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Intermolecular Interaction in the Formation of Dimers & Excimers of Naphthalene, Anthracene & Pyrene

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Calculations are reported concerning the structures of the stable dimers and excimers of naphthalene, anthracene and pyrene. The results show that the perfect sandwich-pair geometry is not the stable conformation for the ground state dimers. While the singlet excimers of anthracene and naphthalene have the symmetric sandwich structures, the singlet excimers of pyrene do not have the perfect sandwich-pair geometry. The computational results also suggest that the conformation of the triplet excimer is different from that favoured by the corresponding singlet excimer. The binding in excimers, photo-dimerisation and the role of σ-π interaction are also examined.

SINCE the pioneering work of Forster and Kasper[1] on the pyrene excimer, the phenomenon of transannular interaction between two closely lying and parallel aromatic hydrocarbons in excimers and ground dimers has become the object of many theoretical[2-5] and experimental works[6-8]. All these treatments dealt with the symmetric sandwich structures of singlet excimers of aromatic hydrocarbons. There are, however, evidences which indicate that an aromatic hydrocarbon in its lowest triplet state can associate with a ground state molecule to form a triplet excimer[9,10]. The recent experimental[10] as well as theoretical studies[11] have established that the singlet and triplet excimers of naphthalene have different configurations.

Similarly there are a few theoretical treatments[12,13] on the formation of dimers between two ground state aromatic hydrocarbons. Low temperature absorption spectra of aromatic hydrocarbons [14,15] have shown features that can be ascribed to dimers. A detailed analysis of the absorption spectrum of anthracene dimer led Chandross *et al.*[15] to conclude that anthracene forms a stable dimer of non-sandwich configuration at low temperature.

However, no unified and consistent overall interpretation of the phenomena associated with the formation of ground state dimers, the singlet and triplet state excimers of aromatic hydrocarbons seem to have been attempted. The object of the present investigation is to examine the energies of excimer luminiscence, both fluorescence and phosphorescence and the binding and structures of ground dimers and excimers. Besides these aspects, the σ-π interaction and its role in the spectroscopy of excimers are also examined. The breakdown of the σ-π separation has been found to have an important consequence on the spin-forbidden electronic transition in the naphthalene excimer[11].

In this paper we report calculations on the interaction potentials of the ground dimers, singlet and triplet excimers of naphthalene, anthracene and pyrene. Our previous treatment[12,16] of the excimers and dimers of naphthalene and anthracene involves the use of Slater $2p$-orbital with $Zc = 3.18$ which is inappropriate for the treatment of intermolecular interactions.

Three different steric conformations of dimers have been considered. They are : (i) Symmetric sandwich structures in which each monomer is exactly superimposed over the other separated by a distance D (Fig. 1a); (ii) tilted structures in which the relative orientation of two molecules is so chosen that their long in-plane axes are parallel while their short axes are inclined by an angle α keeping the distance between the pivot points (denoted by D) fixed (Fig. 1b); and (iii) rotated sandwich structures in which one of the monomers is rotated around the intermolecular axis with respect to the other monomer by an angle θ while keeping the two aromatic planes parallel and separated by a distance D (Fig. 1c).

These considerations do not, however, rule out the other possible structures of dimers. For example, the pyrene crystal is dimeric with two molecules arranged in sandwich pairs such that their long-axes coincide but their short-axes are separated by one C—C bond length. This arrangement maintains the C_{2h} symmetry and minimises the intermolecular repulsion. The object of this work should not therefore be treated as an attempt to predict the observed geometries of the dimers and excimers.

1. Computational Procedure

A perturbative approach for the calculation of the interaction potential in the ground dimers has been followed. The important first-order and second-order terms contributing to the interaction potential of the ground dimers are discussed in an earlier paper[12]. They are electrostatic, π-overlap repulsion, non-bonded repulsion, charge transfer, π-π and σ-σ dispersion energies. The σ-π contributions to the dispersive forces are shown to be directional following the method developed by Rein

