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A QUANTUM MECHANICAL STUDY OF THE PHOTODIMERIZATION OF ANTHRACENE AND ITS DERIVATIVES

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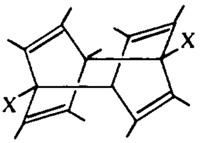
Abstract—Calculations based on the delocalized model of the transition state have been found to be in qualitative accord with the experimental results of the photodimerization of anthracene and its derivatives.

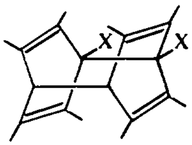
INTRODUCTION

THE PHOTODIMERIZATION reaction of anthracene was first reported in 1866.[1] A systematic study of this reaction has only recently been undertaken principally by Calas, Lalande, Bouas-Laurent *et al.*[2–17] They have extensively studied the effect of substituents, particularly in the 9,10 positions, on the photodimerization and have found the following facts:

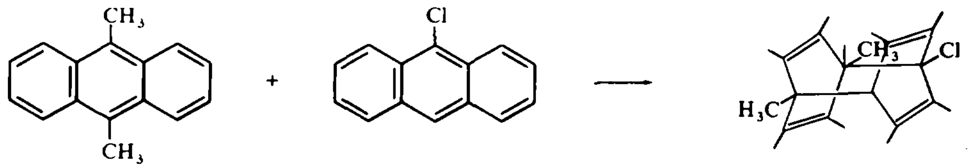
(1) Substitution in the 9,10 positions retards the rate of photodimerization compared to anthracene.[2–5]
(2) A 9,10 non-identically disubstituted anthracene will photodimerize[4, 14–17] whereas an anthracene with identical substituents in the 9,10 positions will not.[5, 18–20]
(3) The structure of the photodimer indicates that the two molecules are joined at the 9,10 position.[2]
(4) For 9-substituted and 9,10 non-identical disubstituted anthracenes two structures of the dimer are possible; one a head-to-head or *cis*, and the other a head-to-tail or *trans* structure. The head-to-tail structure (I) has been established as the correct one.[6]



I



(5) The photodimerization of a mixture of anthracene derivatives leads preferentially to mixed photodimers.[21–24] Thus the photoreaction of 9,10-dimethylanthracene and 9-chloroanthracene forms 9′-chloro-9,10-dimethyl dianthracene (II).
(6) It is commonly accepted that the dimer is formed by the encounter of a molecule in its first excited state with another in its ground state.[18, 19, 25, 26]



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The traditional explanations of organic chemistry based upon steric, resonance and inductive effects have so far failed adequately to explain these experimental results. Explanations based upon quantum mechanical calculations have fared only slightly better.

An argument based upon free valence has been used to explain why the two molecules in the dimer are joined at the 9,10 positions.[27] An approach based upon the difference of charge on the carbon atoms in the 9,10 position has been correlated to the photoreactivity in some examples.[28] The energy required to distort each molecule in the formation of the dimer[29] has recently been invoked to try to explain the experimental facts.

In this paper we will examine the application of the delocalized model of the transition state,[30] to the problem of the dimerization of anthracene and its derivatives.

CALCULATION AND CHOICE OF PARAMETERS

The calculations based on the delocalized model of the transition state were carried out according to the method previously described.[30, 31] Let us discuss the conditions where this method may be applied to intermolecular cycloadditions of conjugated systems.

Both conjugated molecules are assumed to have well-separated bands of σ and π orbitals. For the entire activated complex each molecular plane is no longer a symmetry element. Nevertheless at a large intermolecular distance, Hamiltonian operator will be only slightly different from the original on each molecule, and the overlap between peripheric π orbitals of the two molecules will be only appreciable. The wave function of the transition state may be built out of intermolecular orbitals covering the entire system for the π electrons of the two molecules. The σ electrons on each molecule act only as a hard core which forbids too close an approach. The extension of the Hückel method to the whole delocalized electron system is found in an orbital overlap argument and not in a symmetry one. It may be done because the notion of delocalized bond does not include any symmetry elements. In the framework of perturbation theory, this way of studying the photodimerization of two conjugated molecules has been used previously.[32, 33] Salem introduced a crucial assumption concerning the atomic orbital overlap integrals.[33] All are taken to be small compared with unity (*i.e.*, $\leq 0{\cdot}2$). This condition is fulfilled up to distances of 2·5 Å. To those distances the atomic 2p orbitals, which are sticking out from each molecule, overlap only slightly when the molecules come together with their planes roughly parallel.

