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CONSEQUENCES OF LATTICE RELAXABILITY IN SOLID STATE PHOTODIMERIZATIONS

G. S. MURTHY, P. ARJUNAN, K. VENKATESAN * AND V. RAMAMURTHY *

Department of Organic Chemistry, Indian Institute of Science,
Bangalore 560 012, India.

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Abstract - With the view to understand the photobehaviour of olefinic crystalline compounds lattice energy calculations have been performed for a number of photodimerizable olefins. It is shown that to rationalize the photoreactivity of the compounds, dynamic topochemical concepts have to be invoked. Although the calculations have been carried out using the ground state geometry with the dispersion constants applicable to the ground state, the results are in agreement with the experimental observations. The limitations of the approach employed are pointed out.

INTRODUCTION

The science of solid state organic chemistry, and particularly the area of lattice control over reaction pathways now seems to be entering a period of flowering and growth. There is no doubt that with deeper understanding of intermolecular interactions and of topochemistry, solid state organic reactions could be planned and exploited in synthetic organic chemistry. Schmidt and co-workers[1] at the Weizman Institute studied systematically the factors that govern the course of organic solid state, especially photoinduced reactions. As a result of their extensive studies on the photodimerization of cinnamic acids, Schmidt has drawn attention to the fact that not only must the double bonds of the reacting monomers be within ~ 4.2 Å, they must also be aligned parallel for cycloaddition to occur[2]. Schmidt has formulated the geometrical criteria for dimerization only with the view of inferring how precisely the π -electron system of the reacting double bonds must be aligned in the crystal lattice for reaction to occur. The Schmidt's criteria for dimerization are landmarks in organic solid state photochemistry and are used as rules for an understanding of a large number of $[2+2]$ photodimerization reactions of widely varying structures. However, very recent studies on the photodimerization of olefinic crystals have brought to light several examples which deviate significantly from the well accepted topochemical principles[3-18]. However, the exceptions observed and discussed in detail below should not be construed as serious violations of Schmidt's rules. Rather all the experimental observations should be integrated into the original basic ideas by widening apparent limitations and scope. Examples of exceptions to original topochemical principles are summarized in Tables 1 and 2.

The topochemical postulates as understood now are with reference to molecules which have in their ground state π -orbitals favourably juxtaposed and upon excitation small movements of atoms take place leading to a dimer of specific stereochemistry. This concept of preformation is obviously deficient in atleast two respects. Firstly, it does not take into consideration the importance of nearest neighbours. The role of the nearest neighbours is reduced to that of passive spectators during the evolution of the dimer. Secondly, it does not give due consideration to the changes those may be caused by molecular excitation. In this context, Cohen[19] has introduced the concept of "reaction cavity" which gives due importance to the presence of nearest neighbours. More recently, Craig[20] has emphasized the possible effect of electronic excitation in a molecular crystal. He has advanced a new concept termed "dynamic preformation". We illustrate below that these concepts which are important refinements of original "topochemical principles" allow one to understand many photoreactions which are apparent violations of original topochemical rules.

The observed situation with 7-methoxycoumarin[16] is of special importance in this connection as this crystal was the precursor to all the attempts at unification discussed in this paper. X-ray crystal structure analysis of 7-methoxycoumarin reveals that the reactive double bonds are rotated by 67.5° with respect to each other, the centre-centre distance between the double bonds being 3.83 Å. Inspite of this unfavourable arrangement, photodimerization occurs in the crystalline state yielding syn head-tail dimer as the only product. From the irradiation time versus % yield of dimer for cases in which the reactions must be defect-initiated (e.g. 7-methylcoumarin and 4-methyl-6-chlorocoumarin) as well as those in which the reaction is topochemical (e.g. 7-acetoxycoumarin and 7-chlorocoumarin) it was observed that in the former situation, there is a significant induction period whereas in the latter no induction period was observed. As 7-methoxycoumarin behaves very much like the ones in which the reaction is topochemical it seems reasonable to rule out defects as the possible loci for the reaction.[4,16,21] Thus the reactivity of 7-methoxycoumarin necessiated that the motional aspects of the molecules in the crystal lattice during the course of the reaction must be introduced when we try to understand the photoreactivity via topochemical postulates.

