BINDING IN SINGLET- AND TRIPLET-STATE EXCIMERS

II. Role of Subjacent Orbital Interactions*

B. S. SUDHINDRA AND A. K. CHANDRA

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012

ABSTRACT

Theoretical studies on excimers have invariably been restricted to treating excimers as a four-electron problem and are unsatisfactory both with respect to accounting spectral characteristics, and geometry of snglet/triplet excimer. In a previous paper [*Mol. Phys.* 30, 319 (1975)], we have studied the possible geometries of singlet/triplet excimer, based on the 4-electron problem and concluded that the perfect sandwich structure is the most stable conformation for an excimer. In the present work, an excimer is treated as an $4n$-electron problem ($n = 2, 3$) and the results for naphthalene and anthracene systems indicate that singlet and triplet excimers can have different geometries. The role of subjacent orbitals is also discussed.

1. INTRODUCTION

AN excimer is a dimer, which is associated in an excited electronic state, and dissociative (*i.e.*, would dissociate in absence of external restraints) in its electronic ground state[1]. Collisional interaction between a singlet/triplet excited atom/molecule ($^{1,3}M^*$) and an unexcited atom/molecule ($^{1,3}M$).

$$^{1,3}M^* + {}^{1,3}M \rightleftharpoons {}^{1\ 3}D^*$$

may yield a singlet/triplet excimer. While much experimental data are available[1-3], a satisfactory theory to account for the spectral characteristics, differences in stability and geometry of singlet/triplet excimer is lacking. Theoretical studies have invariably been restricted to treating an excimer as a 4-electron problem[4-8]. In this work, we report the preliminary results of our efforts to extend 4-electron model to a $4n$-electron model ($n = 2, 3$), which takes into account not only the highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO) of each monomer, but also the next highest (occupied) and lower (unoccupied) molecular orbitals—the subjacent orbitals of each monomer. The importance of inclusion of subjacent orbitals has been shown by Berson and Salem[9], in their work on forbidden reactions, in Woodward-Hoffman's sense.

2. METHOD

We use the super-molecular-orbital theory[8], and the method is similar to our earlier work[10] (appendix, for some details on evaluation of integrals).

3. RESULTS AND DISCUSSION

In Fig. 1 is shown the dimer orbitals (in super-molecular-orbital approach) for naphthalene and anthracene excimer, in the $4n$-electron model, where dimer orbital $2k$ and $2k - 1$ belong to k^{th} parentage (of monomer). As regards geometry, we consider two cases :

(i) a perfect sandwich structure (D_{2h} symmetry).

(*ii*) a 'tilted' structure in which long axes of the molecules are parallel and short axes make an angle 'α'.

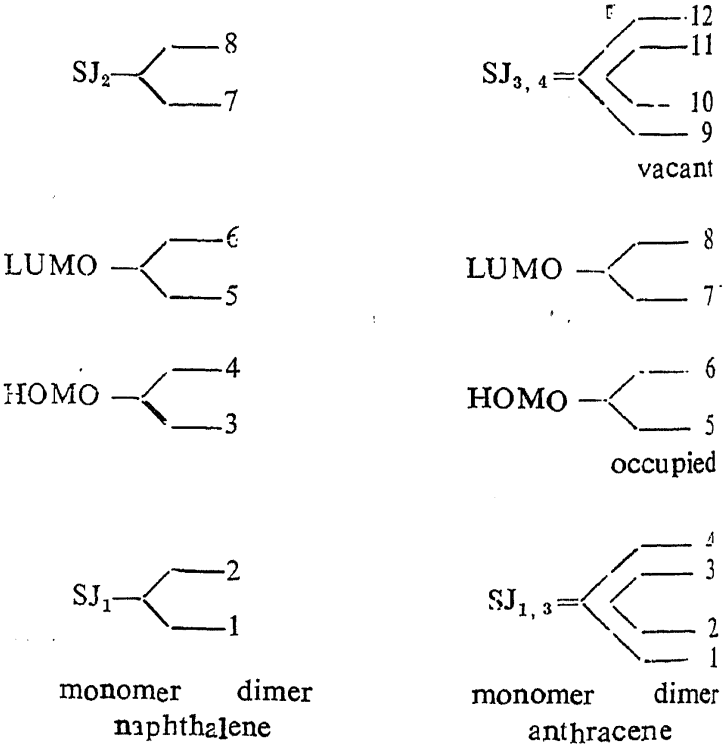

FIG. 1. Numbering (and parentage from monomer) of MO's in excimer of naphthalene and anthracene (schematic).

