho+1)] \quad (53)$$

The *intermolecular* Coulomb penetration integral $(q_A : r_B r_B)$ is in all cases, neglected.

The Correction for Infinite Separation

The energies of the excited excimer states are obtained by solving secular equations of the form:

$$|\,\boldsymbol{H} - E\boldsymbol{S}\,| = 0 \quad (54)$$

where $\boldsymbol{H}$ and $\boldsymbol{S}$ represent, respectively, Hamiltonian and overlap matrices, the elements of which are given in Eqs. 19—39. It is convenient to calculate the energy with respect to the ground-state energy at $\alpha=0°$, E_0^0; for this purpose Eq. 54 is rewritten as:

$$|\,(\boldsymbol{H} - E_0^0\boldsymbol{S}) - E'\boldsymbol{S}\,| = 0 \quad (55)$$

where:

$$E' = E - E_0^0 \quad (56)$$

and where the calculated energy, E', is now the energy scaled from the ground state of the dimer of $\alpha=0°$.

The direct use of the theoretical Hamiltonian matrix elements reveals one significant difficulty. From the viewpoint of physical significance, $H_{AA} - E_0^0$ should converge on the ^1L_a excitation energy of the monomer at an infinite separation of the two molecules. As is evident from Eqs. 18 and 22, $H_{AA} - E_0^0$ equals $(12|12)$ at an infinite separation. $(12|12)$ is also the result of the theoretical evaluation of the ^1L_a monomer energy in a two-electron treatment; thus, H_{AA} extrapolates to a correct energy limit. However, the value of $(12|12)$ is 0.491 eV., whereas ^1L_a is at 4.290 eV., and there exists great numerical discrepancy. This discrepancy, which may be due to the incompleteness of the simple four-electron treatment, needs to be calibrated. In this regard, the experimental ^1L_a monomer energy is obtained at an infinite separation. In other words, the monomer contribution is made as empirical as possible, while the dimerization effects are left in their fully theoretical form. This attitude is also adopted for charge resonance states. In sum, the $^1L_a - (12|12)$ term is added to all the diagonal terms of Eq. 55.

Results and Discussion

Calculations were carried out at intervals of five degrees in α. The lowest of the four excited states is the excimer state which is responsible for the excimer luminescence. The wave function of this state is expressed in the form of:

$$\psi = a\psi_A + b\psi_B + c\psi_C + d\psi_D \quad (57)$$

The energy of the excimer state, E', and the normalized mixing coefficients are summarized in Table I. The energy of the ground state scaled from that of $\alpha=0°$:

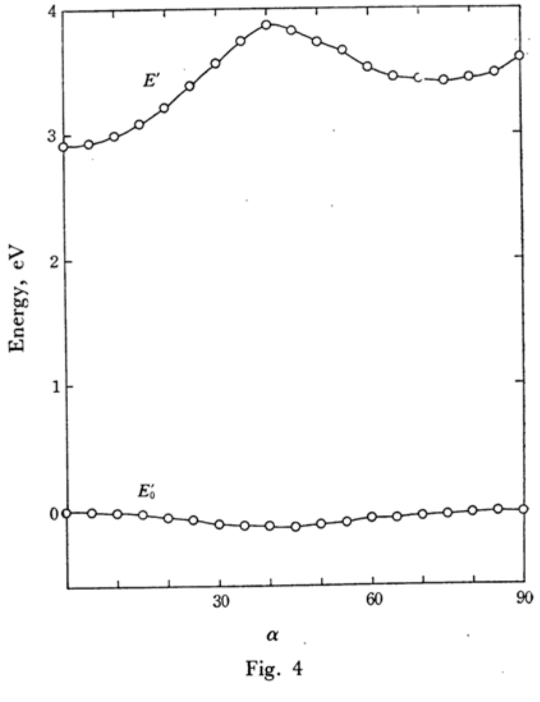

Fig. 4

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[17] R. G. Parr, ibid., **33**, 1184 (1960).

[18] The unit of energy equals e^2/a_0, where e is the charge on an electron and a_0 is the Bohr radius.

