Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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Version of record first published: 04 Oct 2006.

To cite this article: N. W. Thomas (1990): Computer Simulation of a Solid-State [2 + 2]-Photodimerisation, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 188:1, 273-289

To link to this article: http://dx.doi.org/10.1080/00268949008047823

Mol. Cryst. Liq. Cryst., 1990, Vol. 188, pp. 273–289
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Printed in the United States of America

Computer Simulation of a Solid-State [2 + 2]-Photodimerisation

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(*Received November 1, 1989; in final form May 29, 1990*)

The solid-state [2 + 2]-photodimerisation of three members of the 2-benzyl-5-benzylidenecyclopentanone (BBCP) family of compounds is simulated. Two empirical parameters, R_1 and R_2, are defined, which are calculated from the crystal structures of monomer and dimer compounds. R_1 is correlated with the tendency of the compounds to crack upon photodimerisation. The rates of reaction and the wavelengths of radiation required to effect reaction can be understood in terms of the geometry of overlap of the two monomeric double bonds that react to form the cyclobutane rings of the dimer molecules. The structural factors governing whether the reactions proceed homogeneously or heterogeneously are examined by using the model of a regular solid solution, with interaction energies calculated with (6-exp) atom-atom non-bonded potentials. The importance of the mechanisms of photon absorption, reaction to form a dimer, and exciton transport in determining the phase characteristics of the reaction is also discussed.

Keywords: photodimerisation BBCP potential solid-state computer-modelling

INTRODUCTION

Our understanding of the pathways of solid-state reactions has been guided by the topochemical principle, which states that reactions in crystals proceed with a minimum of atomic and molecular movement. An important consequence of this principle is that the fluid-state reactivity of a given molecule may differ from its reactivity in the solid state, where the crystalline matrix severely restricts its translational and rotational motion. However, this restriction in molecular movement is not necessarily disadvantageous, since it offers the prospect of greater stereochemical control, and in some cases enhanced reactivity.

A natural type of reaction to be exploited in solid-state synthesis is the photochemical reaction. The first stage of such a synthesis involves the crystallisation of the reactant molecules in a structure with the reactive functions of the molecule correctly oriented for reaction. The second stage involves irradiation of the crystal with light of the appropriate wavelength, at a suitable temperature. It is often the first stage of a synthesis which is more difficult, since the relationship between the structure of a molecule and the crystal structure(s) it adopts cannot normally be deduced from first principles. Further, the second stage need not be straightfor-

ward, since the photo-reaction does not necessarily proceed homogeneously, and a heterogeneous mechanism may obtain. Such heterogeneous reactions sometimes involve crystalline defects as an integral part of the reaction pathway. It is also frequently the case that the stress developed in the course of the reaction gives rise to cracking and/or amorphous products, so that the crystallinity of the reactant phase is impaired. In extreme cases, this degradation in crystallinity can cause incomplete reaction.

With so many factors influencing the progress of a solid-state reaction, one way to proceed is to study a model family of compounds in depth, in order to appreciate the potential for optimising techniques in solid-state synthesis. Cohen and Schmidt[1] have pioneered this approach with their work on cinnamic acids. These undergo photochemical [2+2]-cycloadditions, as does distyrylpyrazine when it reacts to form a polymer in the solid state.[2] A number of anthracene derivatives have been studied which are capable of [4+4]-photoadditions,[3] and the solid-state polymerisation of diacetylenes (R—C≡C—C≡C—R) has been studied in depth.[4,5,6]

Another model family of compounds, which react in a [2+2]-photoadditive manner, has the parent 2-benzyl-5-benzylidene-cyclopentanone (BBCP),[7] with a molecular structure as shown in Figure 1(a). The cyclopentanone ring and the benzylidene group can be regarded as forming a rigid sub-molecular unit, owing to the presence of a conjugated π-electron system. Some molecular flexibility is afforded, however, by the possible rotation of the benzyl phenyl ring about the bond RS, although the vast majority of derivatives of BBCP have similar conformations in the crystalline state.[8]

The parent compound reacts with uv light to form a dimer in a reaction that is both topochemical and topotactic.[9] The dimer is thought to form in solid solution within the monomer phase, so that the overall reaction proceeds homogeneously from a single-crystal monomer to a single-crystal dimer. The criterion of topotaxy requires that a chemical reaction leads to a material with crystal orientations correlated with the crystal orientation of the reactant.[10]

Some fifteen compounds have been synthesised with chloro, bromo and methyl substituents at X and Y positions, and their crystal structures have been determined by X-ray diffraction.[11,12] The aim of this work was to relate the molecular structure of a BBCP derivative to the crystal structure it adopts, and thereby rationalise its solid-state photo-reactivity or photo-stability.[13,14] A sufficient condition for photoreactivity was found to be the presence of parallel double bonds in adjacent

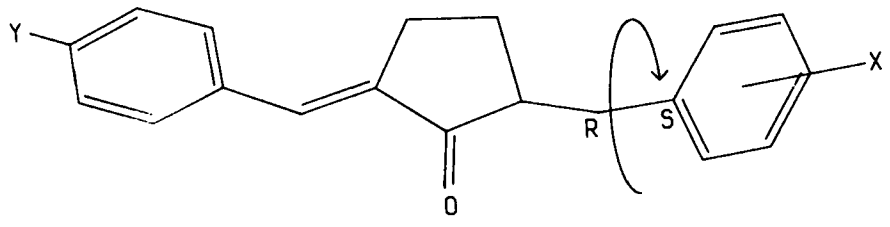

FIGURE 1(a) The molecular backbone of 2-benzyl-5-benzylidene-cyclopentanone (BBCP), showing positions of substituents *X*,*Y* in the benzyl and benzylidene rings, respectively. Rotation of the benzyl moiety about bond RS is possible.

