Theoretical Study of Excimers in Crystals of Flexible Conjugated Molecules. Excimer Formation and Photodimerization in Crystalline 1,4-Diphenylbutadiene

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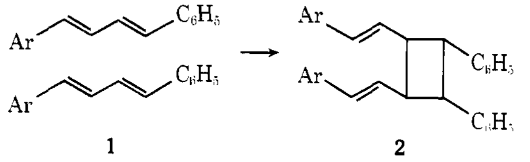
Abstract: A method for theoretical study of excimers in crystals of flexible conjugated molecules is presented. The method provides analytical potential surfaces which include the π electron surfaces, the hard core interaction between the σ electrons, and the crystal potential. The equilibrium geometry of a crystalline excimer is evaluated by complete minimization of its energy with respect to all the independent degrees of freedom. The method is applied to the study of the excimer formation step in the photodimerization of crystalline 1-(2,6-dichlorophenyl)4-phenylbutadiene. It is found that the close approach of the two monomers in the excimer state results in a considerable intramolecular deformation relative to the ground state dimer. It is also found that the intra- and intermolecular nonbonded interactions play an important role in determining the equilibrium geometries of such flexible nonplanar excimers. The possible existence of a preferred direction for the photodimerization in the crystal is examined by simulating the process of excimer formation. It is concluded that the crystal forces induce asymmetry in the process of relaxation of an excited monomer into the excimer state. The preferred direction for the excimer formation and hence for the subsequent photodimerization is predicted.

I. Introduction

The theoretical analysis of solid state reactions has the very important advantage over solution and gas-phase reactions in that the initial geometry of the system is uniquely defined, and the path of the reaction is largely restricted by the crystal forces. The knowledge of the initial geometry and the spatial restriction on the reaction path may provide important information on the reaction mechanism. One of the most studied examples of crystal effects on chemical reactivity is the solid state photodimerization of flexible molecules. In this type of reaction the study of the molecular deformation which takes place as the molecules move toward each other can throw light on the type of molecular interaction which is responsible for the passage from the pair of excited and ground state monomers to the ground state dimer.[2a] A well characterized intermediate in the path of photodimerization is the excimer species.[2b] In this work we study the geometrical relaxation process involved in the formation of the excimer state.

The study of excimer formation and photodimerization of flexible conjugated molecules requires a method which enables one to minimize the energy with respect to all independent coordinates. A complete minimization is important as the interplay between different degrees of freedom provides many possibilities for energy relaxation which cannot be investigated by simple mapping methods. Since we deal with solid-state reactions, it is essential to incorporate the crystal field into the calculations. Here we present a theoretical approach which allows for the detailed study of excimer formation in crystals of flexible conjugated molecules. The method provides realistic potential surfaces which include the effects of the π electrons, the hard-core repulsion of the σ electrons, and the crystal forces. The potential surfaces and its derivatives are given in an analytical form, so that it is possible to apply efficient minimization techniques for evaluating the minimum in the multidimensional surface. The method is applied here to the study of excimer formation of crystalline 1,4-diphenylbutadiene.

While α,ω-diphenyl all-trans polyenes are photoreactive in solution they are all light stable in the crystal.[3] However, substituted molecules of this series which crystallize in a structure with a short unit-cell axis (4 Å) have been found to display excimer emission and to undergo photodimerization in the solid (affording the topochemically expected mirror dimer),[3] thus indicating that the spectroscopic and photochemical properties of solid polyenes may be determined by their crystal structures. Here we present a theoretical study of excimer formation in crystalline 1-(2,6-dichlorophenyl)-4-phenyl-*trans,trans*-1,3-butadiene (**1**)



1 2

Ar = 2,6-$C_6H_3Cl_2$

which belongs to the category of 4 Å compounds and undergoes photodimerization yielding a single mirror-symmetric cyclobutane (**2**).[3]

The substituted butadiene **1** crystallizes in a space group $P2_12_12_1$ with a = 9.39 Å, b = 4.03 Å, c = 35.31 Å, and z = 4. The X-ray analysis of **1**[4] has shown that the molecule is heavily distorted from planarity; this must be due to combined effects of intra- and intermolecular forces.

While there is little intramolecular reorganization of fused-ring monomers such as pyrene[5] during the formation of an excimer, considerable changes in molecular conformation are expected in the reaction of open-chain systems such as **1**. The present calculation of the equilibrium geometry of the excimer species of **1** may test this expectation. The geometry of the excimer may throw light on the possibility of generating optically active dimers in a chiral two-component system since dimerization within molecular stacks of twisted monomer units may proceed in a preferred direction.[6] In other words, the initial geometrical relaxation of the excited guest molecule may lead to different approach configurations with the nearest upper and lower ground state molecules of the host of which one may be more favorable for excimer formation and subsequent dimerization. The existence of a preferred direction of dimerization along the 4 Å axis has been detected experimentally in a mixed crystal system consisting of **1** as a host and its thiophene analog (where the phenyl ring of **1** is replaced by a thienyl ring) as a guest. The selective excitation of the guest (due to its lower excitation energy) led to the formation of an optically active heterodimer.[7] In the present work we make an attempt to study the favorable path of excimer formation in such a system using the pure crystal of **1** as a model for our calculations.