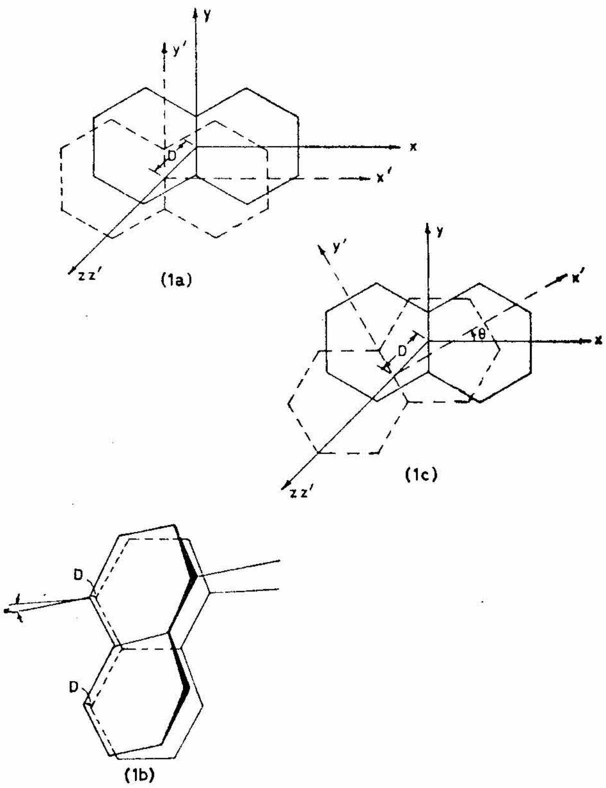

Fig. 1 — Axes-system for a pair of naphthalene molecules for three different steric conformations where D, α and θ are defined

et al.[17], but they are much smaller than the σ-σ and π-π terms.

Our calculations of the interaction energy associated with the formation of singlet and triplet excimers involves the computation of the excitation energy from the ground state of the dimer to the lowest energy excimer state (singlet or triplet), and the interaction energy of two ground state monomers for different steric configurations. For the calculation of the transition energies in excimers we have chosen a SCF-LCAO-MO calculation within the frame work of the super-molecule approach[4] which includes now the interaction between all singly excited configurations in the singlet and triplet manifolds separately. Since the configuration interaction in the triplet-mainifold is larger than in the singlet-manifold, we observe higher stability of the triplet excimers (see sec. 2.3). It is to be noted that in our previous papers[4] we determined the stability of triplet excimer from the singlet-triplet splitting in the state of excimers. This led to a wrong conclusion that an excimer triplet is unstable relative to a monomer triplet and a monomer ground states.

The coordinates of the two molecules in excimers are chosen so that the integral β' defined as

$$< i \mid H \mid j' > = \beta'_{ij} \quad ..(1)$$

is negative and the corresponding overlap is positive, where i and j' are the molecular orbitals of the molecules A and B, respectively and H is the hamiltonian of the composite system. β' is assumed proportional to the overlap and the proportionality constant is approximately chosen as -10eV as in the ref. 4. For the non-parallel dimers, the molecular integrals depend on the orientation of the $2p$-orbitals of the atoms of the two monomers and are evaluated by a standard procedure which is briefly described in the appendix.

The excimer potential ^{1,3} U for the singlet and triplet states is given by[11,16].

$$-{}^{1,3}U = \triangle E_M\,({}^{1,3}p) - \triangle E({}^{1,3}\sigma) - \triangle E_G \quad ..(2)$$

where $\triangle E_M({}^{1,3}p)$ is the transition energy from the ground state of the monomer to the excited electronic state with which the lowest energy excimer state correlates, $\triangle E({}^{1,3}\sigma)$ is the energy of excimer luminiscence (fluorescence or phosphorescence) and $\triangle E_G$ is the interaction energy of the ground state dimer. It is to be noted that both $\triangle E_G$ and $\triangle E({}^{1,3}\sigma)$ are functions of the structural parameters of the dimer.

In a previous publication Chandra and Lim[11] used the Slater carbon $2p$-orbital with the orbital exponent $Z = 2.55$ that fits best with the atomic SCF functions[18] in the region of $3 \sim 4$Å. Since the intermolecular separation in a dimer is of the order of $3 \sim 4$ Å, we expect that the use of such orbital should lead to more accurate predictions.

