

A THEORETICAL STUDY OF THE REACTION PATHWAY IN THE PHOTODIMERIZATION OF ANTHRACENE

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Abstract—The approximation proposed by Salem to calculate the interaction energy between conjugated systems has been used to obtain different potential surfaces for anthracene photodimerization in order to establish the reaction pathway.

INTRODUCTION

The photodimerization reaction of anthracene was first reported in 1866.¹ It is commonly accepted that the dimer is formed through the encounter of a molecule in its first singlet excited state with another in its ground state.^{2,3}

Crystal structure analysis of the photodimer of anthracene indicates that the two molecules are joined at the 9,10 positions⁴ (Fig 1). The dimer looks

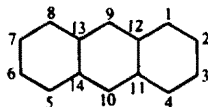


Fig 1. Anthracene center numbers.

like two butterflies facing each other. Each outer ring is bent around its meso axis at a 23° angle⁷ (Fig 2).

An argument based on free valence has been used to explain why the two molecules in the dimer are joined at the 9,10 positions. Results from MO calculations indicate that the free valence of C₉ and C₁₀, already large in the ground state, increases considerably in the first excited state.^{8,9} The energy required to distort each molecule in the formation

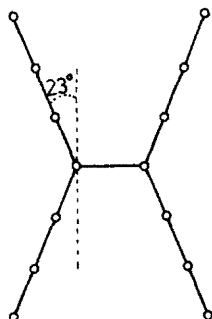


Fig 2. Dimer structure.

of the dimer has also been invoked to try to explain the experimental facts in the photodimerization of anthracene and its meso derivatives.¹⁰ Finally, calculations based on the delocalized model of the transition state have been found to be in qualitative agreement with the experimental results.¹¹ The butterfly shape of the outer rings in the transition state was taken into account by considering only the resonance integrals between meso atoms of the two molecules.

The experimental results are consistent with those predicted by the Woodward-Hoffmann rules^{12,13} for concerted reactions. In order to establish the reaction mechanism of a one step reaction, it is necessary to study the stereochemistry of the process. In this paper we will study the stereochemistry of the photodimerization of anthracene as the reaction progresses.

METHOD OF CALCULATION

The most favorable reaction pathway may be obtained from potential surfaces. Frequently the potential surface is calculated by computing the total energy of the systems for different positions of the reactants. A second way to calculate the potential surface is to evaluate directly the variation of energy, as the reaction is progressing, by means of a perturbation method. When the reactants are large molecules as is anthracene, perturbation method is the only feasible one for reasons of economy.

The calculations have been carried out using the approximation proposed by Salem.^{14,15} In this approximation the interaction energy between two conjugated molecules with overlapping p orbitals is described in terms of the π electrons of the separate systems. An analytical expression of the interaction energy is obtained as a function of the overlap between the atomic orbitals 2p_x of both molecules. Three main limitations are imposed. Both conjugated molecules are assumed to have

well separated bands of σ and π orbitals, the σ bonds acting only as a hard core which forbids too close an approach. Each atomic centre only interacts with one centre of the other molecule. And finally, the overlap integrals are small when compared with the unit.

The interaction energy between molecule in their ground state is given by the expression:

$$E_{int} = - \sum_{rr'} (q_r + q_{r'}) \eta_{rr'} S_{rr'} \\ - 2 \sum_r^{occ} \sum_{r'}^{unocc} \left[\frac{\left(\sum_{rr'} c_{kr} c_{k'r'} \eta_{rr'} \right)^2}{E_k - E_{k'}} \right. \\ \left. + \frac{1}{2} (E_k - E_{k'}) \left(\sum_{rr'} c_{kr} c_{k'r'} S_{rr'} \right)^2 \right] \\ - 2 \sum_r^{occ} \sum_{r'}^{unocc} \left[\frac{\left(\sum_{rr'} c_{kr} c_{j'r'} \eta_{rr'} \right)^2}{E_k - E_{j'}} \right. \\ \left. + \frac{1}{2} (E_k - E_{j'}) \left(\sum_{rr'} c_{kr} c_{j'r'} S_{rr'} \right)^2 \right] \quad (1)$$