Theoretical Methods. Our treatment of excited conjugated molecules is based on the potential surface of the quantum mechanical extension of the consistent force field to π electron systems (QCFF/PI).[8] In this method we assume σ–π separability and describe the σ potential surface by empirical potential functions whereas the ground and excited π potential surfaces are described analytically by a semiempirical SCF-MO-CI scheme of the PPP type (corrected for nearest neighbor overlap). The reliability of this potential surface (including minor modifications) was demonstrated in calculations of the ground state equilibrium geometry of some flexible conjugated molecules in the crystalline state.[9]

The present approach treats the excimer as a supermolecule consisting of two monomers. The π potential is modified in order to include σ type interactions between $2p_z$ orbitals of the two monomers. These interactions are introduced by resonance integrals of the form

$$\beta_{2p\sigma,2p\sigma} = I_{2p}S_{2p\sigma,2p\sigma} \qquad (1)$$

where the effective ionization potential is $I_{2p} = -10.5$ eV, and the effective charge in the overlap integral S is chosen as $Z = 2.8$ by fitting the calculated and observed shift between the absorption and emission of the pyrene excimer.[5] The form of the repulsive integrals between $2p_z$ orbitals on different molecules is assumed to be identical with that between $2p_z$ orbitals on the same molecule.

The basic assumptions in the present treatment are as follows: (1) The excimer formation is determined mainly by the interactions of the π electrons. Therefore, the π electrons are treated quantum mechanically and the hard-core repulsions between the σ electrons are described by empirical nonbonded functions.

(2) The excimer is treated by the SCF-MO method as a supermolecule so that the molecular orbitals of the monomers are being already mixed before the CI calculations. Such a mixing of molecular orbitals is equivalent to the configuration interaction mixing of exciton states with charge resonance states[10] which has been shown to be essential for reproducing the observed red shift of excimer emission.[11]

(3) The overlap between the monomer molecules is introduced effectively by considering all semiempirical π integrals as integrals in the Löwdin base and performing the SCF calculations in the zero differential overlap approximation.

(4) The relaxation process involved in the formation of the excimer in the crystal is assumed to occur in a rigid environment of ground-state molecules.

According to the above assumptions the potential surface of the N'th electronic state of an excimer consisting of two monomers **a** and **b** is given in the following way

$$V^N(\mathbf{r}^a, \mathbf{r}^b) = V_{\mathrm{intra}}{}^N(\mathbf{r}^a, \mathbf{r}^b) + \sum_{l} \sum_{i,j} [V_{\mathrm{inter}}(r_{ia,jl}) + V_{\mathrm{inter}}(r_{ib,jl})] \qquad (2)$$

where $V_{\mathrm{intra}}{}^N$ is the N'th intramolecular energy surface of the excimer, and $\mathbf{r}^a$ and $\mathbf{r}^b$ are the Cartesian coordinate vectors of molecules **a** and **b** respectively. V_{inter} is an atom-atom nonbonded potential. $r_{ia,jl} = \mathbf{r}_i{}^a - \mathbf{r}_j{}^l$ where i and j are the atomic indices while l runs over the neighboring ground-state molecules which are related to the reference ground-state molecule by the crystal symmetry. The intramolecular energy is given by

$$V_{\mathrm{intra}}{}^N(\mathbf{r}^a, \mathbf{r}^b) = V_\sigma(\mathbf{r}^a) + V_\sigma(\mathbf{r}^b) + V_\pi{}^N(\mathbf{r}^a, \mathbf{r}^b) + \sum_{ij} V_{\mathrm{inter}}(r_{ia,jb}) \qquad (3)$$

The V_σ and V_π contributions are obtained by using the QCFF/PI scheme. The σ surface is given by empirical potential functions while the π surface is expressed by the following.

$$V_\pi{}^N(\mathbf{r}^a, \mathbf{r}^b) = V_\pi{}^0(\mathbf{r}^a, \mathbf{r}^b) + \Delta V_\pi{}^N(\mathbf{r}^a, \mathbf{r}^b) \qquad (4)$$