TABLE I. ENERGY AND MIXING COEFFICIENTS OF NAPHTHALENE EXCIMER

α	E', eV.	E_0', eV.	a	b	c	d
0	2.909	0	0.5461	−0.5461	0.3948	−0.3948
5	2.930	−0.009	0.5534	−0.5323	0.4471	−0.3479
10	3.005	−0.023	0.5565	−0.5362	0.4427	−0.3508
15	3.123	−0.042	0.5617	−0.5429	0.4349	−0.3548
20	3.278	−0.063	0.5696	−0.5535	0.4219	−0.3584
25	3.460	−0.084	0.5817	−0.5700	0.4003	−0.3581
30	3.659	−0.101	0.6023	−0.5970	0.3610	−0.3441
35	3.855	−0.123	0.6437	−0.6437	0.2799	−0.2798
40	3.992	−0.134	0.7091	−0.7002	0.0687	−0.0423
45	3.964	−0.139	0.6680	−0.6696	−0.2236	0.2169
50	3.851	−0.111	0.6142	−0.6195	−0.3586	0.2942
55	3.729	−0.098	0.5874	−0.5828	−0.4182	0.3212
60	3.622	−0.082	0.5741	−0.5553	−0.4489	0.3352
65	5.538	−0.064	0.5673	−0.5333	−0.4669	0.3458
70	3.482	−0.046	0.5638	−0.5145	−0.4787	0.3561
75	3.458	−0.031	0.5624	−0.4975	−0.4874	0.3669
80	3.466	−0.020	0.5627	−0.4806	−0.4953	0.3780
85	3.504	−0.014	0.5682	−0.4585	−0.5069	0.3852
90	3.622	−0.014	0.5372	0.5372*i*	0.4285	0.4285*i*

$$E_0' = E_0 - E_0^0 \qquad (58)$$

is also shown in Table I. The calculated energies are also plotted in Fig. 4 as a function of α. It seems reasonable to assume that the mutual repulsion of the two cores, a repulsion which is not included in the present calculation, is nearly independent of α. Figure 4 may then be considered to be the potential energy diagram expressed as a function of α. As may be seen in Fig. 4, there are two minima in the potential of the excited states, one at $\alpha=0°$ and one at $\alpha=75°$; consequently, the excimer is stable at these two configurations. We assume that when two molecules approach, by diffusion, to form an excimer, there is no specific orientation of the two molecules. If this assumption is true, various configurations (namely, various α values) of the excimer are formed, with nearly equal probabilities. They will immediately undergo relaxation according to the potential of Fig. 4. The potential barrier of 0.5 eV. between the two stable configurations is too high compared with the thermal kinetic energy of $1.5\boldsymbol{k}T=0.04$ eV., and the mutual transformation of the two is impossible at ordinary temperatures. It may well, then, be said that at an equilibrium state two kinds of excimers exist; the one with $\alpha=0°$ is hardly ever interpreted as being responsible for excimer fluorescence because of the forbidden character of the transition, while the one with $\alpha=75°$ may contribute to the observed excimer fluorescence.

The calculated energy of excimer fluorescence at $\alpha=75°$,

$$E' - E_0' = 3.46 \text{ eV}.$$

may seem to be too high compared with the observed energy (3.13 eV.)[19] of the naphthalene excimer fluorescence. However, to discuss this discrepancy is trivial, since, in the present calculations, the interplanar distance of 3 Å and the orbital exponent of $Z=3.18$ have been tentatively chosen rather arbitrarily. If smaller values of Z are used, as has been suggested[3,20] the calculated energy would surely become lower, and an agreement with the observed energy might well be obtained.

Concluding Remarks

It has been shown that there is considerable configuration interaction between molecular exciton states and charge resonance states. As may be seen in Table I, all of the four zeroth order states, the two molecular exciton states and the two charge resonance states, contribute to the excimer states in nearly equal measure. It has also been shown that the energy of the excited state varies significantly with the α value, and a stable configuration may be obtained at $\alpha \neq 0°$. It has been suggested that these configurations should, in general, be included in the calculation of this sort.