2. Results and Discussions

2.1. *Interaction potentials for the ground state dimers and their equilibrium conformations* — It is seen that the interaction operator 'V' has not been defined explicitly hence the matrix elements $\eta_{ij'}$ (see Eq. 7 of ref. 12) where i and j' are the molecular orbitals of the molecules A and B, and have to be evaluated by semi-empirical means. We assume that $\eta_{ij'}$ is proportional to the corresponding intermolecular overlap, $S_{ij'}$. In our earlier papers[11,12,16] this proportionality constant, K was given the value of -10 eV arrived at by comparing $\eta_{ij'}$ with the resonance integral β_0 (-2.4eV) between two adjacent $2p$-orbitals in benzene. This is not justifield as β_0 involves both the kinetic and potential energy terms whereas 'V' involves only the potential energy term. Salem[19] chose K $= -3$eV, somewhat arbitrarily, in the estimation of the interaction energies between two conjugated systems. We have estimated the value of K by invoking the available experimental data on the interactions between two pyrene molecules. Birks and Kazzaz[20] have reported from the observed binding and the fluorescence energies of the pyrene excimer that the total interaction energy of the two ground state pyrene molecules separated by 3.34 Å in the perfect sandwich configuration is 7.9 kcal/mol. Our calculated total interaction energy for this configuration of pyrene dimer fits with the observed value for $K = -1$ eV. We have therefore adopted this value of K for the estimation of the π-overlap repulsion and the charge-transfer interactions. Although this choice of $K = -1$eV seems to be low, the variation of K in the range of -1eV $\sim$ -3eV does not affect the trends of our results for the intermonomer separation greater than 3Å, hence our conclusions are not modified by such variations. It is to be noted that in our previous treatment[11] of naphthalene dimer and excimer the value of K was chosen as -10 eV which grossly overestimated the overlap repulsion and charge-transfer interaction terms. It is found here that the charge-transfer interaction term is very small compared to the other terms in the dimer potential because of low value of K and is therefore neglected.

In Figs 2 and 3 are shown the variations of the total interaction potential and its constituent terms with D, the inter-planar separation of symmetric sandwich configuration of naphthalene and pyrene dimers. The results for anthracene are very similar to those of naphthalene. We have then examined other possible steric configurations of dimers. In Figs 4 and 5 are shown the variation of the total interaction potentials with α and θ respectively for the dimers of naphthalene, anthracene and pyrene. The results for pyrene are somewhat different from those of anthracene and naphthalene. For example, while there is a continuous decrease of the π-overlap repulsion term for anthracene and naphthalene dimers when θ is increased from 0° to 90° for any given value of D, such term for pyrene dimer does not decrease continuously with θ but shows a minimum around $\theta = 50°$. This behaviour is also noticed in the variation of the electrostatic energy. These trends are expected because pyrene has a sheet-like structure while naphthalene and anthracene are linear polynuclear hydrocarbons. It is important to mention that the above trends in the variation of electrostatic and π overlap repulsion terms which are quite dominant are also reflected in the total interaction potential of pyrene dimer which shows a minimum for θ in the region of 40° ~ 50° (Fig. 5). When the total energy is minimised with respect to the structural parameters (D, α, and θ) the possible equilibrium

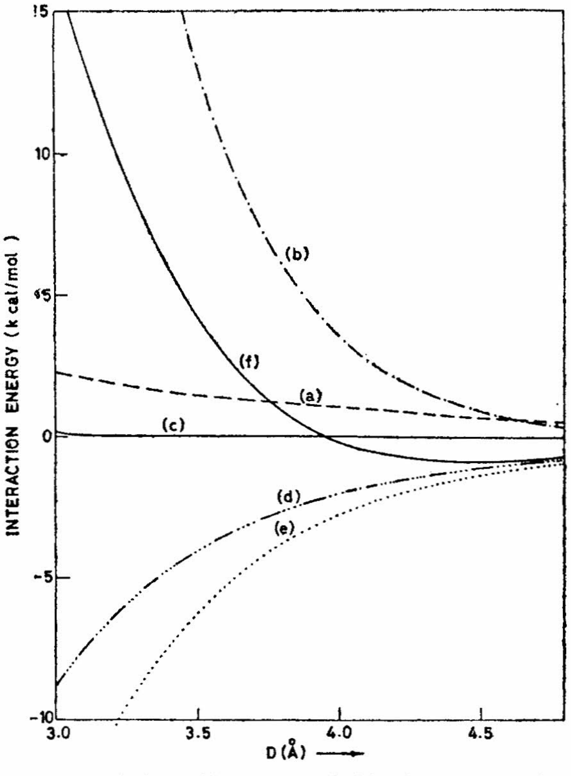

Fig. 2 — Variation with D(A°) of (a) the electrostatic, (b) the π-overlap repulsion (c) the non-bonded repulsion ($Z_H = 1.2$) (d) the π-π dispersion, (e) the σ-σ dispersion and (f) the total interaction energies in naphthalene dimmer of the perfect sandwich pair geometry