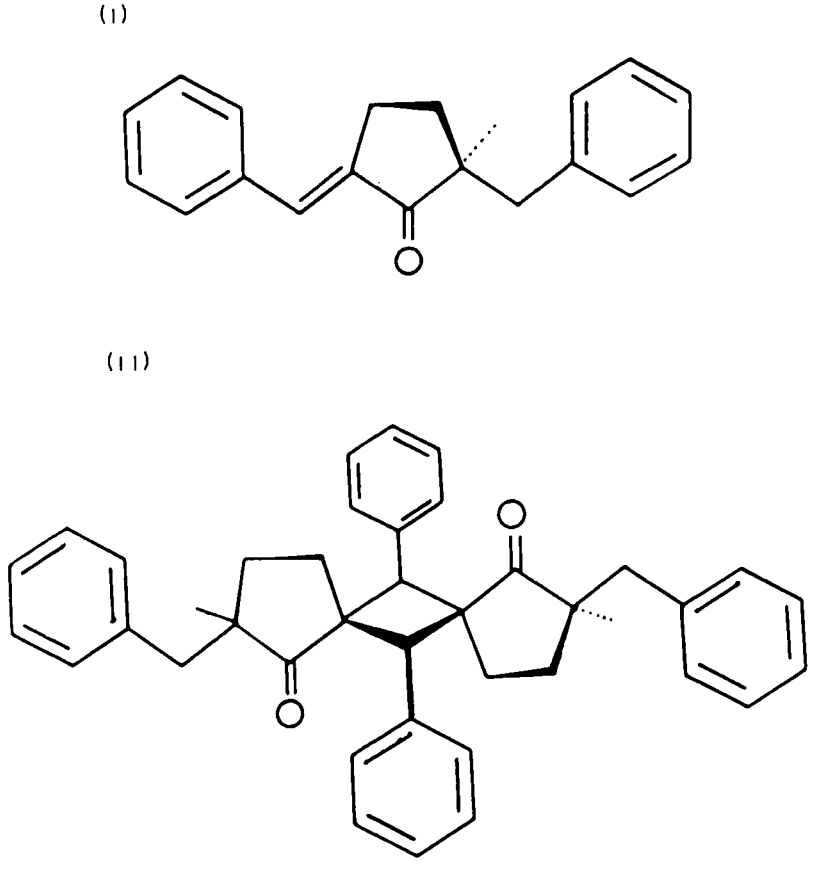

FIGURE 1(b) Molecular structures of the monomer (i) and dimer (ii) of BBCP. The dimer is formed with a 100% yield upon irradiation in the crystalline state.

monomers, separated by a centre-to-centre distance, $d < 4.2$ Å, as found in the work on cinnamic acids.[1] A predictive framework, applicable to all derivatives of BBCP, has also been defined, which is capable of predicting whether a given derivative of the parent compound will be photoreactive or photostable, merely from the positions of its Cl, Br and/or Me substituents.[15,16] This framework is sufficiently general to be applied to other families of molecular crystals in which dispersive non-bonded interactions are the dominant mechanism of stabilising the molecules in the crystalline state.

Work on the BBCP system to date has been concentrated on the prediction of the crystal structure of a particular derivative from a knowledge of its molecular structure. It thus refers to the first stage of a solid-state synthesis. This paper addresses the issues connected with the second stage, i.e. irradiation of the crystal with light of a suitable wavelength. Experimental information has been obtained in previous studies for the photodimerisation of three compounds, the parent BBCP, *p*Cl-BBCP (X = *p*Cl) and B-*p*Br-BCP (Y = *p*Br), as summarised in Table I.[8,17] This notation reflects the positions of the substituents in the molecules: *p*Cl-BBCP

TABLE I

Experimental information on the photo-dimerisation of BBCP, *p*Cl-BBCP and B-*p*Br-BCP[8,17]

	Rate of reaction*	Tendency to crack*	Radiation required
BBCP	1	1	broadband uv
*p*Cl-BBCP	2	2	broadband uv
B-*p*Br-BCP	3	3	visible light

*expressed on a scale of 1 to 3, with 3 representing the greatest rate of reaction or tendency to crack

has a chloro group substituted at the *para*-position in the benzyl moiety, whereas B-*p*-BrBCP has a *bromo* substituent at the *para* position in the benzylidene group.

A unique feature of this family of compounds is that 100 percent conversion from monomeric reactants to dimeric products can be obtained, as shown schematically in Figure 1(b). No intermediates are formed, as the reaction is a concerted [2+2]-photoaddition reaction. This 100 per cent conversion from monomer to dimer is a consequence of the crystal structures of the monomers, in which the two monomeric double bonds, which react to form dimers, are parallel.[11,12,17] These double bonds are also related by a centre of symmetry, which is retained in the dimeric product.

It has also been possible to monitor the course of the photo-reaction by means of a diffraction study of single crystals, whilst being irradiated.[17] This study utilised a four-circle diffractometer and a broad-band 100W mercury lamp, filtered so that $\lambda > 320$ nm. The observations recorded in Table I refer to irradiation under these conditions. The rate of reaction is a qualitative indication of the number of monomers per unit volume reacting to form dimers in a given time. Owing to the similarities in molecular and crystal structure between all three compounds,[15,16] the rate of absorption of photons is likely to be relatively invariant. Consequently the rates of reaction given in Table I can be regarded as approximate indicators of the quantum yields in the dimerisation reactions. The entry in the table that B-*p*-BrBCP requires only visible light to form the dimer is based on the observation that a crystal of this compound will dimerize merely by being exposed to sunlight on a window-ledge. This is not observed in the other two compounds.[8]

This paper examines each of the three dimerization reactions in terms of the crystal structures of monomers and dimers. The trends in Table I are rationalised, and an analytical framework is developed to indicate, from structural considerations alone, the tendency of a given compound to react in a homogeneous or a heterogeneous manner in forming photo-products.