A number of questions remain. We have excluded the configuration of $\alpha=0°$ as the one responsible for excimer luminescence. Whether or not we are justified in doing so is a difficult question. Group theoretically, the excimer state at $\alpha=0°$ is of the B_{3g} symmetry in the D_{2h} point group,[11] and the transition to the A_g ground state is forbidden. Further, different from, say,

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[19] E. Döller and Th. Förster, *Z. Physik. Chem. N. F.*, **31**, 274 (1962).

[20] G. C. Nieman and G. W. Robinson, *J. Chem. Phys.*, **37**, 2150 (1962).

the benzene fluorescence, there is no vibrational coupling to acquire an allowed transition moment in the excimer fluorescence, unless we consider hot bands, since the ground state is dissociative. These considerations favor our treatment; however, further investigations might be necessary. These will be the subject of ensuing publications.

In the present calculation we have considered only the excimer configurations in which two molecular planes are parallel and their principal axes coincide. This may actually seem rather a freakish situation. However, to treat excimers of random orientations is quite difficult, if not impossible; at any rate, it is beyond the limits of the present paper.

The present calculations are based upon the above-specified model, just one of many models we may think of; therefore, too much emphasis should not be placed upon our suggestion of the $\alpha=75°$ configuration. It is, however, of interest to add that our calculations on the radiative lifetime of the excimer fluorescence yield 6×10^{-6} sec. at $\alpha=75°$, which is in good agreement with the observed value[21] of $1.2-1.4\times10^{-6}$ sec. The details of the calculations will be published in the next paper.[22]

TABLE II. IN-PLANE COMPONENT OF CARBON-CARBON DISTANCE, h

α	1-1′	1-2′	1-3′	1-4′	1-5′	1-6′	1-7′	1-8′	2-1′	2-2′
0	0	1.39000	2.40755	2.77999	3.67759	4.16999	3.67759	2.40755	1.39000	0
5	0.16041	1.23450	2.25429	2.67233	3.67409	4.21864	3.77348	2.52652	1.54887	0.21860
10	0.32052	1.08528	2.09814	2.55958	3.66359	4.25947	3.86248	2.64068	1.70914	0.43679
15	0.48002	0.94669	1.93974	2.44196	3.64613	4.29240	3.94441	2.74981	1.86939	0.65416
20	0.63860	0.82542	1.77986	2.31969	3.62172	4.31736	4.01908	2.85371	2.02855	0.87027
25	0.79597	0.73127	1.61945	2.19301	3.59042	4.33431	4.08636	2.95218	2.18577	1.08473
30	0.95183	0.67648	1.45975	2.06215	3.55228	4.34319	4.14609	3.04503	2.34038	1.29712
35	1.10587	0.67123	1.30248	1.92736	3.50738	4.34401	4.19815	3.13208	2.49178	1.50705
40	1.25781	0.71664	1.15005	1.78891	3.45580	4.33675	4.24244	3.21317	2.63947	1.71410
45	1.40735	0.80386	1.00611	1.64705	3.39765	4.32143	4.27886	3.28814	2.78301	1.91790
50	1.55421	0.92056	0.87620	1.50206	3.33303	4.29808	4.30735	3.35686	2.92200	2.11415
55	1.69812	1.05628	0.76867	1.35420	3.26206	4.26676	4.32783	3.41918	3.05607	2.31415
60	1.83879	1.20377	0.69500	1.20377	3.18489	4.22751	4.34027	3.47499	3.18489	2.50585
65	1.97596	1.35827	0.66710	1.05105	3.10165	4.18044	4.34464	3.52420	3.30813	2.69279
70	2.10938	1.51664	0.69077	0.89632	3.01250	4.12562	4.34094	3.56669	3,42552	2.87460
75	2.23877	1.67676	0.76105	0.73989	2.91763	4.06318	4.32917	3.60239	3.53679	3.05093
80	2.36391	1.83711	0.86622	0.58205	2.81720	3.99324	4.30936	3.63124	3.64169	3.22146
85	2.48454	1.99656	0.99464	0.42311	2.71140	3.91595	4.28155	3.65317	3.73999	3.38586
90	2.60045	2.15424	1.13765	0.26336	2.60045	3.83148	4.24579	3.66815	3.83148	3.54381