The results of the present calculations are given in terms of the delocalization energy ΔE^*. This is the difference in energy, in units of β, between the transition state containing the whole delocalized system in its first excited state and the initial state of two molecules of anthracene derivatives, one in its ground state and the other in its first excited state. The larger the value of ΔE^*, the lower in energy is the transition state for formation of the photodimer. Again the simple Hückel method was used since it does not require precise knowledge of the geometry of the transition state. The resonance integrals for the bonds being formed between the two molecules in the transition state are assumed to be equal to 0·5 β. This value corresponds to "σ"-type overlap of 0·125 between two carbon 2p orbitals with atoms 3 Å apart. This distance is common for all charge transfer complexes, fundamentally stabilized by the same phenomena of electronic delocalization. The butterfly shape of the outer rings in the transition state is taken into account by considering only the resonance integrals between meso atoms of the two molecules. Because of this slight distortion in the transition state, the resonance integrals around a meso atom should be reduced. Nevertheless this effect has been neglected because of our lack of precise knowledge of the transition state geometry.

A variety of different parameters have been suggested to take into account heteroatoms in the simple Hückel method.[34] Rather than use a fixed value for a given heteroatom, we have chosen to study the effect on ΔE^* of varying the value of h in the coulomb integral α_x and k of the resonance integral β_x between the heteratom substituent and the adjacent carbon atoms at the 9,10 positions of anthracene. The purpose of this method is twofold. Firstly it ensures that the parameters chosen are not a unique set which provides good agreement between the theoretical and experimental results. Secondly it makes it possible to see trends in the values of ΔE^* as the nature of the substituent is changed. This technique has been used successfully in explaining the effects of substituents on the photo-oxidation of anthracene[31] whose similarity to the photodimerization has been emphasized.[2,3,5,12] To represent a heteroatom which is an electron donor, two electrons are added to the anthracene system and the values of h vary from 0 to +3. To represent an electron acceptor, no electrons are added to the anthracene system and the values of h_x vary from 0 to −3. The value of k was taken equal to 0·4, 1·0 and 1·3 for 9-monosubstituted anthracenes and equal to 1·0 for the 9,10-disubstituted anthracenes.

RESULTS AND DISCUSSION

The variation of ΔE^* with the change in the parameters h_x and k_{cx} for anthracenes containing an electron donor substituent in the 9-position is illustrated in Figs 1 and 2 for the transition states leading to the *trans* and *cis* dimers respectively. These plots show that the value of ΔE^* for all 9-substituted anthracenes is less than that for anthracene. Qualitatively this means that the rate of formation of these dimers would be slower than the rate of formation of the dimer of anthracene in agreement with the observed experimental results. Similar variations of ΔE^* with change in the parameters h_x and k_{cx} are obtained for anthracenes containing an electron withdrawing substituent in the 9-position.

Figs 3 and 4 illustrate the variation of ΔE^* with change in the parameters h_x for one of the two substituents of an unsymmetrically 9,10-disubstituted anthracene. The parameters of the other substituent have been kept constant at $h_x = 2·0$ and $k_{cx} = 1·0$. Again a slower rate of dimerization is predicted for the unsymmetrically 9,10-disubstituted anthracene than for anthracene which is in accord with experimental results. A similar plot for the dimerization of anthracenes containing identical substituents