ANALYSIS OF THE CRYSTAL STRUCTURES OF THE THREE REACTIVE SYSTEMS

The maintenance of a centre of symmetry in the conversion from monomer to dimer[11,12,17] is important for a modelling of atomic movements that take place during the reaction, as inversion symmetry may be maintained about the 'reaction

centre' at all stages of reaction. Consequently movement by one monomer of the reacting pair will be accompanied by an equivalent displacement of the other monomer. Indeed this is likely to be the case for a concerted $[_\pi 2 + _\pi 2]$-cycloaddition reaction between like molecules. A second point to be considered is the change in unit cell parameters between monomer and dimer structures. The extent of this change may be monitored quantitatively by defining a parameter, R_1, such that

$$R_1 = \{1/3[(\mathbf{a}_d - \mathbf{a}_m)^2 + (\mathbf{b}_d - \mathbf{b}_m)^2 + (\mathbf{c}_d - \mathbf{c}_m)^2]\}^{1/2} \quad (1)$$

In this equation, $\mathbf{a}_m$ and $\mathbf{a}_d$ are the unit-cell vectors parallel to the x-axis for the monomer and dimer crystal structures respectively, with similar interpretations for $\mathbf{b}_m$, $\mathbf{b}_d$, $\mathbf{c}_m$ and $\mathbf{c}_d$. R_1 represents the r.m.s. change in the lengths of the unit cell vectors in passing from monomer to dimer, and its value for the three systems is given in Table II, together with values of the unit cell constants.

The values of R_1 are interesting in that they reflect the observed tendency for cracking to occur during photodimerisation in the three systems. BBCP has the smallest value, indicating that the topotaxy is more exact than in the other two cases. This is important, irrespective of whether the mechanism of reaction is homogeneous or heterogeneous. In the former case, elastic strain can arise from a mismatch at unit cell level. Similar considerations hold for a heterogeneous mechanism, as interfaces between monomeric and dimeric regions will be associated with considerable elastic strain if the topotaxy is inexact. This can have two effects: first, the elastic strain increases the tendency for cracking to occur; secondly, defects may be set up at the monomer/dimer interfaces, in order to relieve strain. In systems where defects are an integral part of a heterogeneous reaction pathway, it is necessary that they are created at the reaction front, which separates monomeric and dimeric regions.

Whereas R_1 gives an indication of the topotaxy of the reactions, a second parameter, R_2, may be introduced, to quantify the degree of net atomic movement that takes place in these reactions:

$$R_2 = \left\{1/N \sum_i (\mathbf{t}_{im} - \mathbf{t}_{id})^2\right\}^{1/2} \quad (2)$$

R_2 represents the r.m.s. displacement of the atoms in the reaction from monomer

TABLE II

Values of the unit cell constants and the parameter R_1 for the systems BBCP, *p*Cl-BBCP and B-*p*Br-BCP

System		Space Group	a/Å	b/Å	c/Å	β	R_1/Å
BBCP	monomer	Pbca	31.293	10.779	8.689		
	dimer		31.321	10.811	8.629		0.042
*p*Cl-BBCP	monomer	$P2_1/c$	17.175	10.587	8.796	103.7°	
	dimer	$P2_1/c$	16.688	10.719	8.702	103.6°	0.296
B-*p*Br-BCP	monomer	Pbca	34.222	10.923	8.427		
	dimer	Pbca	32.960	10.270	8.980		0.880

to dimer, where N is the number of atoms constituting a monomer-pair (or dimer). Hydrogen atoms have been omitted from the summation, since their positions are known with less precision, and they cannot be considered to be an integral part of the molecular backbones in the three systems. $\mathbf{t}_{im}$ and $\mathbf{t}_{id}$ are the positional vectors of the i^{th} atoms with respect to the common origin, which is taken as the centre of symmetry. R_2 is thus a crude measure of the extent to which the shape of the reaction cavity changes in the course of the dimerisation.

The idea of a reaction cavity has been introduced by Cohen[18,19] as a refinement of the topochemical principle. According to this concept, the preferred reaction pathway is that which involves the minimal change in shape of the reaction cavity. In the present case, the reaction cavity is the region in space which contains the monomer molecules prior to reaction, and the dimer molecules after the product-determining step. For a homogeneous reaction mechanism in BBCP, the reaction cavity is coordinated by monomer molecules at the initial stage of the reaction, as shown in Figure 2(a). The formation of a dimer within this reaction cavity is shown in Figure 2(b).

In order to calculate values of $\mathbf{t}_{id}$ in Equation (2), an assumption must be made about the manner in which the dimer molecules are formed within the monomer matrix. A straightforward method, which will be termed 'Mechanism 1,' is to assume that the initial orientation of a dimer molecule in the monomer matrix is identical to its final orientation in the dimer crystal, at 100 per cent conversion from monomer to dimer. The coordinates, $\mathbf{t}_{id}$ may thus be obtained directly from the known dimer crystal structure, together with the assumption of topotaxy, i.e. $\mathbf{a}_d \| \mathbf{a}_m$, $\mathbf{b}_d \| \mathbf{b}_m$ and $\mathbf{c}_d \| \mathbf{c}_m$. The centre of symmetry of the dimer is placed at the centre of symmetry relating the two monomers that react to form the dimer.

However, the value of R_2 calculated by this method is not necessarily a *minimum*. It is possible to obtain a lower value of R_2 by allowing the dimer molecule to rotate about its centre of coordinates. This possibility, which will be termed 'Mechanism 2,' has been investigated by rotating the dimer by up to $\pm$ 45° from its 'Mechanism 1' position about the x, y and z axes, in steps of 1°. From all of these alternative positions of the dimer molecule, a minimum value of R_2 was calculated. The results are given in Table III.