α	2-3′	2-5′	2-6′	2-7′	3-1′	3-2′	3-5′	3-6′	4-1′	4-5′
0	1.39000	4.16999	5.01171	4.81510	2.40755	1.39000	3.67759	4.81510	2.77999	2.40755
5	1.17864	4.11363	5.00694	4.87114	2.55737	1.59870	3.57502	4.74988	2.88236	2.28399
10	0.96504	4.04966	4.99264	4.91792	2.70329	1.80437	3.46600	4.67563	2.97925	2.15609
15	0.74961	3.97823	4.96884	4.95533	2.84487	2.00660	3.35077	4.59247	3.07046	2.02409
20	0.53274	3.89948	4.93557	4.98331	3.98173	2.20501	3.22958	4.50057	3.15583	1.88823
25	0.31487	3.81357	4.89291	5.00181	3.11353	2.39923	3.10272	4.40011	3.23519	1.74877
30	0.09639	3.72070	4.84094	5.01078	3.23992	2.58887	2.97050	4.29127	3.30839	1.60599
35	0.12226	3.62105	4.62658	4.65761	3.36062	2.77359	2.83322	4.17426	3.37529	1.46015
40	0.34068	3.51484	4.47733	4.46715	3.47535	2.95303	2.69127	4.04930	3.43577	1.31154
45	0.55846	3.40232	4.31991	4.27015	3.58384	3.12685	2.54501	3.91664	3.48971	1.16042
50	0.77518	3.28372	4.54215	4.95140	3.68585	3.29471	2.39487	3.77652	3.53701	1.00710
55	0.99042	3.15933	4.44544	4.91287	3.78117	3.45631	2.24135	3.62921	3.57757	0.85186
60	1.20377	3.02943	4.34027	4.86499	3.86959	3.61132	2.08500	3.47500	3.61132	0.69500
65	1.41483	2.89434	4.22683	4.80786	3.95092	3.75946	1.92644	3.31416	3.63820	0.53681
70	1.62320	2.75440	4.10535	4.74157	4.02499	3.90044	1.76647	3.14702	3.65815	0.37760
75	1.82848	2.60999	3.97606	4.66625	4.09164	4.03400	1.60607	2.97389	3.67114	0.21768
80	2.03028	2.46151	3.83919	4.58205	4.15073	4.15988	1.44650	2.79510	3.67714	0.05734
85	2.22821	2.30942	3.69502	4.48913	4.20215	4.27785	1.28952	2.61099	3.67614	0.10310
90	2.42191	2.15424	3.54381	4.38766	4.24579	4.38766	1.13765	2.42191	3.66815	0.26336

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21) J. B. Birks and T. A. King, *Proc. Roy. Soc.* **A291**, 244 (1966).

22) T. Azumi and H. Azumi, This Bulletin, in press (1966).

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Appendix I

Table II presents the in-plane components of distance, *h*, between two carbon atoms which belong to different molecules (see Fig. 3). These values are required in evaluating integrals over atomic orbitals. The atom positions are indicated by numbers, and those in different molecules are indicated by primed numbers, as is shown in Fig. 1. Since the Hückel coefficients for molecular orbitals, ϕ_1 or ϕ_2, are zero for atoms 9 and 10, the summation over *r* in Eqs. 40—44 may be carried out only from 1 to 8. There are still $8\times8=64$ pairs of carbons whose distances are required, but only twenty of these need be obtained; these are shown in Table II in Å units. Any other pair is identical to one of the pairs given in the table by symmetry considerations.

Appendix II

The numerical results for intramolecular and intermolecular MO integrals are tabulated in Tables III and IV. All integrals except the overlap integrals are in eV. units.