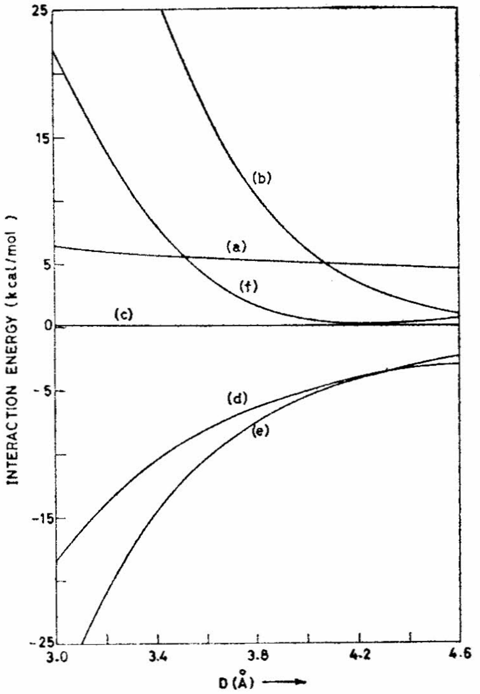

Fig. 3 — Variation with D(Å) of (a) the electrostatic, (b) the π-overlap repulsion, (c) the non-bonded repulsion, (d) the π-π dispersion, (e) the σ-σ dispersion and (f) the total interaction energies in pyrene dimer of the perfect sandwich-pair geometry

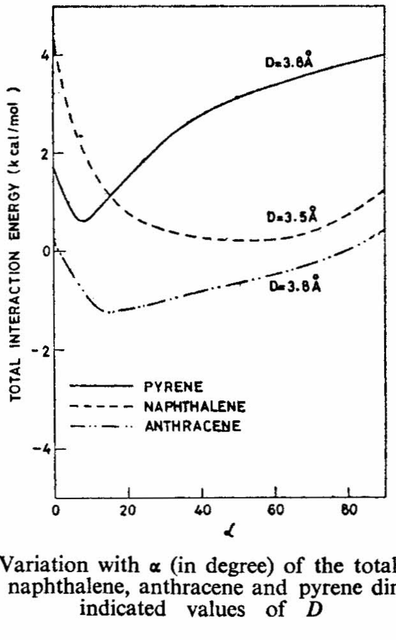

Fig. 4 — Variation with α (in degree) of the total interaction energies in naphthalene, anthracene and pyrene dimers for the indicated values of D

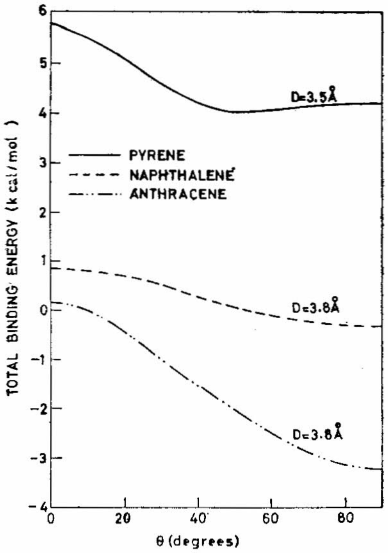

Fig. 5 — Variation with θ (in degree) of the total interaction energies in naphthalene, anthracene and pyrene dimers for the indicated values of D