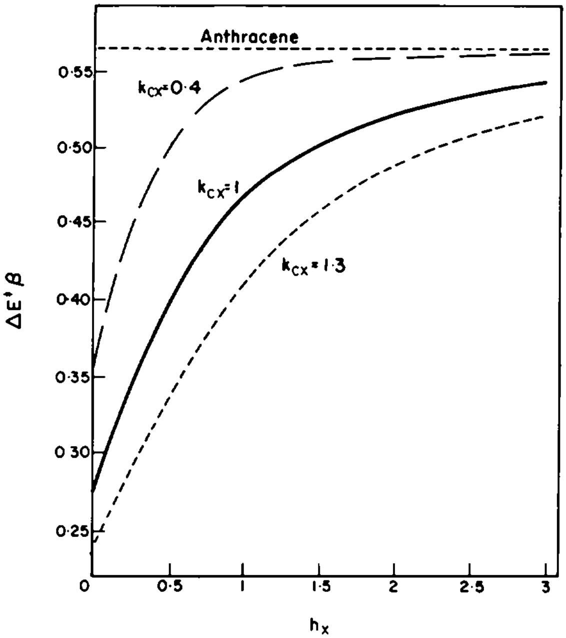

FIG 1 The effect on ΔE^{*} of variations of h_x and k_{cx} in the Coulomb integral α_x and the Resonance integral β_x respectively for the photodimerization of 9-X-anthracene leading to the *trans* isomer.

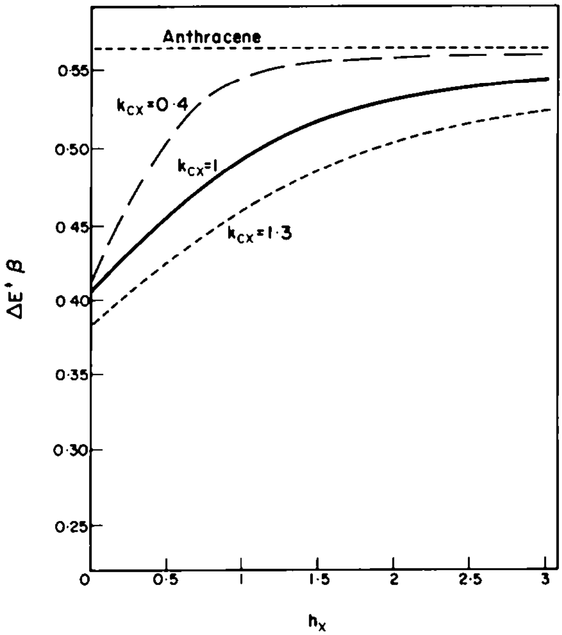

FIG 2 The effect on ΔE^{*} of variations of h_x and k_{cx} in the Coulomb integral α_x and the Resonance integral β_x respectively for the photodimerization of 9-X-anthracene leading to the *cis* isomer.

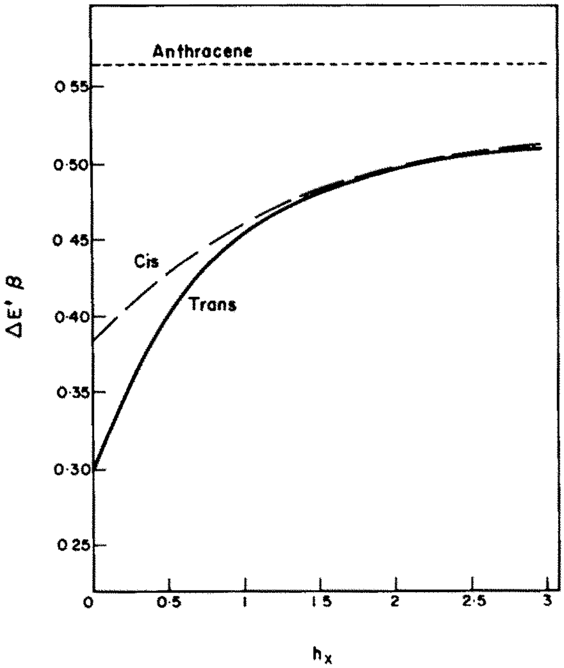

FIG 3 The effect on ΔE^* of variations of h_x in the Coulomb integral α_x of one substituent for the photodimerization of an unsymmetrically 9,10-disubstituted anthracene (h_x for the other substituent kept constant at 2·0; k_{cx} = 1·0).