TABLE III. INTRAMOLECULAR MO INTEGRALS

(11 | 11)	5.75862
(12 | 12)	0.94098
H_{11}^c	−21.37112

TABLE IV. INTERMOLECULAR MO INTEGRALS

α	S_1	S_2	(11 | 1′1′)	(12 | 1′2′)	(11 | 11′)	(11 | 22′)	(11′ | 11′)
0	−0.06685	−0.03690	3.71823	0.20429	−0.31670	−0.17524	0.02117
5	−0.06549	−0.03566	3.71887	0.20388	−0.31029	−0.16939	0.02033
10	−0.06193	−0.03247	3.71870	0.20060	−0.29360	−0.15442	0.01824
15	−0.05637	−0.02761	3.71782	0.19482	−0.26747	−0.13156	0.01519
20	−0.04908	−0.02147	3.71643	0.18705	−0.23317	−0.10265	0.01163
25	−0.04039	−0.01450	3.71474	0.17786	−0.19221	−0.06988	0.00801
30	−0.03064	−0.00720	3.71297	0.16778	−0.14616	−0.03554	0.00478
35	−0.02017	−0.00001	3.71376	0.15734	−0.09655	−0.00175	0.00227
40	−0.00929	0.00662	3.71374	0.14656	−0.04489	0.02949	0.00074
45	0.00167	0.01236	3.71421	0.13549	0.00736	0.05652	0.00031
50	0.01246	0.01682	3.70854	0.12366	0.05860	0.07751	0.00100
55	0.02275	0.01988	3.70861	0.11137	0.10771	0.09197	0.00268
60	0.03226	0.02133	3.70916	0.09805	0.15317	0.09891	0.00513
65	0.04073	0.02110	3.71008	0.08348	0.19370	0.09802	0.00805
70	0.04792	0.01924	3.71124	0.06735	0.22820	0.08948	0.01108
75	0.05367	0.01588	3.71251	0.04981	0.25581	0.07398	0.01387
80	0.05786	0.01130	3.71373	0.03099	0.27591	0.05270	0.01610
85	0.06039	0.00583	3.71482	0.01121	0.28813	0.02728	0.01754
90	0.06125	−0.00008	3.71570	−0.00907	0.29225	−0.00029	0.01804

α	(11′ | 22′)	(12 | 12′)	(12 | 1′2)	(12′ | 12′)	(12′ | 1′2)	$H_{11'}^c$	$H_{22'}^c$
0	0.01171	−0.02461	−0.03521	0.00165	0.00150	2.04484	1.13049
5	0.01109	−0.02376	−0.03461	0.00162	0.00139	2.00338	1.09260
10	0.00954	−0.02165	−0.03312	0.00158	0.00112	1.89523	0.99564
15	0.00737	−0.01843	−0.03075	0.00153	0.00074	1.72595	0.84762
20	0.00497	−0.01436	−0.02757	0.00146	0.00032	1.50388	0.66047
25	0.00272	−0.00974	−0.02362	0.00135	−0.00007	1.23889	0.44837
30	0.00097	−0.00490	−0.01897	0.00122	−0.00038	0.94129	0.22603
35	−0.00008	−0.00010	−0.01370	0.00105	−0.00054	0.62100	0.00722
40	−0.00038	0.00429	−0.00788	0.00087	−0.00056	0.28780	−0.19507
45	0.00000	0.00805	−0.00165	0.00073	−0.00044	−0.04901	−0.36998
50	0.00091	0.01083	0.00480	0.00064	−0.00024	−0.37948	−0.50590
55	0.00207	0.01277	0.01123	0.00063	0.00000	−0.69569	−0.59928
60	0.00320	0.01366	0.01739	0.00069	0.00024	−0.98822	−0.64389
65	0.00402	0.01346	0.02304	0.00083	0.00042	−1.24887	−0.63772
70	0.00433	0.01222	0.02795	0.00100	0.00052	−1.47061	−0.58189
75	0.00401	0.01003	0.03196	0.00118	0.00051	−1.64795	−0.48085
80	0.00307	0.00704	0.03491	0.00133	0.00040	−1.77702	−0.34236
85	0.00166	0.00349	0.03672	0.00143	0.00021	−1.85540	−0.17708
90	−0.00002	−0.00034	0.03734	0.00147	−0.00001	−1.88184	0.00220