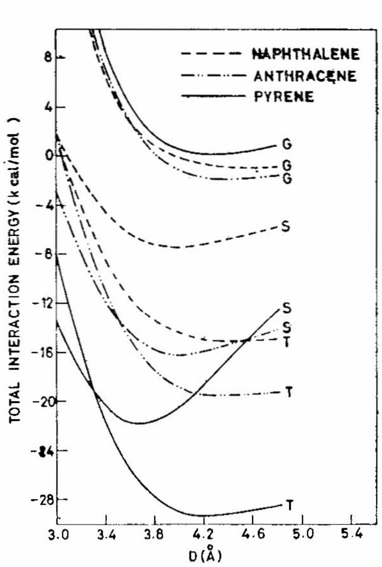

Fig. 6 — Variation with $D(\alpha = 0, \beta = 0)$ of the total interaction energy in the ground state (G), the excimer singlet state (S) and the excimer triplet state (T) of naphthalene, anthracene and pyrene dimers

conformations of the dimers are obtained. They are given in Table 1 along with their binding energies. Our conclusions regarding the ground state dimers are as follows : (i) The perfect sandwich configuration is not the stable configuration of the aromatic hydrocarbon dimers. If however the sandwich configuration is formed in a rigid medium it could change into a rotated form if the restraining matrix is allowed to soften; and (ii) anthracene and naphthalene could form weakly stable dimers while the pyrene dimer is metastable.

These conclusions are of very broad validity. Although Chandross *et al.*[14,15] from the spectral analysis concluded that anthracene forms a weak dimer of non-sandwich conformation, the structure of dimer they arrived at is different from the non-sandwich structure we have arrived at theoretically. This is because we have not examined theoretically the translated structure in which one molecule is displaced from the perfect sandwich arrangement maintaining C_{2h} symmetry as in pyrene crystal. The main point that emerges from this analysis is that the totally eclipsed sandwich structure of dimers cannot be the stable structure in view of very large intermolecular repulsion.

2.2. *Excimer potentials, excimer fluorescence and phosphorescence energies* — The interaction energies of excimers for the singlet and triplet states are obtained from equation 2 where the transition energies $\triangle E(^{1,3}\sigma)$ have been estimated for different steric conformations of excimers using a semi-empirical theory developed earlier[4] and employing the configuration interaction in the singlet and triplet manifolds respectively. In Fig. 6, is shown the plot of the total interaction energy vs D for the perfect sandwich structures of the singlet and triplet state excimers of naphthalene, anthracene and pyrene. The corresponding ground state interaction energies i.e. $\triangle E_G$ are also shown for comparision. The results show that the phenomenon of photo-association resulting in the formation of singlet excimers is generally accompanied by a decrease in the interplanar separation, normally expected in a ground state Vander Waal's dimer. These results also suggest that the triplet state of a monomer could be strongly bound with its ground state in a sandwich pair without any change in the intermolecular separation. It is quite significant to note that the singlet and triplet state excimers of pyrene have larger binding energies with well-defined minima in their excimer potentials than the excimers of naphthalene and anthracene, although the reverse order is noticed in the stability of their ground-state dimers.

We have examined other steric conformations of excimers. In Fig. 7 are shown the variations of the interaction potentials for the singlet and triplet excimers with the tilt angle α. The minima in Fig. 7 do not correspond to the equilibrium structures of excimers because the positions of the potential minima vary with D. The results for the rotated sandwich structures of excimers, presented in Fig. 8, reveal that while in the lowest excited singlet state, particularly for naphthalene and anthracene excimers, there is a small barrier for rotation of one monomer relative to the other, in the lowest triplet state the perfect sandwich form passes to the rotated structure without an energy barrier as in the ground dimer.

When the total interaction potentials for each excimer state are minimised with respect to the various structural parameters such as D, α, and θ (Fig. 1), the equilibrium steric conformations of the singlet and triplet state excimers are obtained. In Table 1 are given the probable equilibrium conformations of the singlet and triplet state excimers of naphthalene anthracene and pyrene, their binding energies, and the fluorescence and phosphorescence energies from their equilibrium structures observed in solution. The corresponding observed values,