Here V^0 is given by

$$V_\pi{}^0(\mathbf{r}^a, \mathbf{r}^b) = V_\pi{}^0(\mathbf{r}^a) + V_\pi{}^0(\mathbf{r}^b) + 2\sum_{ij} P_{ia,jb}(\mathbf{r}^a, \mathbf{r}^b)\bar{\beta}_{ia,jb}(\mathbf{r}^a, \mathbf{r}^b) - \sum_{i,j} [{}^1\!/_2 P^2{}_{ia,jb}(\mathbf{r}^a, \mathbf{r}^b) - Q_{jb}(\mathbf{r}^a, \mathbf{r}^b)Q_{ia}(\mathbf{r}^a, \mathbf{r}^b)]\gamma_{ia,jb}(\mathbf{r}^a, \mathbf{r}^b) \qquad (5)$$

where $\bar{\beta}$ is the previously defined $\beta_{2p\sigma,2p\sigma}$ (for definition of the other quantities, see ref 8a). Equation 5 gives essentially the $V_\pi{}^0$ potential of ref 8 modified by the incorporation of $\bar{\beta}$. $\Delta V_\pi{}^N$ is obtained similarly by incorporating $\bar{\beta}$ in the $\Delta V_\pi{}^N$ of ref 8. The parameters which are used here are those of set B in ref 9.

The intermolecular nonbonded potential V_{inter} in eq 2 and 3 is the exp-6 potential of ref 8. The nonbonded parameters of the exp-6 potential involving chlorine atoms were taken from set B of ref 12. In V_{inter} we neglect the possible interaction between the π charges of the N'th state of the excimer with the surrounding molecules.

The σ and π potential surfaces in our method are expressed analytically as a function of the Cartesian coordinates of the excimer, thus allowing the use of efficient minimization techniques[13,14] which are essential for determining the equilibrium geometry of excimers consisting of flexible conjugated molecules. The minimization is performed in the $3n$ dimensional space of the Cartesian coordinates of the excimer.

II. Results and Discussion

The validity of our ground state potential surface has been examined by minimizing the lattice energy with respect to the $3n$ Cartesian coordinates of the n (=30) atoms in the asymmetric unit. The agreement between the observed and calculated geometry in the ground state is fairly good (see Table I) and hence one may expect a reliable prediction of the excited state geometry as both potential surfaces (ground and excited states) are evaluated by using the same semiempirical integrals.

(a) The Excimer State. The equilibrium geometry of the excimer was evaluated by minimizing $V^N(\mathbf{r}^a,\mathbf{r}^b)$ (where N is the lowest singlet excimer state) with respect to all Cartesian components of $\mathbf{r}^a$ and $\mathbf{r}^b$. The results are presented in Figure 1 and in Table II. The torsion angles of the central chains of both molecules (**a** and **b**) are listed in Table III. The relaxation of the two monomers in the excimer state is quite different. The main reorganization occurs in the butadiene chains whereas the phenyl rings are less shifted from their initial positions in the ground state crystal. The twist about the central bond (8–9) is essentially zero in both molecules, thus preserving the coplanarity of the butadiene system. The close approach of the two butadiene systems (~3 Å) results in considerable twists about bonds 7–8 and 9–10 of **a** and **b** in opposite directions (see Table III) which destroy the coplanarity of the end atoms (4 and 11) with the butadiene moiety, the effect being larger in **b**. This relaxa-

Table I. Ground-State Conformation

Torsion angle[a]	Obsd[b]	Calcd
5–4–7–8	–14.4	–15.1
4–7–8–9	178.6	177.9
7–8–9–10	178.8	179.0
8–9–10–11	175.6	176.0
9–10–11–12	40.8	39.7

[a] In degrees. [b] Reference 4.

tion leads to considerable overlap between the π orbitals of the central atoms (as may be seen from comparing Figures 2A and 2B) yet avoiding too close contacts between the bulky phenyl rings.

The geometry of the excimer species cannot explain the fact that the dimerization occurs at the 7-8 bond but not at the 9-10 bond, as the center-to-center distances between parallel bonds at the excimer state are similar (3.04 and 3.05 for 7-8 and 9-10, respectively). The steric effects of the dichlorophenyl groups probably begin to be considerably larger than those of the phenyl groups at shorter distances where it hinders close approach of the 9-10 bonds.

Although it is rather difficult to distinguish between the contributions of nonbonded and π energies in determining the equilibrium geometry of the excimer, it is clear that nonbonded effects are very important in such systems consisting of flexible nonplanar molecules where intra- as well as intermolecular forces are opposing the close approach of the two interacting molecules.

An important indication of the reliability of our calculations is the agreement between the calculated and observed spectroscopic properties of the excimer. The calculated maxima of the excimer and monomer emissions are 21,680 and 26,750 cm^{-1}, respectively; the corresponding experimental values are 21,276 and 25,700 cm^{-1}, respectively.