A comparison of Tables III and I reveals that neither set of values of R_2 can be correlated with rate of reaction, or tendency to crack. Thus the parameter R_2 appears not to be a useful quantitative indicator of the solid-state reactive properties of this family of compounds. A more discriminating structural feature is to be found from a consideration of the movement of the two parallel double bonds alone, in forming the cyclobutane ring of the dimer. The relative disposition of the two monomeric double bonds, AB and CD, can be described in terms of the parallelogram ABCD, as shown in Figure 3.

A consideration of the values of BC shows that the separation of the double bonds is least in B-*p*Br-BCP and greatest in BBCP. Similarly, γ is closest to 90° in B-*p*Br-BCP, indicating that the intermolecular overlap of the *p*-atomic orbitals which form the intramolecular π-bonds between atoms A and B and between atoms C and D is greatest in B-*p*Br-BCP and least in BBCP. This trend is reproduced in the displacements of atoms A and B in passing from the monomer to the dimer, as given in Table IV. The smallest displacements are to be found in B-*p*Br-BCP

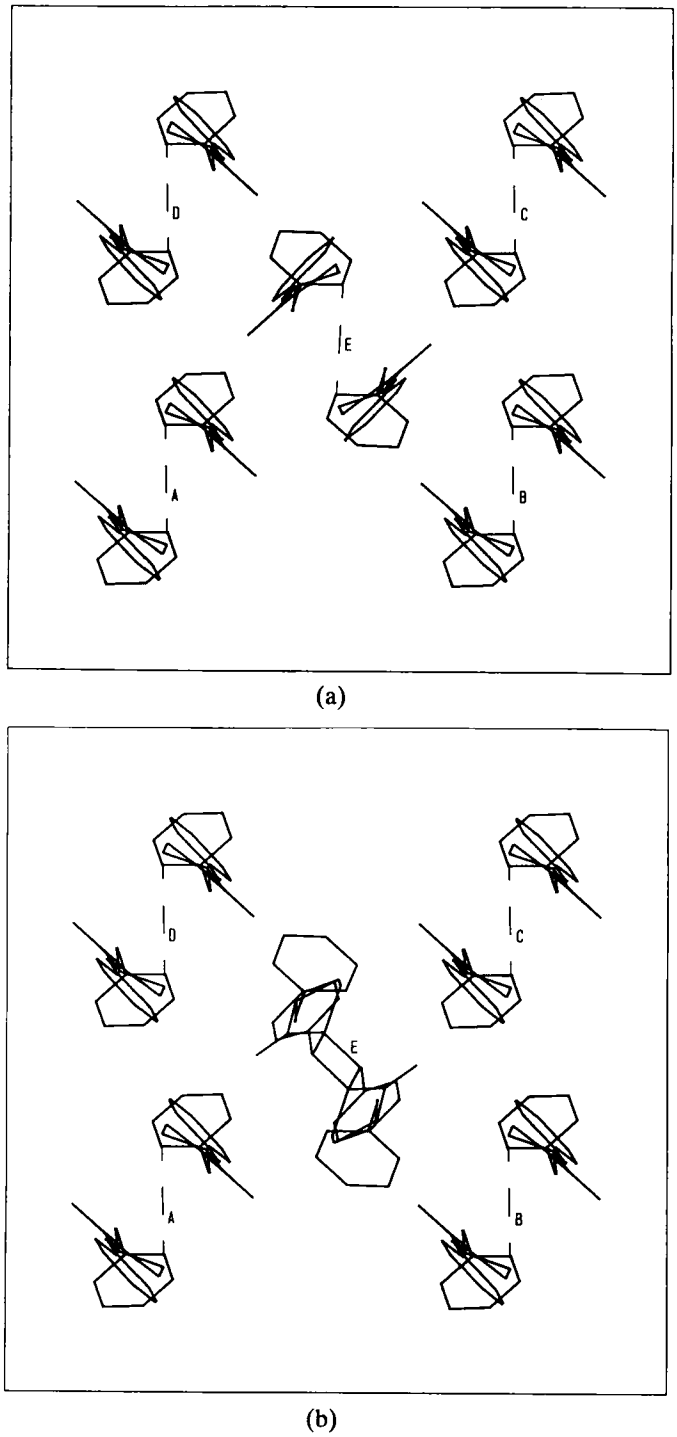

FIGURE 2 Formation of the reaction cavity in BBCP by monomer-pairs A, B, C and D. Monomer pair E in Figure 2(a) reacts to form dimer E in Figure 2(b). At later stages of reaction, monomer-pairs A, B, C and D also form dimers.

TABLE III

Values of R_2 for the systems BBCP, *p*Cl-BBCP and B-*p*Br-BCP, with the angles of rotation required for a minimum value of Mechanism 2

System	MECHANISM 1 R_2/Å	R_2/Å	MECHANISM 2 Rotation, θ, about axes *x*, *y* & *z* θ_x	θ_y	θ_z
BBCP	0.725	0.639	−1	4	−2
p-Cl-BBCP	0.641	0.602	2	16	−1
B-*p*Br-BCP	0.664	0.594	−2	−1	4

and the largest displacements in BBCP. Thus B-*p*Br-BCP in its monomeric structure already lies further along the reaction coordinate from monomer to dimer than the other two compounds: its rate of reaction is correspondingly faster.