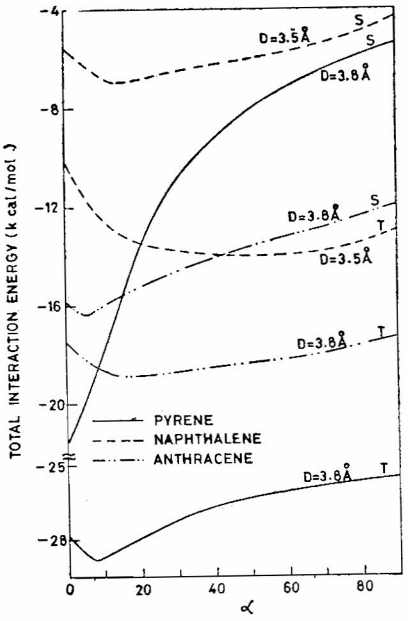

Fig. 7 — Variation with α (in degree) at the indicated values of D, of the total interaction energy in the singlet (S) and triplet (T) state excimers of naphthalene, anthracene and pyrene

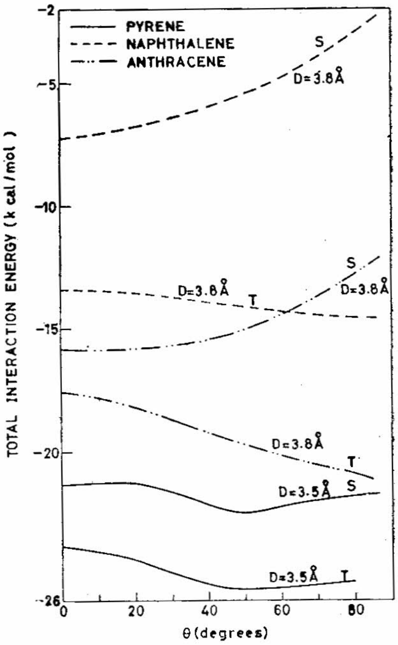

Fig. 8 — Variation with θ (in degree) at the indicated values of D, of the total interaction energy in the singlet (S) and triplet (T) state excimers of naphthalene, anthracene and pyrene

wherever available are also recorded in Table 1 for comparison. The agreement between the calculated and observed emission energies is reasonably satisfactory. The results of Table 1 reveal that the geometries of the triplet excimers of naphthalene and anthracene are distinctly different from the perfect sandwich pair conformation favoured by the corresponding singlet excimers while the singlet and triplet excimers of pyrene have almost similar steric conformations. The data in Table 1 further reveal that for all the systems, the ground dimers and the corresponding triplet excimers have nearly the identical steric conformations.

2.3. *Binding in singlet and triplet excimers* — Although the calculated binding energies of the singlet excimers do not agree satisfactorily with the observed values, they nevertheless predict the right trends in the stability of the different excimers. However, according to the results of Table 1 the triplet excimers have greater binding energies than the corresponding singlet excimers. This seems to be a quite an unusual result and does not explain the failures to observe the excimer phosphorescence in aromatic hydrocarbons.

Binding in excimers is essentially due to the exciton resonance and the charge resonance effects[21]. The wavefunction for the singlet state excimer of an aromatic hydrocarbon can be given by

$$\psi = a\,\psi_{\mathrm{ER}} + b\,\psi_{\mathrm{CR}} + \ldots \qquad \ldots (3)$$

where ψ_{ER} and ψ_{CR} are the wavefunctions for the exciton resonance and charge-resonance states, a and b are the mixing coefficients. Since the exciton resonance states refer predominantly to the ^1L_a state of the monomer, the relative stability of the hydrocarbon-excimers can be understood from the different degrees of mixing with their charge-resonance states. In Table 2 are given the values of the mixing coefficients a and b for the equilibrium structures of the singlet excimers of naphthalene, anthracene and pyrene. The increased stability of pyrene excimer over that of naphthalene and anthracene excimers is therefore due to the increased charge-transfer contribution. This seems quite reasonable because the difference between the ionisation potential and electron affinity i.e. I—A of pyrene is smaller than those of naphthalene and anthracene.

2.4. *Photo-dimers* — In some aromatic hydrocarbons, the excimer interaction leads to the formation of stable photo-dimer. Ferguson and Mau[22] reported that the excimer state is an intermediate in the photo-dimerisation reaction of anthracene. The fact that excimer fluorescence in anthracene is not readily observed is due to the rapid rate of photodimerisation. Hyashi *et al.*[23] found that for the perfect sandwich pair structure of anthracene, the activation energy for the photodimerisation is only 1 kcal/mol.