And the interaction energy E_{int}^* between the excited conjugated molecule and an identical partner in its ground state is $E_{int}^* = E_{int} + \Delta E_{int}$, being:

$$\Delta E_{int}^{(j-k)} = - \left(\left| \sum_{rr'} c_{kr} c_{j'r'} \eta_{rr'} \right| \right. \\ \left. + \left| \sum_{rr'} c_{kr} c_{k'r'} \eta_{rr'} \right| \right) \\ + \sum_{rr'} (c_{jr}^2 - c_{kr}^2) \eta_{rr'} S_{rr'} \\ + \sum_{all(\sigma)j} \left[\frac{\left(\sum_{rr'} c_{kr} c_{j'r'} \eta_{rr'} \right)^2}{E_j - E_k} \right. \\ \left. + \frac{1}{2} (E_j - E_k) \left(\sum_{rr'} c_{kr} c_{j'r'} S_{rr'} \right)^2 \right] \\ - \sum_{all(\sigma)k} \left[\frac{\left(\sum_{rr'} c_{kr} c_{j'r'} \eta_{rr'} \right)^2}{E_j - E_k} \right. \\ \left. + \frac{1}{2} (E_j - E_k) \left(\sum_{rr'} c_{kr} c_{j'r'} S_{rr'} \right)^2 \right] \quad (2)$$

In both expressions $\eta_{rr'}$ is taken as proportional to $S_{rr'}$.

These analytical expressions of the interaction energy allow an easy evaluation of the reaction surface as a function of parameters connected with the reaction coordinate. Overlap integrals are calculated using equations suggested by Roothaan.¹⁶

Reaction paths are drawn in units of β starting from a parallel position of both molecules at great distances from each other and perpendicular to the isoenergetic lines in the direction of the gradient to higher interaction energies. This path corresponds to the maximum stabilization.

It must be remarked that the reaction surfaces employed are simplified potential surfaces, lacking chiefly the σ interaction and the electrostatic interaction, since the Hamiltonian is an effective one-electron Hamiltonian.

RESULTS AND DISCUSSION

The analytical expression of the interaction energy in the photodimerization of anthracene includes first and second order terms in overlap which are given by equations (1) and (2). The eigenvalues and eigenfunctions of anthracene π electrons are taken from Huckel molecular orbitals of Heilbronner-Straub.¹⁷ It is assumed that each atomic centre only interacts with an identical partner of the other molecule, S_r being the overlap between the atomic orbitals $2p_z$ of r centers of both molecules. Table 1 presents the coefficients of the different terms.

At large distances, the terms of the first order will be predominant. Among these, those which affect the 9 and 10 centers have the highest coefficients, owing to the high coefficients of the frontier orbitals in these positions. For this reason, the rate at which the newly forming bonds are established will be higher at the 9 and 10 positions than at other positions. Nevertheless, it is necessary to carry out a quantitative computation of interaction energy in order to reach a definitive conclusion.

The parameters chosen to study the reaction coordinate were the angle between facing planes bent around different axes, and the distance between respective anthracene axes. Given the loss of planarity of both conjugated systems, the method adopted can be applied only if the molecular distortion is small. In the present study the maximum angle considered of each outer ring outside of the planarity is 15° .

Fig 3 presents the interaction energy surface when the anthracenes are bent around the 9-10 axes. The most favourable pathway shows that, after an initial approach of facing outer rings (negative angles), both are bent in opposite directions (positive angles). As the reaction advances, a strong repulsive barrier forces the butterfly shape of both anthracenes to increase. Fig 4 presents the interaction energy surface when the anthracenes are bent around the 1-4 axes while Fig 5 shows the interaction energy surface when they turn around the 2-3 axes. The pathway is unfavourable in both instances, with the most stable position at an angle of about 3° at 3.3 Å. It must be remembered that the repulsive σ interaction is not taken into account in