The observation that B-*p*Br-BCP merely requires sunlight to be dimerised, whereas the other two systems require irradiation by broad-band uv light, can also be rationalised in terms of the molecular geometries at the reaction centres. Assuming that the [2+2]-dimerisation requires one of the monomers to undergo a π to π^* electronic excitation in order to proceed to the transition state, the photon energy required to excite the electron depends on the separation of the π and π^* energy

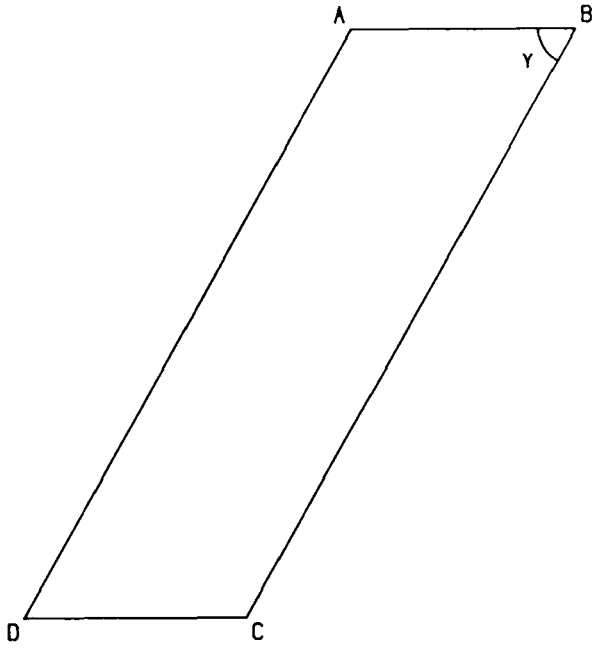

FIGURE 3 Relative disposition of reactive double bonds AB and CD. The lengths of AB and CD, and the angle γ are given in Table IV.

TABLE IV

Magnitudes of AB, BC and γ Fig. 3, and displacements of atoms A and B in passing from monomer to dimer (Mechanism 1)

System	AB/Å	BC/Å	γ	$\lvert {}^{t}A,d - {}^{t}A,m \rvert$ /Å	$\lvert {}^{t}B,d - {}^{t}B,m \rvert$ /Å
BBCP	1.325	4.167	68.2°	1.16	1.46
*p*Cl-BBCP	1.331	4.027	70.3°	1.11	1.37
B-*p*Br-BCP	1.336	3.798	88.0°	1.01	1.31

levels, $E_{\pi^*} - E_{\pi}$. For two monomeric double bonds separated by a large distance, $E_{\pi^*} - E_{\pi}$ depends on intramolecular factors alone, which will be virtually constant in each of the three systems. As the double bonds approach each other, they begin to interact, so that the intramolecular energy levels of the π and π^* orbitals are perturbed. This process is illustrated in Figure 4.

The analysis in the figure considers the *p* atomic orbitals which form the π_{AB}, π_{CD}, π^*_{AB} and π^*_{CD} molecular orbitals of the monomers. At close monomeric separations, a better approximation to the orbital wave functions is given by mixing the monomeric π-orbitals, to give the four linear combinations $(\pi_{AB} + \pi_{CD})$, $(\pi_{AB} - \pi_{CD})$, $(\pi^*_{AB} + \pi^*_{CD})$ and $(\pi^*_{AB} - \pi^*_{CD})$. When the two monomers are separated by a large distance, the required photon energy is given by $E_{\pi^*_{AB}} - E_{\pi_{AB}}$. However, when the monomers are in close proximity, as in B-*p*Br-BCP, the required photon energy is $E(\pi^*_{AB} + \pi^*_{CD}) - E(\pi_{AB} - \pi_{CD})$, which is considerably smaller. Thus as the monomers approach one another, the minimum frequency of the light required for dimerisation passes from the uv into the visible region of the electromagnetic spectrum.

It appears, for these three systems at least, that the overlap of the monomeric orbitals is the criterion by which the degree of solid-state reactivity can be understood, and possibly predicted. The influence of the shape of the reaction cavity on the reactivity of a particular compound is minimal, as the disposition of the monomer reactive centres appears to be more important. The parameter R_2 seems not to be a useful structural parameter in considering the reactivity or tendency to crack of a given system. But the concept of the reaction cavity will be seen to be helpful in rationalising whether a given system prefers to react in a homogeneous or a heterogeneous manner in forming photo-products.

THE ROLE OF THE REACTION CAVITY IN DETERMINING WHETHER THE PREFERRED DIMERISATION MECHANISM IS HOMOGENEOUS OR HETEROGENEOUS

Elementary equilibrium thermodynamics are capable of describing the phase characteristics of the photo-dimerisation in terms of the model of a regular solid solution. Suppose that, at the start of the reaction, $2N$ monomer molecules are present (i.e. N monomer-pairs), and at the end of the reaction, N dimers are present. At a