Note: $2k^{th}$ and $(2k-1)^{th}$ dimer orbitals belongs to k^{th} parentage (of monomer).

Primary motivation in considering these two types only is that, our previous experience[10] suggests that rotated sandwich structure is less stable when compared to sandwich structure. Moreover, Ferguson *et al.*[11] have clearly ruled out the possi-

* Presented in part, at the Seminar on 'Molecular Interactions', Department of Chemistry, Sri Venkateswara University, Tirupati 517 502 (A.P.), February 19–21 (1977).

bility of a rotated structure. Further, we wish to study theoretically, the possibility of singlet and triplet excimers having different structures. It is increasingly felt[12,13] that singlet and triplet excimer may have different steric configurations.

3.1. *Role of Subjacent Orbitals*

In Table I are given the coefficients for the various configurations [after configuration interaction (CI)] for the lowest excited state, in naphthalene excimer. It is clear that for the singlet state, the subjacent orbitals interaction is important, while for the triplet states, the HOMO/LUMO interaction is important. In Table II is shown the non-zero (and $> 0{\cdot}1$) coefficient of the various configurations (after CI) for the lowest excited state of anthracene excimer. It is obvious from a close analysis of the data that in the case of singlet state, HOMO/LUMO interaction is predominant, while for the triplet states, there is some contribution from subjacent orbitals [*i.e.*, transition from HOMO (and subjacent occupied MO) to vacant subjacent orbital]. We feel that in higher polyacenes excimers, say, pyrene, perylene, etc.; the 4-electron model may be sufficient for describing singlet excimers, while transitions from/to subjacent orbitals are important for describing triplet excimers.

3.2. *Stability of Singlet/Triplet Excimer*

Of the several low lying excimer states, we shall be concerned with only the lowest state, σ-state, the emitting state of excimer. To examine the stability of σ-state (singlet/triplet) of an excimer with respect to dissociation into a monomer ground and a monomer singlet/triplet states, we need to examine the differences between the energy. $E_{1,3\sigma}$ of the singlet/triplet σ-state of an excimer and the sum of $E_{,3p}$, the energy of the singlet/triplet p-state and E_M–the energy of ground state of the monomer. The interaction energy is given by

$$E_{1,3\sigma} - E_{1,3p} - E_M = {}^{1,3}\Delta E + y \qquad (1)$$

where

$${}^{1,3}\Delta E = E({}^{1,3}\sigma) - E({}^{1,3}p) \qquad (2)$$

and $E({}^{1,3}\sigma)$ and $E({}^{1,3}p)$ are the energies of singlet/triplet excimer σ, and the monomer p bands respectively. Both ${}^{1,3}\Delta E$ and 'y' are functions of the structural parameters in the dimer structure. In Table III is shown the binding energy of an excimer both in tilted and sandwich conformation

TABLE I

Coefficients of the various configurations, in the lowest excited state of naphthalene excimer. Pivotal distance $D = 3{\cdot}5$ *Å*

Tilt angle α		(*m*, *n*) 4, 5*	4, 7	3, 6	3, 8	2, 5	2, 7	1, 6	1, 8
0°	Singlet	0·0	−0·2940	0·0	−0·3803	0·4764	0·00	0·7362	0·0
	Triplet	0·6061	0·0	0·7836	0·0	0·0	0·0884	0·0	0·1041
40°	Singlet	0·0	−0·3702	0·0	−0·4035	0·5643	0·0	0·6178	0·0
	Triplet	0·6671	0·0	0·7321	0·0	0·0	0·0961	0·0	0·0989
70°	Singlet	0·0	−0·3983	0·0	−0·4197	0·5643	0·0	0·5888	0·0
	Triplet	0·6786	0·0	0·7214	0·0	0·0	0·0972	0·0	0·0981

* (*m*, *n*) indicates transition from m^{th} occupied dimer orbital to n^{th} vacant orbital. Similar is the behaviour for all D's and tilt angles.