It is important to note that the dependence of the electronic levels of an excimer of flexible molecules on its geometry is quite different from that of the more familiar case of excimer of rigid molecules. In the case of flexible molecules there is a large difference between the geometry of the ground and the excited monomers. In the excited state the torsional deformations around single bonds decrease and those around double bonds increase as the bond order of the single bond increases and that of the double bond decreases. These geometrical changes lead to a strong correlation between the wave functions (as well as the excitation energies) and the conformation of the monomers. This point can be clarified by examining the dependence of the wave functions of the excimer state on the molecular coordinates in two limiting cases denoted as **a*b**^{0} and **a*b***, where (0) and (*) stand for the equilibrium geometries of the ground and excited states of the monomer, respectively. For the sake of simplification we shall use the exciton and charge transfer wave functions rather than the supermolecule wave functions. The wave function of the excimer can be represented by the wave functions of the unperturbed monomers in the following way

$$\Psi = C_{\mathrm{I}}(\mathbf{r}_a, \mathbf{r}_b)\phi_a{}^*\phi_b{}^0 + C_{\mathrm{II}}(\mathbf{r}_a, \mathbf{r}_b)\phi_a{}^0\phi_b{}^* + C_{\mathrm{III}}(\mathbf{r}_a, \mathbf{r}_b)\phi_a{}^-\phi_b{}^+ + C_{\mathrm{IV}}(\mathbf{r}_a, \mathbf{r}_b)\,\phi_a{}^+\phi_b{}^- \quad (6)$$

where ϕ^0 and ϕ^* are the wave functions of the ground and excited states of the monomer, respectively, and ϕ^- and ϕ^+ are the ionic wave functions of the monomer. The coefficients ($C_{\mathrm{I}} \ldots C_{\mathrm{IV}}$) depend strongly on $\mathbf{r}_a$ and $\mathbf{r}_b$. Thus while for the **a*b*** geometry $C_{\mathrm{I}} = -C_{\mathrm{II}}$ (in the lowest excimer state), one finds that for the **a*b**^{0} geometry $|C_{\mathrm{I}}| \gg |C_{\mathrm{II}}|$ (see Table IV). This result is due to the fact that for weakly interacting monomers the diagonal Hamiltonian matrix element $\langle\phi_a{}^*\phi_b{}^0|H|\phi_a{}^*\phi_b{}^0\rangle$ can be approximated by $\langle\phi_a{}^*|H_a|\phi_a{}^*\rangle + \langle\phi_b{}^0|H_b|\phi_b{}^0\rangle$ which has a minimum at the **a*b**^{0} geometry. The dependence of the excitation energy of the system on the intramolecular geometry has been examined for the medium interaction region where one can still distinguish between exciton states and charge resonance states even in the supermolecule approach. The results are presented in Table IV and show that the excitation energy is highly dependent on the geometry even for the isolated monomer. It is also shown that for the **a*b*** geometry the lowest excimer state is described by the commonly used wave function with $C_{\mathrm{I}} = -C_{\mathrm{II}}$ whereas for the **a*b**^{0} case the exciton is localized mainly on one monomer. The dependence of the wave functions on the geometry should provide a guide for the study of the process of exciton trapping.

(b) The Favorable Direction of Excimer Formation. In a mixed crystal system where the guest has a lower excitation energy than the host,[7] the mixing between the electronic levels of the reacting molecules is smaller than in the pure crystal. Therefore it is reasonable to assume that the first step in the exciton trapping process involves the relaxation of the guest molecule to its equilibrium geometry whereas the subsequent step involves the formation of the excimer

Table II. Calculated Cartesian Coordinates (Å) of the Nonhydrogen Atoms in the Ground and Excimer States