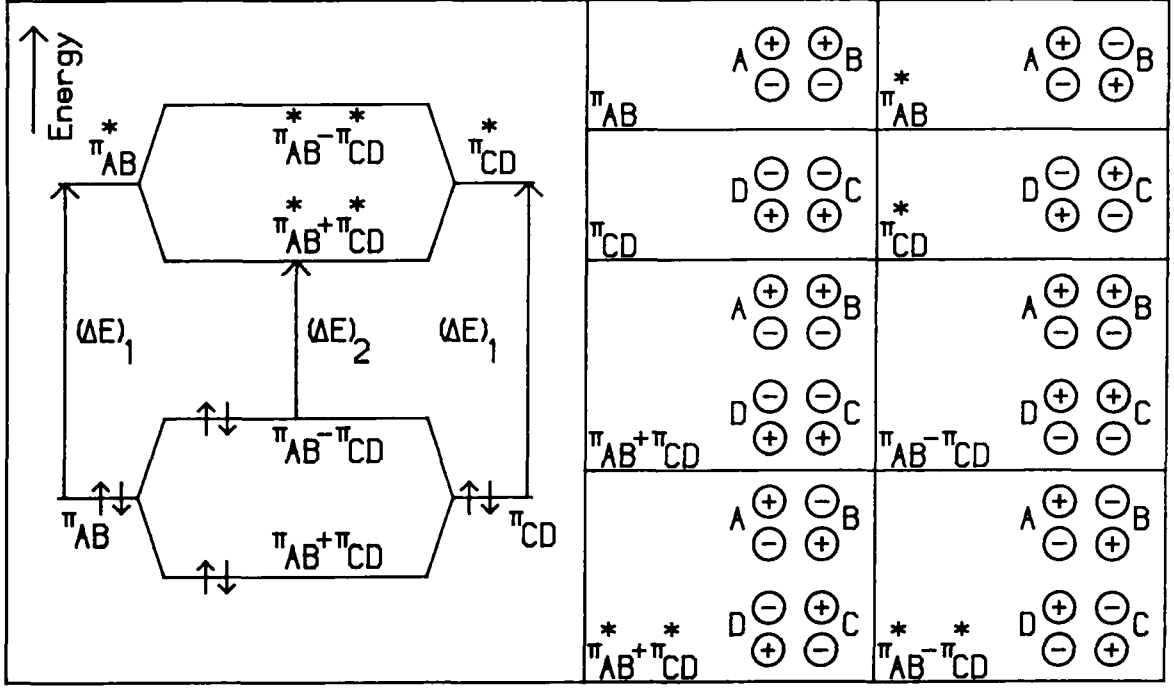

FIGURE 4 An analysis of the photon energy required to excite an electron from a π to π^* orbital in one of the reacting monomers. At large monomeric separations, this energy corresponds to $(\Delta E)_1$, but at smaller separations, intermolecular orbitals are formed, thereby reducing the excitation energy to $(\Delta E)_2$.

fractional conversion, x, $(1 - x)N$ monomer-pairs are present, together with xN dimers. At fractional conversion x, a given monomer-pair, or dimer, will be coordinated by Zx dimers and $Z(1 - x)$ monomer-pairs, where Z is the number of monomer-pairs (or dimers) coordinating a given monomer-pair (or dimer) in the structure. This is given the value of 4, in accordance with Figures 2(a) and (b). Consequently the number of (monomer pair)-(monomer pair) pairs in the crystal is equal to $4N(1 - x)^2/2$, the number of dimer-dimer pairs is equal to $4Nx^2/2$, and the number of (monomer pair)-dimer pairs is $4Nx(1 - x)/2 + 4N(1 - x)x/2 = 4Nx(1 - x)$. The factor of two enters the denominators in order to avoid counting pairs twice.

Thus the internal energy of the system at conversion x is given by

$$U = 4N(1 - x)^2 V_{MM}/2 + 4Nx^2 V_{DD}/2 + 4Nx(1 - x) V_{DM} \tag{3}$$

In order to calculate the internal energy of *mixing*, the energy of pure monomer and pure dimer existing in separate phases at conversion x (as in a heterogeneous mechanism) must be subtracted away. So the internal energy of mixing, ΔU, is given by

$$\Delta U = \{4N(1 - x)^2 - 4N(1 - x)\} V_{MM}/2 + \{4Nx^2 - 4Nx\} V_{DD}/2 + \{4Nx(1 - x)\} V_{DM} \tag{4}$$

which reduces to

$$\Delta U = 4wNx(1 - x) \tag{5}$$

where

$$w = V_{DM} - 1/2 (V_{MM} + V_{DD}) \tag{6}$$

V_{DM} is the interaction energy of a dimer-(monomer pair) pair, and V_{MM}, V_{DD} correspond to the energies of interaction of two monomer pairs and two dimers respectively. Since the molar entropy of mixing of a monomer-dimer solid solution is given by

$$\Delta S = -R \{x \ln(x) + (1 - x) \ln(1 - x)\} \tag{7}$$

the Helmholtz molar free energy of mixing is

$$\Delta F = 4wx(1 - x) + RT \{x \ln(x) + (1 - x) \ln(1 - x)\} \tag{8}$$

The parameter w has been calculated for the three different systems, by employing pairwise (6-exp) atom-atom potentials of the form $u = -A/r^6 + B \exp(-Cr)$, for which the A, B and C parameters are quoted in Table V.

These values have been extracted from a review by Ramdas and Thomas,[20] with

TABLE V

Parameters A,B and C for the (6-exp) non-bonded potentials used*

Type of interaction	A	B	C	Type of interaction	A	B	C
C . . . C	2376.5	349908	3.60	H . . . Cl	837.1	106267	3.70
C . . . H	523.0	36677	3.67	H . . . Br	1316.0	112071	3.51
C . . . O	1606.0	337274	3.89	O . . . O	1085.3	325097	4.18
C . . . Cl	3818.7	596535	3.63	O . . . Cl	2580.6	574997	3.92
C . . . Br	6003.3	629113	3.44	O . . . Br	4056.9	606399	3.73
H . . . H	114.2	11104	3.74	Cl . . . Cl	6136.2	1016994	3.66
H . . . O	352.1	60082	3.96	Br . . . Br	15165.0	1131108	3.28

*units of A, B, C such that potential u has units kJ mol^{-1} for an interaction distance, r, specified in Å

the assumption of a geometric mean combining law for the majority of the A and B parameters, and an arithmetic mean combining law for the C parameters.[21] Calculation of V_{MM} and V_{DD} is straightforward, since the known monomer and dimer crystal structures are used. However, calculation of V_{DM} is not quite so simple, as the value obtained is strongly dependent on the coordinates chosen for the dimer in the monomer matrix.

An appropriate choice of dimer coordinates can be guided by potential energy-minimisation techniques, which give an optimised value of V_{DM}. The PCK6 package[22] had been adapted expressly to calculate the energies of point defects in molecular crystals,[23] and the inclusion of a dimer within the monomer crystal structure can be regarded as a special type of point defect. A problem regularly encountered with this technique, however, is that the refined energy of interaction of a dimer in a monomeric matrix will depend, to some extent, on the coordinates assigned to the dimer at the *start* of the refinement. Thus one cannot be confident that the energy obtained corresponds to a *global*, and not a local minimum. In order to tackle this problem, one author has expressed support for a stochastic (or Monte Carlo) method, in which each atom in a molecule is subjected to a sequence of random "kicks," prior to an energy minimisation procedure.[24] If this iterative process is carried out over a long timescale, it is argued, the exploration of crystal and molecular conformational space will be sufficiently extensive to identify the global energy minimum.