TABLE II

Coefficients of the various configurations, in the lowest excited state of anthracene excimer, for privotal distance $D = 3{\cdot}2$ *Å*

Tilt angle (°)		(*m*, *n*) 6, 7[a]	5, 8	4, 9	3, 10[b]
0	Singlet	0·269	0·955	0·0	0·00
	Triplet	0·506	0·816	0·158	0·215
45	Singlet	0·522	0·837	0·0	0·0
	Triplet	0·619	0·732	0·183	0·202
90	Singlet	0·620	0·764	0·0	0·0
	Triplet	0·651	0·703	0·189	0·198

[a] (*m*, *n*) indicates the transition from m^{th} occupied dimer orbital to n^{th} vacant orbital.
[b] Only those configurations for which the coefficients are at least 0·1 are included in this table. Similar behaviour is noticed for other distances and tilt angles

TABLE III

Binding energies in naphthalene excimer (in eV)

Tilt angle α (°)	Tilted conformation				Pivotal distance D (Å)	Sandwich conformation (zero tilt angle)	
	Pivotal distance D (Å)						
	3·2		3·5				
	Singlet	Triplet	Singlet	Triplet		Singlet	Triplet
0	−0·401	−0·571	−0·707	−1·054	3·3	−0·5483	−0·851
10	−0·622	−0·964	−0·745	−1·123	3·4	−0·6451	−0·973
20	−0·654	−1·038	−0·724	−1·121	3·5	−0·7067	−1·054
30	−0·649	−1·057	−0·699	−1·109	3·6	−0·7432	−1·104
40	−0·639	−1·064	−0·677	−1·098	3·7	−0·7626	−1·134
50	−0·625	−1·060	−0·658	−1·088	3·8	−0·7702	−1·149
60	−0·605	−1·048	−0·630	−1·076	3·9	−0·7703	−1·155
70	−0·573	−1·022	−0·618	−1·061	4·0	−0·7655	−1·154
80	−0·521	−0·975	..	..	4·1	−0·7580	−1·150
90	−0·447	−0·903	..	..			

TABLE IV

Binding energies in anthracene excimer (in eV)

Pivotal distance D (Å) Tilt angle	Tilted conformation				Pivotal distance D(Å)	Sandwich conformation	
	3·2		3·5				
	Singlet	Triplet	Singlet	Triplet		Singlet	Triplet
0°	−0·0930	−0·3459	−0·4897	−0·9087	3·2	−0·0930	−0·346
10°	−0·4490	−0·7780	−0·6085	−1·0285	3·4	−0·418	−0·792
20°	−0·4407	−0·8817	−0·5614	−1·0114	3·5	−0·490	−0·909
30°	−0·4321	−0·9051	−0·4930	−0·9770	3·6	−0·526	−0·981
40°	−0·4150	−0·9090	−0·4395	−0·9505	3·7	−0·539	−1·022
50°	−0·3928	−0·9018	−0·3918	−0·9228	3·8	−0·538	−1·043
60°	−0·3558	−0·8817	−0·3635	−0·9125	3·9	−0·527	−1·047
70°	−0·3043	−0·8363	−0·3374	−0·9074	4·0	−0·512	−1·045
80°	−0·2224	−0·7624	−0·2645	−0·8575			
90°	−0·1055	−0·6525	+0·0390	−0·8110			

for different values of pivotal distances for naphthalene excimer. An examination of the data reveals that at lower values of 'D' it is the 'tilted' conformation that is stable while at larger values of 'D' (> 3·5 Å) it is the sandwich form that is stable. Similar results have been obtained for anthracene excimer also (Table IV). Further, for any given value of D (and α) triplet excimer is more stable than the singlet excimer. This result contradicts the experimental data[12]. The possible reasons for this discrepancy is under investigation. In this context, it is interesting to note the observation of Schweitzer *et al*[18], that the wavefunction in a singlet excited state is more diffuse than the wavefunction for the corresponding triplet state, which is rather contracted towards the nuclei. This result together with the increasing feeling that one must use different parameters for singlet and triplet states[19] may be a source for seeking an explanation for the observed differences in stability (and possibly structure) of singlet and triplet excimer. Another important factor, which has great influence on the calculations, is the choice of orbital exponent. In this and earlier works, a constant value of $Z = 3{\cdot}18$ has been employed for all distances. Different sets of values for

different distances could be expected to yield interesting results.

ACKNOWLEDGEMENTS

Authors thank the Central Instruments and Services Laboratory, Indian Institute of Science, for computer facilities. One of us (B. S. S.) thanks the Council of Scientific and Industrial Research (Government of India), for a post-doctoral fellowship.