	Ground state			Excimer state					
				a			b		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
C (1)	2.089	1.427	–3.214	2.046	1.652	–3.050	2.254	5.395	–3.372
C (2)	0.946	2.141	–2.818	0.872	2.359	–2.327	1.049	5.976	–2.934
C (3)	0.762	2.478	–1.470	0.631	2.757	–1.408	0.811	6.157	–1.568
C (4)	1.714	2.092	–0.491	1.561	2.444	–0.367	1.779	5.749	–0.598
C (5)	2.859	1.365	–0.903	2.741	1.716	–0.713	2.994	5.160	–1.060
C (6)	3.043	1.042	–2.258	2.974	1.332	–2.041	3.224	4.996	–2.433
C (7)	1.488	2.501	0.912	1.280	2.908	0.986	1.485	5.967	0.809
C (8)	2.151	2.007	1.984	2.058	2.595	2.100	2.278	5.591	1.885
C (9)	1.876	2.519	3.333	1.705	3.022	3.420	1.947	6.052	3.210
C (10)	2.504	2.038	4.429	2.511	2.694	4.507	2.694	5.739	4.329
C (11)	2.314	2.589	5.796	2.252	3.005	5.909	2.469	6.326	5.663
C (12)	1.044	3.077	6.284	0.941	3.246	6.441	1.175	6.705	6.154
C (13)	0.931	3.580	7.560	0.787	3.652	7.771	1.042	7.281	7.424
C (14)	2.059	3.725	8.380	1.900	3.776	8.621	2.162	7.486	8.244
C (15)	3.310	3.283	7.926	3.181	3.450	8.144	3.435	7.117	7.784
C (16)	3.444	2.716	6.650	3.366	3.057	6.816	3.597	6.541	6.520
Cl (1)	–0.443	2.767	5.403	–0.532	2.919	5.561	–0.319	6.441	5.293
Cl (2)	5.040	2.212	6.152	4.992	2.651	6.320	5.229	6.184	6.017

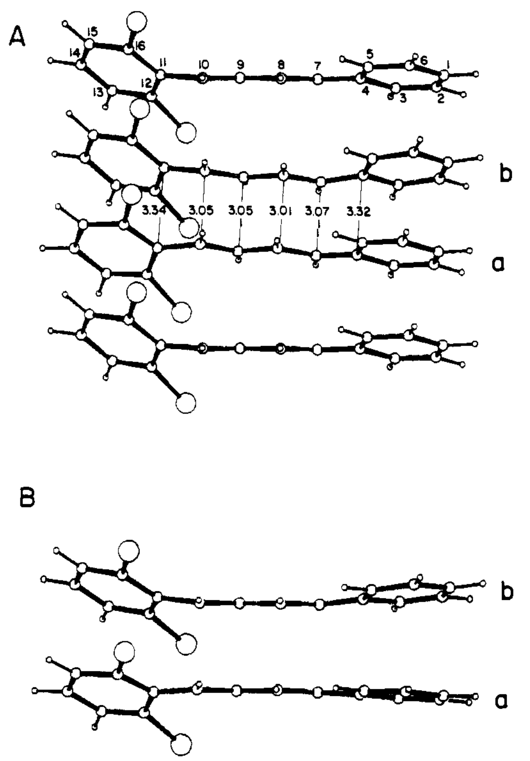


Figure 1. (A) Equilibrium geometry of the excimer along the 4-Å axis. The view is edge-on along the butadiene plane of the ground state molecule. (B) Equilibrium geometry of the excimer. The view is edge-on along the butadiene planes of **a** and **b**.

Table III. Excimer-State Conformation

Torsion angle[a]	Molecule a	Molecule b
5–4–7–8	−5.6	−3.3
4–7–8–9	183.2	171.1
7–8–9–10	180.2	180.1
8–9–10–11	183.5	172.8
9–10–11–12	23.8	32.5

[a] In degrees.

either with the upper or lower host molecule in the 4 Å translation stack. The excimer may be formed preferentially with one of these two neighboring host molecules.

It should be noted here that the mechanism of exciton trapping in excimer of large flexible conjugated molecules might be quite different from the corresponding mechanism in the more frequently studied case of excimers of rigid planar aromatic molecules. It is quite possible that the intramolecular torsional relaxation contributes to the exciton trapping process as much as the translational relaxation. That is, the transfer of the excess intramolecular energy to the lattice modes by the low frequency torsional modes of a flexible molecule is as fast as the transfer of the excess intermolecular energy by the translational modes.

The general features of the process of excimer formation in the mixed crystal (and to some extent in the pure crystal[15]) may be obtained by simulating the corresponding reaction paths in the pure crystal system. That is, as the guest has a similar conformation to that of the host,[16] the hypothetical geometrical relaxation of an excited monomer of **1** surrounded by rigid ground state molecules of **1** may be used to simulate the relaxation of the excited guest in a rigid host crystal. Similarly the subsequent steps in the excimer formation in the mixed crystal can be examined using the pure crystal model.