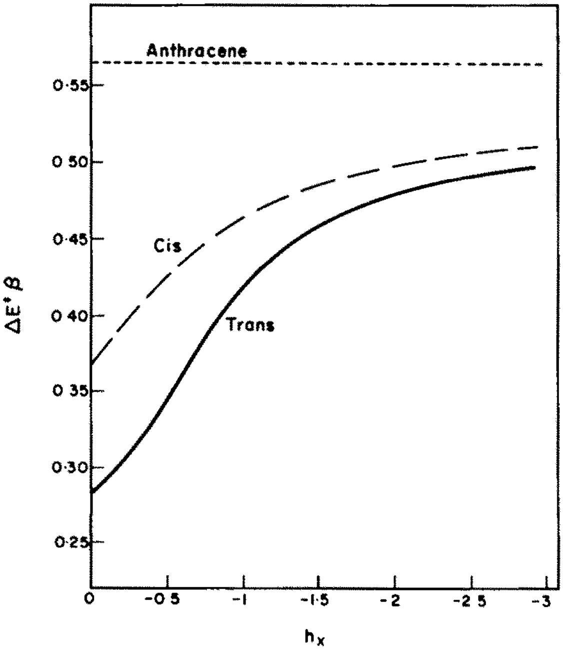

FIG 4 The effect on ΔE^* of variations of h_x in the Coulomb integral α_x of one substituent for the photodimerization of an unsymmetrically 9,10-disubstituted anthracene (h_x for the other substituent kept constant at 2·0; k_{cx} = 1·0).

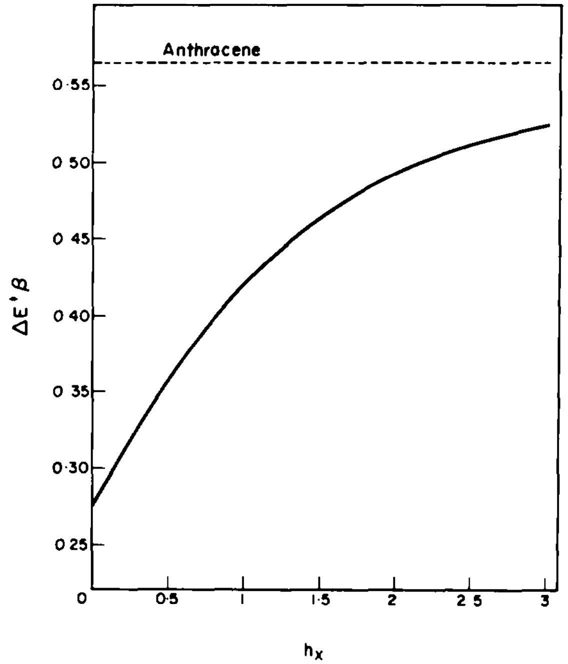

FIG 5 The effect on ΔE* of variations of h_x in the Coulomb integral α_x for the photodimerization of a symmetrically 9,10-disubstituted anthracene (k_{cx} = 1·0).

in the 9,10 positions is shown in Fig. 5. Again, the values of $\Delta E^{\neq}$ predict that the symmetrically disubstituted anthracene will dimerize slower than anthracene. However the numerical values of $\Delta E^{\neq}$ for any value of h_x in Fig. 5 are not very different from those in Figs 1, 2, 3 and 4. Yet experimentally it is known that symmetrically 9,10-disubstituted anthracenes do not dimerize while monosubstituted and unsymmetrically 9,10-disubstituted anthracenes do dimerize. Clearly the data in Fig. 5 are incapable of explaining this experimental fact.