Table 1. Interaction energy in the photodimerization of anthracene

		First order terms in overlapping						Second order terms in overlapping										
		S ₅	S ₄	S ₃	S ₂	S ₆	S ₇	S ₈	S ₆	S ₅	S ₄	S ₃	S ₂	S ₁₀	S ₁₁	S ₁₂	S ₁₃	S ₁₄
S ₁	0.58													1.16	0.05	0.05	0.05	0.05
S ₂	-3.46													-0.79	-0.09	-2.37	-0.14	0.05
S ₃	-1.47													-0.32	-0.95	0.18	-0.07	-0.16
S ₄														-0.40	0.17	-0.96	-0.14	0.05
S ₅														-0.26	-2.34	-0.06	0.04	-0.15
S ₆														-0.13	0.02	0.02	-0.09	-2.32
S ₇														-0.46	-0.08	-0.16	-0.91	0.21
S ₈														-0.47	-0.17	-0.07	0.20	-0.90
S ₉														-0.46	0.07	0.18	-2.30	-0.10
S ₁₀														-1.05	0.14	-2.41	-2.41	0.14
S ₁₁														-2.65	-2.41	0.14	0.14	-2.41
S ₁₂														-1.13	-2.41	-1.62	-0.43	0.09
S ₁₃														-1.13	-2.17	-2.17	0.08	-0.44
S ₁₄														-1.13	-2.17	-2.17	-2.17	-1.62

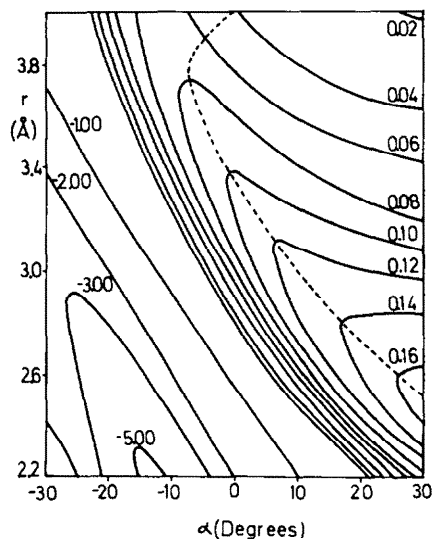


Fig 3. Interaction energy surface between two anthracenes: r is the distance between the 9-10 axes; α is the angle between facing planes.

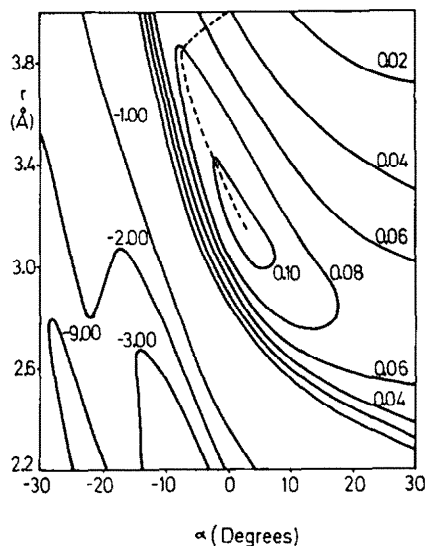


Fig 4. Interaction energy surface between two anthracenes: r is the distance between the 1-4 axes; α is angle between facing planes.

calculating the interaction energy. On the other hand, given the apolar nature of anthracene molecules, the electrostatic effect will be small.

The theoretical pathway of anthracene photodimerization agrees with the experimental angle of 46° between facing outer rings of the final dimer.⁷ It also agrees with one of two proposed mechanisms for the photodimerization in single crystals of anthracene from crystallographic data, the particular mechanism depending on the geometry of the sur-

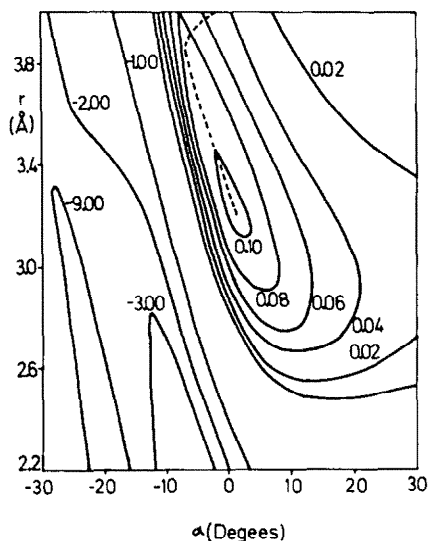


Fig 5. Interaction energy surface between two anthracenes: r is the distance between the 2-3 axes; α is the angle between facing planes.

face where the dimerization begins.¹⁸ The present kinetic investigation supports the aforementioned theoretical studies involving the energy required to distort each molecule¹⁰ and using a transition state model delocalized across the meso carbons,¹¹ in explaining the experimental facts in the photodimerization of anthracene meso derivatives. It may be concluded that, in spite of the simplicity of the method employed, it seems to be adequate in the study of the theoretical pathway of anthracene photodimerization.

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