Photo-dimerisation of aromatic hydrocarbon is generally a 1, 4-addition process and has been observed for several anthracene and naphthalene derivatives[21]. The photo-dimer, dianthracene, is formed by a pair of covalent σ-bonds joining the *meso*-positions in the two molecules. The structure of such a photo-dimer shows that the perfect sandwich pair conformation of the two interacting molecules is the essential prerequisite. Our results in Table 1 therefore rule out the possibility of the triplet state excimer as an intermediate in the photo-dimerisation reaction of naphthalene and anthracene. The results of Table 1, however, suggest that neither the singlet nor the triplet excimers of pyrene has the favourable

TABLE 1 — POSSIBLE EQUILIBRIUM CONFORMATIONS, BINDING AND EMISSION ENERGIES

System	Ground dimers			Singlet excimers				Triplet excimer			
	Equilibrium conformation	Binding energy (kcal/mole)	Equilibrium conformation	Binding energy (kcal/mole)		Excimer fluorescence (eV)		Equilibrium conformation	Binding energy (kcal/mol)	Excimer Phosphorescence (eV)	
				Calc.	Obs.	Calc.	Obs.			Calc.	Obs.
Naphthalene	Rotated Sandwich $D = 4.3$Å, $\theta = 90°$, $\alpha = 0$	1.2	Symmetric sandwich $D = 4.0$A	7.4	5.8(a)	3.66	3.13(d)	Rotated Sandwich D = 4.3A, $\theta \simeq 85°$, $\alpha = 0$	15.0	2.03	2.3(g)
Anthracene	Rotated sandwich, $D = 3.9$Å, $\theta = 90°$, $\alpha = 0°$	3.2	Symmetric Sandwich D = 4.0A	16.0	8.0(b)	2.64	2.30(e)	Rotated Sandwich D = 3.9A, $\theta \simeq 85°$, $\alpha = 0$	21.0	1.06	—
Pyrene	Rotated metastable sandwith $D = 4.2$A $\theta = 40°$, $\alpha = 0$		Rotated Sandwich D = 3.6A, $\theta = 50°$, $\alpha = 0$	22.5	9.5(c)	2.56	2.59(f)	Rotated Sandwich D = 4.2A, $\theta = 40°$, $\alpha = 0$	29.0	0.81	1.7(h)

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TABLE 2 — CONFIGURATIONAL MIXING COEFFICIENTS, *a* AND *b*, FOR THE EQUILIBRIUM CONFORMATIONS OF THE SINGLET EXCIMERS

Singlet excimer	*a*	*b*
Naphthalene	0.9986	0.0511
Anthracene	0.9974	0.0702
Pyrene	0.9877	0.1578

structure for the formation of photo-dimer. A recent report[24] reveals that, unlike anthracene and naphthalene, pyrene does not form photo-dimer.

2.5 σ-π *interaction in excimers* — The problemof σ-π interaction and its role in enhancing the intensity of $T_1 \rightarrow S_0$ radiative transition of the naphthalene excimer have been discussed earlier by Chandra and Lim[11]. But, because of the large equilibrium separation between two momomers in excimers, the σ-π interaction can never be large and is unlikely to make any significant contribution to the energy. However, its role in the spectroscopy of excimers can not be ignored because the predominantly $|\pi\pi^*|$ configurations of the singlet and triplet excimers contaminate a small amount of the $|\sigma\pi^*|$ and $|\pi\sigma^*|$ configurations.Such mixing of configurations is responsible for the observed greater intensity of excimer phosphorescence[9,10] relative to the intensity of monomer phosphorescence even in very dilute solutions of naphthalene. Besides, the observation[25] of the sizeable out of-plane polarisation in the excimer fluorescence of a sandwich pair of anthracene, produced by the photolysis of dianthracene, is another effect which could be caused by the σ-π interaction in excimers. It has, indeed, been found that the out-of-plane polarisation in the excimer fluorescence of anthracene is greater than that found in the naphthalene excimer[26]. This is quite understandable, because the energy gap between the σ- and π-levels (Fig. 9) in both the filled and the unfilled bands of anthracene is smaller than that of naphthalene. This should lead to an increased contamination of the σ-π configurations in the predominantly π-electron configurational wave-functions of the anthracene excimer.