According to the data in Figs 1, 2, 3 and 4, the value of $\Delta E^{\neq}$ for the transition state leading to formation of the dimer with the *cis* structure is larger than that for the *trans* isomer. Thus these calculations predict that the *cis* isomer should be formed preferentially contrary to experimental fact. However these calculations do not take into account the change in the electrostatic interaction between the reacting molecules. This is particularly important when comparing the photodimerization of anthracene and its 9-mono and 9,10-disubstituted derivatives. In the case of the dimerization of anthracene the charge at each carbon atom is zero in both the ground and excited states and consequently the electrostatic interaction is zero. The same is not true for 9-substituted anthracenes as can be seen from Fig. 6 which plots the calculated electrostatic interaction when both molecules are 3 Å apart versus h_x. The data in this figure are calculated by means of equation 1.

$$E = \sum_{r=1}^{\text{all centers}} \sum_{r'=1}^{\text{all centers}} \frac{q_r q_{r'}}{R_{rr'}} \tag{1}$$

where R is the distance between the centers r and r' on different molecules and q is the effective charge on each center. In the transition state leading to the *cis* isomer a strong electrostatic repulsion is present while in the transition state leading to the *trans* isomer an electrostatic attraction, or a small repulsion, is present. It is interesting to note that the major contributor to the electrostatic effect is due to the charge on the *substituents* in the 9 position, not the charge on the 9 carbon atom. The reason for this is that an electron donor substituent becomes a better donor (and consequently more positive) in the excited state while an electron acceptor substituent becomes a better acceptor (and consequently more negative) in the excited state.[36] As a result the *trans* orientation is the more favourable in terms of electrostatic repulsions. The interaction between the charges on the 9 carbon atom is less important because the charge on these two carbon atoms is reduced in the excited state.

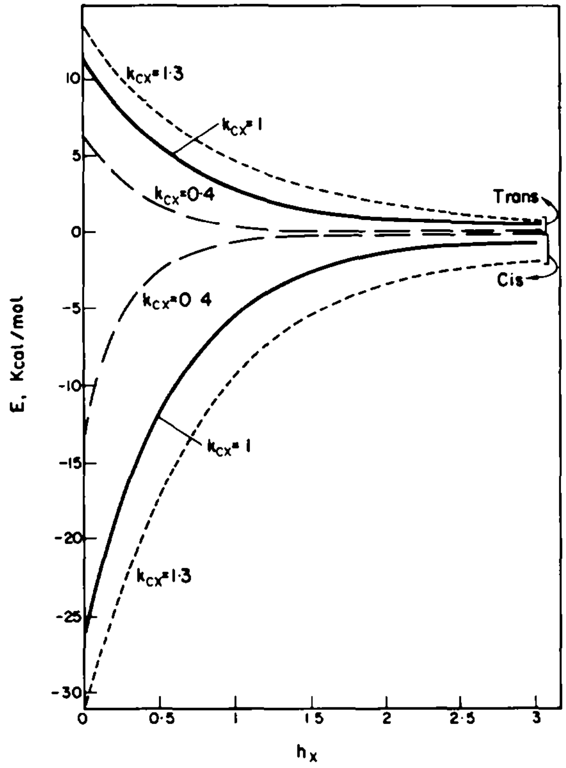

FIG 6 Variation of electrostatic interation with changing h_x for the photodimerization of 9-X-anthracene.

From our qualitative calculations it is impossible to determine the relative importance of the electrostatic interaction versus electron delocalization. However in the case of symmetrically disubstituted anthracenes where the unfavourable electrostatic interactions cannot be minimized by adopting a *trans* configuration, photodimerization should be greatly retarded. Experimentally it is found never to occur. Thus it appears that the electrostatic interaction between the substituents in the 9,10 positions of one molecule in the ground and the other in the excited states do play an important role.

Finally some remark concerning the contribution of σ electrons of the two molecules to the core repulsive wall. The effect will be different in the potential barrier leading to the *cis* and *trans* isomers. The repulsive wall will be higher in the transition state leading to the *cis* isomer than in one leading to the *trans* isomer. The repulsion between dipoles of localized bonds, unchanged by $\pi \rightarrow \pi^*$ electronic transition, will be high in the transition state leading to *cis* isomer. On the other hand the repulsive interaction between non-bonded atoms will be also higher in the transition state leading to *cis* isomer.