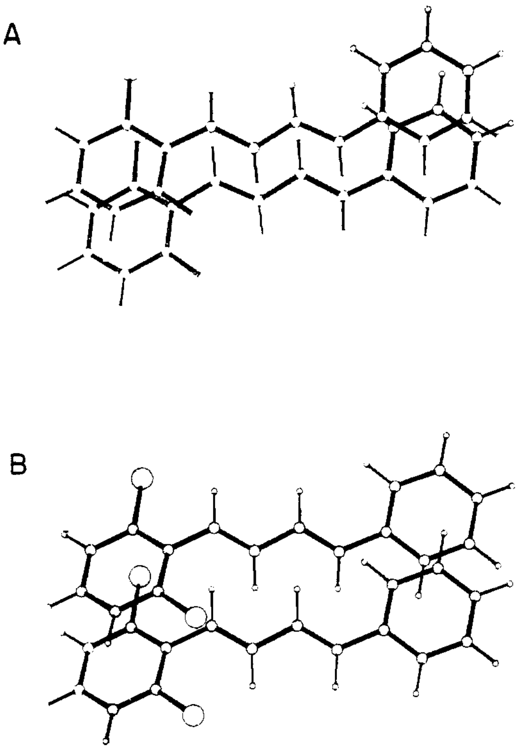


Figure 2. (A) The equilibrium geometry of the excimer. The view is perpendicular to the butadiene plane. (B) The equilibrium geometry of two adjacent ground-state molecules. The view is perpendicular to the butadiene plane.

Table IV. The Dependence of Excitation Energies on the Intramolecular Geometry of the Monomers

Geometry[a]	Excitation energies, cm^{-1}	Approximated excited state wave functions
a*	26,750	$\phi_a{}^*$
a⁰	31,987	$\phi_a{}^*$
a*b* (3.5 A)	23,710	$\phi_a{}^* \phi_b{}^0 - \phi_a{}^0 \phi_b{}^*$
	28,080	$\phi_a{}^- \phi_b{}^+ - \phi_a{}^+ \phi_b{}^-$
	28,970	$\phi_a{}^- \phi_b{}^+ + \phi_a{}^+ \phi_b{}^-$
	31,449	$\phi_a{}^* \phi_b{}^0 + \phi_a{}^0 \phi_b{}^*$
a*b⁰ (3.5 A)	26,080	$\phi_a{}^* \phi_b{}^0$
	31,570	$\phi_a{}^- \phi_b{}^+$
	32,408	$\phi_a{}^+ \phi_b{}^-$
	34,900	$\phi_b{}^* \phi_a{}^0$
a*b⁰ (3.0 A)	21,263	Strong
	27,897	mixing
	31,632	of all
	35,520	configurations

[a] a⁰ and **a*** are the equilibrium geometries of ground and excited monomers, respectively. The excimer geometry has been obtained by translating the rigid monomers along the *b* axis; the average distance between the monomers is given in parentheses.

Our conceptual treatment in simulating the excimer formation is presented by the steps shown in Scheme I (the brackets refer to the rigid environment of ground-state molecules).

In the first stage [1] we calculate the equilibrium geometry of the excited monomer $\mathbf{a}_{\min}$ by minimizing its energy in the lattice of rigid ground-state molecules. The second step [1] → [2] consists of two competing processes as the relaxed molecule (**a**) interacts either with the upper ($\mathbf{b}^1$) or lower ($\mathbf{b}^{-1}$) ground-state neighbors along the 4-Å axis. In this step we minimize separately the energies of the two

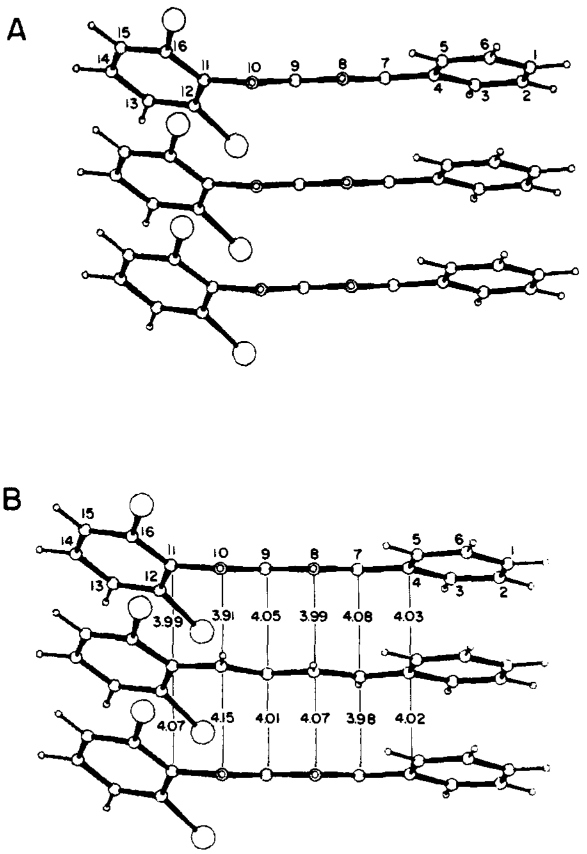


Figure 3. (A) Calculated ground-state geometry. The view is edge-on along the butadiene plane. (B) Stage [1]: the equilibrium geometry of the excited molecule surrounded by two ground-state molecules.