APPENDIX

For the evaluation configuration interaction (CI) matrix elements, we follow the method of Pariser[14]. In the case of naphthalene excimer, the CI matrix is a 17 × 17 determinant, while for anthracene excimer, it is 37 × 37 (because we have a pair of degenerate subjacent orbitals in anthracene). The evaluation of the various inter- and intra-molecular integrals are as follows :

Integral	Over monomer	Intermolecular
Overlap	Parr and Crawford[15]	Parr and Crawford[15]
Coulomb/ exchange (with ZDO approximation)	Mataga and Nishimoto[16]	Parr's multipole[17] expansion
core	HMO	
H_{ij}	$E_i \ \delta_{ij}$	$-10{\cdot}0 \ S_{ij}$

Rest of the calculation/procedure is identical with our earlier work[10].

1. Birks, J. B., *Rep. Prog. Phys.*, 1975, 38, 903.
2. Gordon, M. and Ware, W. R., *The Exciplex*, Academic Press, N.Y., 1975.
3. Forster, Th., *Angew. Chem. Int. Edn. Engl.*, 1969, 8, 333.
4. Murrell, J. N. and Tanaka, J., *Mol. Phys.*, 1964, 4, 363.
5. Konijengerg, E., *Thesis*, Free University, Amsterdam, Holland, 1963.
6. (*a*) Azumi, T. and McGlynn, S. P., *J. Chem. Phys.*, 1964, 41, 3131.
(*b*) Azumi, T., Armstrong, A. T. and McGlynn, S. P., *Ibid.*, 1964, 41, 3839.
(*c*) — and McGlynn, S. P., *Ibid.*, 1965, 42, 1675.
7. — and Azumi, H., *Bull. Chem. Soc. Japan*, 1966, 39, 2317.
8. Chandra, A. K. and Lim, E. C., *J. Chem. Phys.*, 1968, 48, 2589 ; *Ibid.*, 1968, 49, 5066.
9. Berson, J. A. and Salem, L., *J. Am. Chem. Soc.*, 1972, 94, 8917.
10. Sudhindra, B. S. and Chandra, A. K., *Mol. Phys.*, 1975, 30, 319.
11. Ferguson, J., Morita, M. and Puza, M., *Chem. Phys. Lett.*, 1976, 42, 288, and references combined therein.
12. (*a*) Takemura, T., Aikawa, M., Baba, H. and Shindo, Y., *J. Am. Chem. Soc.*, 1976, 98, 2205.
(*b*) Aikawa, M., Takemura, T. and Baba, H., *Bull. Chem. Soc. Japan*, 1976, 49, 431.
13. (*a*) Subudhi, P. C., Kanamara, N. and Lim, E. C., *Chem. Phys. Lett.*, 1975, 32, 503.
(*b*) — and Lim, E. C., *Ibid.*, 1976, 44, 479.
14. Pariser, R., *J. Chem. Phys.*, 1956, 24, 250.
15. Parr, R. G. and Crawford, B. L. Jr., *Ibid.*, 1948, 16, 1049.
16. Mataga, N. and Nishimoto, K., *Z. Physik. Chem.* (Frankfurt), 1957, 12, 335 ; *Ibid.*, 13, 140.
17. Parr, R. G., *J. Chem. Phys.*, 1960, 33, 1184.
18. Schweitzer, D., Clopa, J. P., Behnke, J., Hausser, K. J., Heneel, H. and Staab, H. A., *Chem. Phys.*, 1975, 11, 373, and references therein.
19. (*a*) Zerner, M. C., *Theoret. Chem. Acta*, (*Berl.*), 1976, 42, 223.
(*b*) Gondo, Y. and Kanda, K., *Bull. Chem. Soc. Japan*, 1972, 45, 1612.

CHANGES IN SOLUBLE PROTEINS AND ISOENZYMES IN DEVELOPING SORGHUM GRAINS

R. P. JOHARI, S. L. MEHTA AND M. S. NAIK

Division of Biochemistry, Indian Agricultural Research Institute, New Delhi 110 012

ABSTRACT

Electrophoretic patterns of soluble proteins and isoenzymes of peroxidase and esterase showed qualitative and quantitative differences during grain development. The increase in the intensity of protein bands with low electrophoretic mobility at mature stage suggests synthesis of proteins with higher molecular weight.

INTRODUCTION

SOLUBLE proteins are the physiologically active fractions which constitute major bulk of enzymes involved in plant metabolism. Several workers have observed marked qualitative and quantitative changes in soluble proteins and isoenzyme patterns during grain development of wheat[1,2], maize[3] and barley[4]. The specificity of enzyme pattern implies a role of