An alternative method, which has been adopted here, is to use a computational refinement algorithm together with a systematic and comprehensive (i.e. *non-random*) variation in the starting points of the energy-refinements. A judgment of the appropriate method to use can only be made from a knowledge of the problem in hand. In this case, the structural and conformational refinement variables can be restricted to translations and rotations of rigid dimer molecules about their centres of symmetry. The availability of experimental conformational information for the dimer molecules (from X-ray diffraction studies),[8,17] together with the known monomer crystal structures,[8,11,12] permits the number of refinement variables to be restricted in this manner.

1458 different starting points (sets of dimer coordinates) have been used in each of the BBCP, *p*-ClBBCP and B-*p*-BrBCP systems. These correspond to the dimer coordinates generated by Mechanisms 1 and 2 (see previous section), combined with rotations of these coordinates by up to 16° about the x, y and z Cartesian axes. Thus a range of angles (θ_x, θ_y, θ_z) from ($-16°$, $-16°$, $-16°$) to (16°, 16°, 16°) has been covered. A step-size of 4° between adjacent starting angles has been used, i.e. each angle θ_x, θ_y and θ_x can take on a value of $-16°$, $-12°$, $-8°$ . . . 0° . . . 16°. The subsequent energy-refinements from these starting coordinates, employing a modification of Williams' PCK6 program,[22] permitted translations and rotations of the dimer molecules from their starting positions, with the molecular conformations of the dimers taken as rigid. The assumption of conformational rigidity can be justified on two grounds: first, a limited investigation, in which the dihedral angle about bond RS (Figure 1(a)) was allowed to vary, did not lead to lower interaction energies; and secondly, it is sensible to utilise the experimentally determined dimer conformations in the refinement process.

The results of the energy-minimisation are given in Table VI. The first two columns quote values of V_{MM} and V_{DD}, which are calculated directly from the crystal structures of monomers and dimers respectively. The first V_{DM} column corresponds to the unrefined value given by Mechanism 1; the second V_{DM} entry corresponds to the unrefined value given by Mechanism 2; and the column headed V_{DM} (refined) gives values obtained from the refinement procedure described. These are used to calculate w (equation (6)), since they represent the global energy minima of the dimer molecules in their respective monomeric matrices. From Equation (8), the negative values of w for BBCP and *p*Cl-BBCP mean that ΔF is negative for all values of x in these two systems. By comparison, V_{DM} for B-*p*Br-BCP is sufficiently large and positive to give rise to a positive value of ΔF for essentially all degrees of conversion. This is shown in Figures 5(a) and 5(b), for which T in Equation (8) is taken to be 293 K.

So structural considerations alone show that the coordination of dimer molecules by monomer molecules is favoured in BBCP and *p*Cl-BBCP, but in the B-*p*Br-BCP system, coordination of dimer molecules by other dimer molecules is favoured. Thus in BBCP and *p*Cl-BBCP there is a tendency towards a homogeneous mechanism of dimerisation, but in B-*p*Br-BCP, a heterogeneous mechanism is favoured:

TABLE VI

V_{MM}, V_{DD}, V_{DM} and w for BBCP, *p*Cl-BBCP and B-*p*Br-BCP*

System	V_{MM}	V_{DD}	V_{DM} Mech. 1	V_{DM} Mech. 2	V_{DM} (refined)	w
BBCP	−60.30	−51.93	−52.69	−55.54	−59.44	−3.325
p-Cl-BBCP	−64.83	−58.00	−62.07	+60.42	−64.24	−2.825
B-*p*Br-BCP	−62.65	−60.53	−46.55	−46.02	−55.30	+6.290