Scheme I

$$\begin{tikzcd}
 & {[a_{min}]} \arrow[dl] \arrow[dr] & & {[1]} \\
{[b^{-1}a_{min}]} \arrow[d] & & {[a_{min}b^{1}]} \arrow[d] & {[2]} \\
{[b_{min}{}^{-1}a_{min}]} & & {[a_{min}b_{min}{}^{1}]} & {[3]}
\end{tikzcd}$$

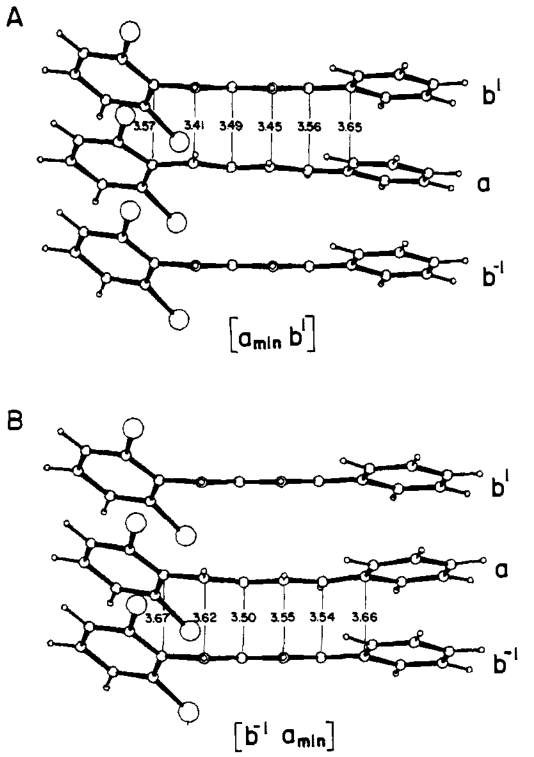


Figure 4. Stage [2]: the two possible excimers $\mathbf{ab}^1$ and $\mathbf{b}^{-1}\mathbf{a}$ where $\mathbf{b}^1$ or $\mathbf{b}^{-1}$ are kept at the ground-state coordinates.

Table V. The Conformation of a in Stages [1] and [2]

Torsion angle[a]	Stage [1] a	Stage [2][b] a(I)	a(II)
4-5-7-8	-4.4	-7.0	-5.0
4-7-8-9	177.5	182.9	174.1
7-8-9-10	182.9	180.6	184.2
8-9-10-11	177.0	181.3	171.9
9-10-11-12	25.2	26.2	31.7

[a] In degrees. [b] a(I) is a in $\mathbf{ab}^1$ while **a**(II) is a in $\mathbf{b}^{-1}\mathbf{a}$.

possible excimers $\mathbf{ab}^1$ (I) and $\mathbf{b}^{-1}\mathbf{a}$ (II) with respect to the coordinate of **a** while $\mathbf{b}^1$ and $\mathbf{b}^{-1}$ are kept at their ground-state coordinates. The last step [2] → [3] involves the minimization of the energies of the two excimers with respect to the coordinates of both molecules. In each case when we treat a given pair of molecules (e.g., $\mathbf{ab}^1$) as an excimer we include the quantum mechanical π electron energy only between this pair while the interaction with the surrounding lattice is represented by the nonbonded functions. The minimum energy geometries of the molecules in the 4-Å stack which corresponds to the three stages are presented in Figures 3 and 4 and 1, respectively. Figure 3B shows the equilibrium geometry of the excited molecule (**a**) surrounded by rigid ground-state molecules. The main relaxation occurs in the butadiene chain whereas the positions of the phenyl rings are almost unchanged. This relaxation results in a more planar conformation compared with that of the ground state as reflected also by the torsion angles (see Table V; stage [1]). The average distance between **a** and $\mathbf{b}^1$ is slightly smaller than that between **a** and $\mathbf{b}^{-1}$ as shown by the intermolecular distances in Figure 3. Figure 4 shows the geometrical relaxation of **a** in the two possible excimers $\mathbf{ab}^1$ (I) and $\mathbf{b}^{-1}\mathbf{a}$ (II) where $\mathbf{b}^1$ and $\mathbf{b}^{-1}$ are kept at their ground-state coordinates. The additional intramolecular relaxation of **a** is smaller in I than in II as may be seen from the comparison between the torsion angles of **a** in I and II to that of the excited monomer in stage [1] (see Table V and compare Figures 3 and 4). The intermolecular contacts in I are shorter than the corresponding contacts in II, particularly at the vicinity of the dichlorophenyl rings, thus demonstrating the dominating effects of these groups in determining the different interactions of **a** with **b** and $\mathbf{b}^{-1}$. The different geometrical relaxation in I and II results also in the stabilization of I by nearly 1 kcal/mol with respect to II. The energy minimization of I and II with respect to the coordinates of both molecules led to equivalent final states of the two excimers (related by translation along the *b* axis) which are identical with the excimer state geometry obtained previously. The comparison of the results of I and II indicates that the process of excimer formation by the relaxed monomer (**a**) with its upper ground state partner ($\mathbf{b}^1$) involves a smaller intramolecular reorganization of the two monomers than that of **a** with its lower partner ($\mathbf{b}^{-1}$). In other words, the final conformations of **a** and $\mathbf{b}^1$ in excimer I are similar to the conformations of the initial excited and ground-state monomers (stage [1]), respectively, whereas the final conformations of **a** and $\mathbf{b}^{-1}$ are quite different from that of the excited and ground-state monomers, respectively.