3. Conclusions

The following conclusions can be drawn from the results reported in this paper : (*a*) The perfect sandwich structures cannot be the stable configuration of the aromatic hydrocarbon dimers and the triplet excimers; (*b*) the singlet excimers of naphthalene and anthracene possess the symmetric sandwich structures while that of pyrene possesses the non-sandwich structure;, (*c*) the σ-π mixing in excimers is responsible not only for the observed intensity of excimer phosphorescence but also for the observed out-of-plane polarisation in the excimer fluorescence; and (*d*) the present approach is not satisfactory for the calculation of binding energies in the singlet and triplet excimers of aromatic hydrocarbon.

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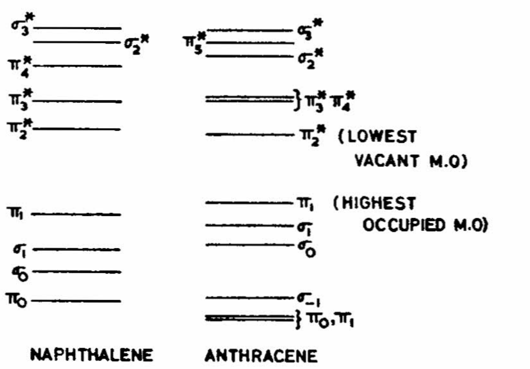

Fig. 9 — Positions, in the order of computed (CNDO) energy, of the highest and a few next-to-highest occupied molecular orbitals and the lowest and a few next-to lowest unoccupied orbitals of naphthalene and anthracene

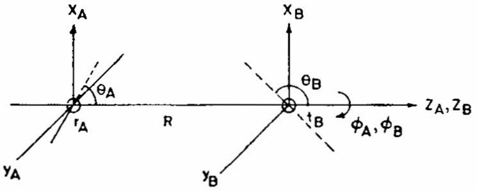

Fig. 10 — Relative orientations of two $2p$-orbitals (denoted by the dotted lines) centered on the atom r of the molecule A and on the atom t of the molecule B

360/44 Computer. One of the authors (A. K. C.) is grateful to Prof. E. C. Lim, Department of Chemistry, Wayne State University, Detroit, Michigan for many helpful discussions.

Appendix

Evaluation of intermolecular integrals — All intermolecular integrals can be expressed in terms of the linear combination of inter-atomic integrals.

The intermolecular atomic orbital overlap $\left\langle \varphi_{r,A} \mid \varphi_{t,B} \right\rangle$ is given by

$$\left\langle \varphi_{r,A} \mid \varphi_{t,B} \right\rangle = S_\pi \operatorname{Sin}\theta_A \operatorname{Sin}\theta_B \operatorname{Cos}(\phi_A - \phi_B) - S_\sigma \cos\theta_A \operatorname{Cos}\theta_B \qquad ..(A.1)$$

where S_π and S_σ are the π-π and σ-σ type of overlap between two $2p$ atomic orbitals φ_r and φ_t and are given by Parr and Crafword[27]. θ_A, θ_B, ϕ_A and ϕ_B define the orientations of the two $2p$-orbitals and are shown in Fig. 10 where the dotted lines through r_A and t_B indicate the axes of two $2p$-orbitals and R, the internuclear distance.

The two-centre intermolecular repulsion integral over the atomic orbitals are evaluated using the multipole expansion method of Parr[28].

$$\left\langle \varphi_{r,A}\, \varphi_{r,A} \mid \varphi_{t,B}\, \varphi_{t,B} \right\rangle = \frac{1}{R} + \frac{Q}{4R^3}[(3 \operatorname{Cos}^2 \theta_A - 1) + (3 \operatorname{Cos}^2 \theta_B - 1)] + \frac{3Q^2}{16R^5}[(1 - 5 \operatorname{Cos}^2 \theta_A - 5 \operatorname{Cos}^2 \theta_B - 15 \operatorname{Cos}^2\theta_A \operatorname{Cos}^2\theta_B) + 2 (\operatorname{Sin}\theta_A \operatorname{Sin}\theta_B \operatorname{Cos}(\phi_A - \phi_B) - 4 \operatorname{Cos}\theta_A \operatorname{Cos}\theta_B)^2] \qquad ..(A.2)$$

$$\text{where } Q = \frac{24}{Zc^2};\ Zc = 2.55 \qquad ...(A.3)$$

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