* all values quoted in kJ mol^{-1}

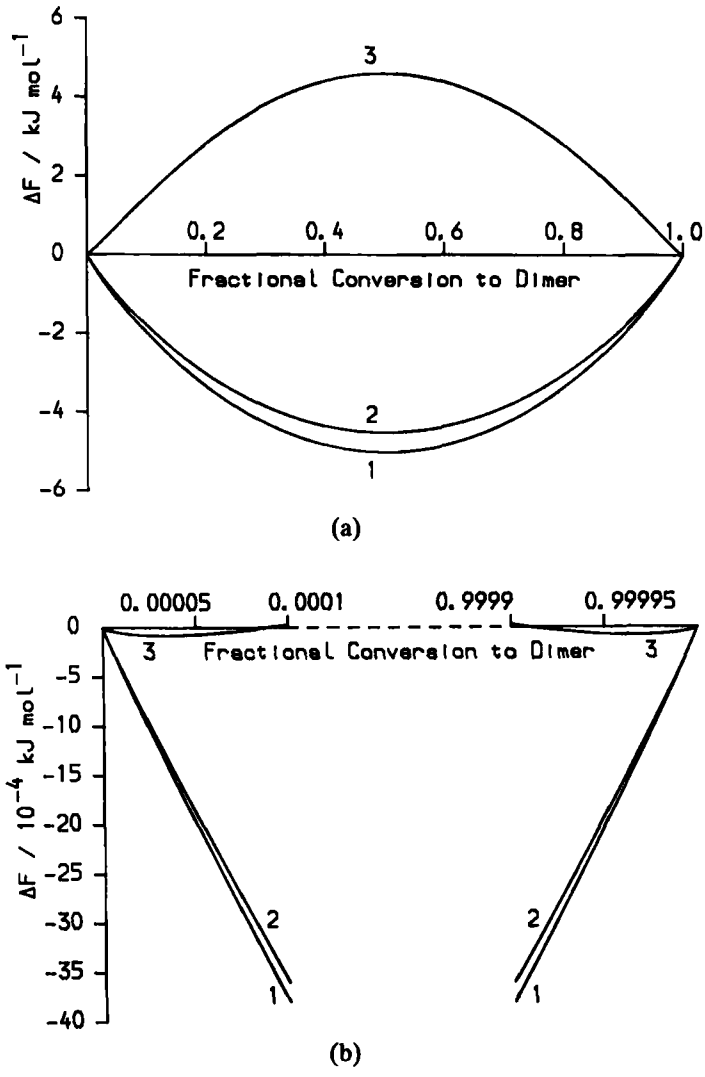

FIGURE 5 Variation of the free energy of mixing as a function of fractional conversion to dimer (1: BBCP; 2: *p*-Cl-BBCP; 3: B-*p*Br-BCP). (a) Variation over the whole course of the dimerisation reaction; (b) Expansion of (a) at very small and very large fractional degrees of conversion. At a very small fractional conversion (< 0.0001), there is a small driving force towards the homogeneous formation of B-*p*-BrBCP dimer within the parent monomer phase. Similar considerations hold at large fractional conversions (> 0.9999), concerning solubility of monomer molecules in the dimer phase.

the monomer and dimer do not mix, but are separated by a reaction front. The physical basis of the positive value of w in B-*p*Br-BCP is the presence of unfavourable Br. . .C and Br. . .H short non-bonded interactions between the dimer molecule and the monomer molecules forming the wall of the reaction cavity.

In a photochemical reaction of this kind, it is not just structural considerations

which determine whether a reaction proceeds homogeneously or heterogeneously. It is also important to consider whether dimerisation occurs at or near the site of photon-absorption, or not. One of the unique features of molecules in the crystalline state is that the excitation energy given to an individual molecule by a photon can pass to another molecule. Whether this transport of excitation energy (manifested by excitons) takes place depends on the extent of exciton delocalisation. The motion of excitons from one molecule to another is strongly dependent on temperature, as a result of electron-phonon coupling, and it can be both wave-like and diffusive in nature. A consequence of strong electron-phonon coupling in a photoreactive crystal is the localisation of excitation energy.[25] In the caseof B-*p*Br-BCP, a heterogeneous mechanism of dimerisation would require the transport of excitons to the reaction front, and *not* prior reaction to form dimers at, or near, the site of absorption. However, the observed cracking of B-*p*Br-BCP[8] is probably due to dimers being formed *homogeneously* at the locations of energy absorption. The particularly favourable overlap of the double bonds in this system is conducive to reaction at the sites of photon-absorption. Br. . .C and Br. . .H repulsive interactions between the dimer and the walls of the reaction cavity would give rise to stress, and consequent cracking.

Control over whether a reaction proceeds homogeneously or heterogeneously is clearly desirable, if cracking is to be avoided. It is conceivable that the homogeneous absorption of energy could be suppressed by irradiation of the crystal at a wavelength for which it has a high extinction coefficient. The photo-product would be expected to form near the surface of the crystal. This technique could be used to good effect in systems such as B-*p*Br-BCP, in which a heterogeneous mechanism of dimerisation is favoured from structural considerations. Investigations of the photo-polymerisation of distyrylpyrazine have shown the potential of this approach.[26] Irradiation of the compound with the 478 nm line of an argon-ion laser can form an oligomeric product, distributed uniformly throughout the monomer structure, without the separation of a separate phase. By comparison, radiation of wavelength 436 or 365 nm, for which the crystal has a high extinction coefficient, can give rise to a separate oligomeric or polymeric phase, which is formed near the surface of the monomer crystal. Some systems react heterogeneously, without the use of special irradiative techniques. Anthracene is a classic example of such a system. It undergoes a [4+4]-photodimerisation reaction at point defects, which act as traps for excitons. These defects are formed at the reaction front, as the reaction proceeds throughout the crystal.[27]

Thus an analysis of the crystal structures of reactants and photo-products, together with a simulation of the reaction cavity, indicates whether a homogeneous or heterogeneous mechanism of reaction is favoured thermodynamically. The type of mechanism which results depends on the transport of excitons from one site to another: delocalised excitons permit a heterogeneous mechanism, whereas strongly localised excitons favour a homogeneous mechanism. The facile reaction of an excited molecule with an adjacent ground-state molecule is also conducive to homogeneous reaction. Further work on the systematic variation of the wavelength of radiation, temperature, and on the crystal structures of the reactive centres would be highly beneficial.

CONCLUSION

The structural characteristics of the second stage of a solid-state photochemical reaction have been simulated on a computer. This stage involves irradiation of the crystal with light of the appropriate wavelength, at a suitable temperature. The systems chosen for simulation belong to the BBCP family of compounds, which undergo [2+2]-photodimerisation reactions. Two empirical parameters, R_1 and R_2 have been defined, which monitor the changes in unit cell constants and the changes in atomic coordinates respectively in passing from monomer to dimer. R_1 can be correlated with the tendency of the crystal to crack, but R_2 cannot be correlated with the characteristics of the reactions. The rates of reaction, and the wavelengths of radiation required to cause reaction can be rationalised in terms of the geometry of overlap of the double bonds in the monomer-pairs related by centres of symmetry.

The question of whether a solid-state photoreaction proceeds homogeneously or heterogeneously is related to structure and to the absorption and transport of excitation energy. A structural study of BBCP, *p*Cl-BBCP and B-*p*Br-BCP, which uses non-bonded potentials to calculate energies of interaction, has shown that there is a thermodynamic driving force towards a homogeneous reaction in BBCP and *p*Cl-BBCP, but a heterogeneous mechanism is favoured in B-*p*Br-BCP. However, a homogeneous mechanism is likely to obtain in the B-*p*Br-BCP system as well, since reaction to form dimers at or near the sites of photon absorption is rapid.

Acknowledgments

A large part of this work was carried out at the University of Cambridge, as a member of Professor J. M. Thomas' Solid State Chemistry group. The author wishes to thank Professor Thomas and his colleagues for their encouragement. Acknowledgement is also made of the University of Leeds Computer Service, for the provision of resources on the AMDAHL 580 Computer.

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