The energy relaxation along the reaction paths of I and II

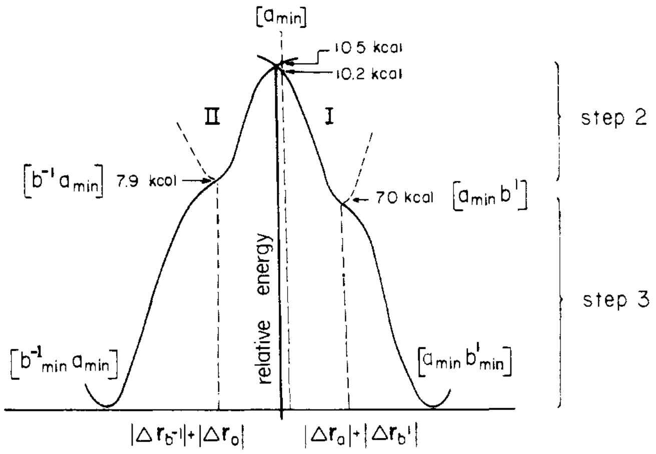


Figure 5. A schematic representation of the energy relaxation along the two possible directions for excimer formation.

is presented schematically in Figure 5. In the upper part of the figure we describe the results of the calculations of step [1] → [2] in which we do not allow the relaxation of $\mathbf{b}^1$ and $\mathbf{b}^{-1}$. In this step the curves of I and II intersect at the ground state equilibrium geometry. On the other hand the energies of curves I and II are not equal at the equilibrium conformation of stage [1] where the energy is lower in I than in II and the distance along the reaction coordinate to the minimum of I (in stage [2]) is shorter than to the corresponding minimum of II. As was shown above the final excimers (stage [3]) are equivalent in I and II and the distance from the minimum of stage [2] to the minimum of stage [3] (the final excimer) is shorter in I than in II. Since the overall geometrical changes involve a large component of translation in the direction of the 4-Å axis, the total displacement is similar in I and II. However, as was mentioned above the intramolecular geometrical changes in I are much smaller than in II.

In comparing the probabilities of I and II we should consider the following results of the calculations. (1) The initial gradient at the point [$\mathbf{a}_{\min}$] is steeper in I than in II. (2) The intramolecular conformational changes upon relaxation to the final excimer are smaller in I than in II. (3) The energy at the minimum of stage [2] is lower in I than in II.

All three points indicate some preference in the formation of the $\mathbf{ab}^1$ (I) excimer.

While the calculations were done by treating only a pair of molecules as excimer it may be argued that a more appropriate treatment should consider the trimer ($\mathbf{b}^{-1}\mathbf{ab}$) as a supermolecule. This, however, would lead to a result which may be approximated by combining curves I and II at the crossing point. In such a case, the beginning of stage [2] from the point [$\mathbf{a}_{\min}$] implies that we start from the right side of the barrier and thus make the direction of I favorable.

The verification of the predicted favorable path may be obtained experimentally using X-ray methods by determining the absolute configuration of the starting monomers in the mixed crystal and that of the enantiomeric cyclobutane obtained in excess.

References and Notes

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(15) At present it is not clear if the first step in excimer formation in the pure crystal is the relaxation of the excited molecule or the immediate trapping into the excimer state. The question of preference of a specific direction in the pure crystal appears only if prior to the excimer formation the crystal symmetry is perturbed by the relaxation of an excited monomer into its equilibrium geometry. In this case (see Figure 3) the interactions of the excited molecule with its upper and lower neighbors are different. Here, however, even if the excimer is formed in a preferential direction it is impossible to detect it by experiment.

(16) The X-ray analysis of the mixed crystal which has been carried out by D. Rabinovich and Z. Shakked shows that the mixed crystal is highly isomorphous with the pure crystal of **1** and the conformation of the guest is very similar to that of the host due to packing requirements.