The calculated delocalization energies for the photoreaction of a mixture of a 9,10-symmetrical, disubstituted anthracene with 9,10-dihydroxyanthracene is illustrated in Figs 7 and 8. In Fig. 7 is illustrated the results with electron donor substituents while Fig. 8 illustrates the case with electron acceptor substituents. For each substituent two values of ΔE^* are possible depending upon which molecule is considered to be in the excited state. In Figs 7 and 8, the dashed line represents the values of ΔE^* for the reaction when the dihydroxyanthracene is in the excited state and di-x-anthracene is in the ground state while the solid line represents the opposite case. The lines in Fig. 7 cross at $h_x = 2{\cdot}0$ since this is the value taken to represent the OH group. From the data in Figs 7 and 8, it is clear that the formation of a mixed dimer is especially favoured. This is so when the substituent x falls within the range $h_x = -2$ to $+1{\cdot}5$. This corresponds to a range of substituent from NO_2 to Cl. Thus the reaction of 9,10-dihydroxyanthracene with such symmetrically disubstituted anthracenes is predicted to result in the preferred formation of the mixed dimer in accord with experimental fact.[24, 27]

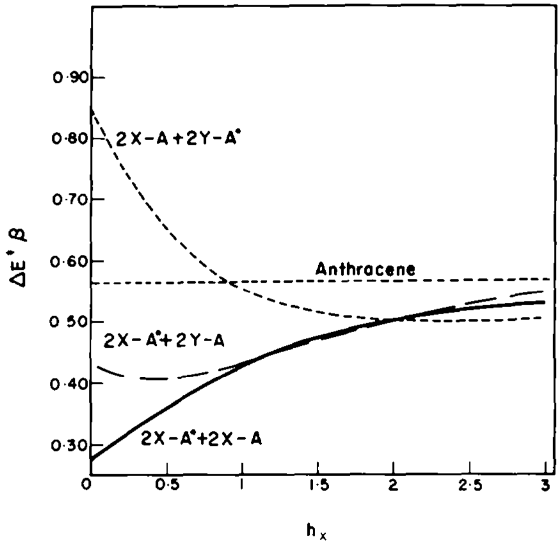

FIG 7 The effect on ΔE^* of variations of h_x in the Coulomb integral α_x of symmetrically 9,10-disubstituted anthracene in its photoreaction with 9,10-dihydroxyanthracene.

The model employed in these calculations represents a transition state near the initial state in which little bond formation between the two molecules has occurred.

The qualitative accord between the calculated values of ΔE^{*} and the experimental results indicate that this model is a good representation of the transition state for the photodimerization of anthracene and its derivatives.

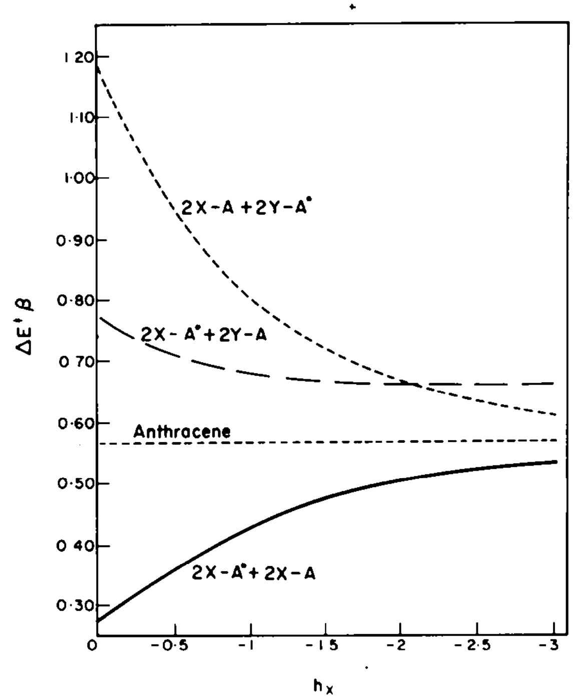

FIG 8. The effect on $\Delta E^{\ddagger}$ of variations of h_X in the Coulomb integral α_X of symmetrically 9,1 - disubstituted anthracene in its photoreaction with 9,10-dihydroxyanthracene.

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