In order to gain an insight into the role of dynamic topochemical factors and environmental effects on the reactivity, lattice energy calculations have been performed on 7-methoxycoumarin.[21] Encouraged by the results, we attempted to generalise this approach by applying the methodology to other reported examples which are apparent violations of the topochemical principles. Although lacking rigour, the results obtained using this approach are revealing. A perusal of the literature shows that the molecules investigated for their photoreactivity in the solid state could be divided broadly into the following categories: (i) crystals with the reacting partners properly juxtaposed and photoreactive; (ii) crystals with the reacting partners improperly juxtaposed and photoinert; (iii) crystals with the reacting partners properly juxtaposed but photoinert and (iv) crystals with the reacting partners improperly juxtaposed yet photoreactive. In addition there are a few examples in which there are more than one topochemically permitted dimers, yet only one of them is preferred. We illustrate below with examples from each one of these categories that the simple lattice energy calculations performed here could be of considerable help in understanding the solid state photobehaviour of organic molecules.

METHODOLOGY

The energy was calculated by a pair-wise van der Waal's attractive and repulsive potentials as follows:

$$E = - \sum_{i}^{\text{one cell}} \sum_{j=1}^{\text{all cells}} A_i A_j / r_{ij}^{6} + \sum_{i}^{\text{one cell}} \sum_{j=1}^{\text{all cells}} D_i D_j / r_{ij}^{12}$$

The first and second terms in the above equation represent the van der Waal's attractive and repulsive contributions respectively; r_{ij} is the distance between ith and jth atoms. The contributions due to Coulombic interactions were not included for the reason to be mentioned in the discussion section. The constants used (A_i and D_i) are given in Table 3.[22] The program WMIN developed by Busing[23] was used in the calculations of the lattice energy.

The ultimate ideal moelcular orientation to be achieved, as proposed by Schmidt[1] is the one in which maximum overlap between the π -orbitals occurs. This is realized when the angles θ_1, θ_2 and θ_3 are 0°, 90° and 90° respectively (Fig. 1). θ_1 is the angle of twist between the double bonds with respect to each other when projected down the line perpendicular to the plane containing one of the double bonds and atoms connected to this double bond. θ_2 is the angle of the parallelogram formed by the pair of potentially reactive double bonds. θ_3 is the dihedral angle between the parallelogram formed by the double bonds and the plane containing one of the double bond carbons and atoms connected to them. D_1 and D_2 are the displacements of the double bonds with respect to each other when looked down the line defined in connection with θ_1 above. d is the centre to centre distance between the double bonds (Table 4). It may be noted that the values of D_1 and D_2 are proportional to the values of θ_2 and θ_3 respectively. More the deviation of θ_2 and θ_3 from 90°, larger would be the values of D_1 and D_2. When the values for these angles differ from ideal values, necessary rotations and translations were given to bring them to ideal geometries for dimerization. A right handed orthogonal system of coordinates was chosen in two different ways with the origin either at the midpoint of the reactive double bond (Fig. 2(b)) or at the centre of gravity of the molecule (Fig. 2(a)). To achieve $\theta_1 = 0°$, rotation was performed about the X-axis as shown in Fig. 2(a). However to reach $\theta_2 = \theta_3 = 90°$ i.e. $D_1 = D_2 = 0$ Å from the initially observed values, rotations or translations along Y and Z-axes were performed Fig. 2(b) . In all the calculations the molecules were treated as rigid-bodies and the neighbouring molecules were also given appropriate rotations (θ_1, θ_2 and θ_3) and translations (D_1 and D_2) so as to preserve the space group symmetry.

In the process of bringing θ_1, θ_2 and θ_3 values to ideal values, the distance (d) between the double bonds decreases except when they are related by a translational symmetry. In order to keep 'd' within ±0.1 Å from the original values, appropriate translations were performed along X-axis (Fig. 2(b)). The final values of the parameters θ_1, θ_2 and θ_3 achieved were within ±1° from the ideal values.

The examples investigated, their crystallographic data, reactivity pattern and the stereochemistry of the dimer, if formed, are given in Table 5. Initial values of θ_1, θ_2, θ_3, D_1 and D_2, initial and final lattice energies and the total increase in the lattice energy are recorded in Table 4.

RESULTS

(I) Properly justaposed and photoreactive molecules:-

In order to test the applicability of the lattice energy calculations of the type performed here and for understanding the dynamics of photoreactivity in the solid state the following five photoreactive systems which generally obey the well accepted topochemical principles were investigated.

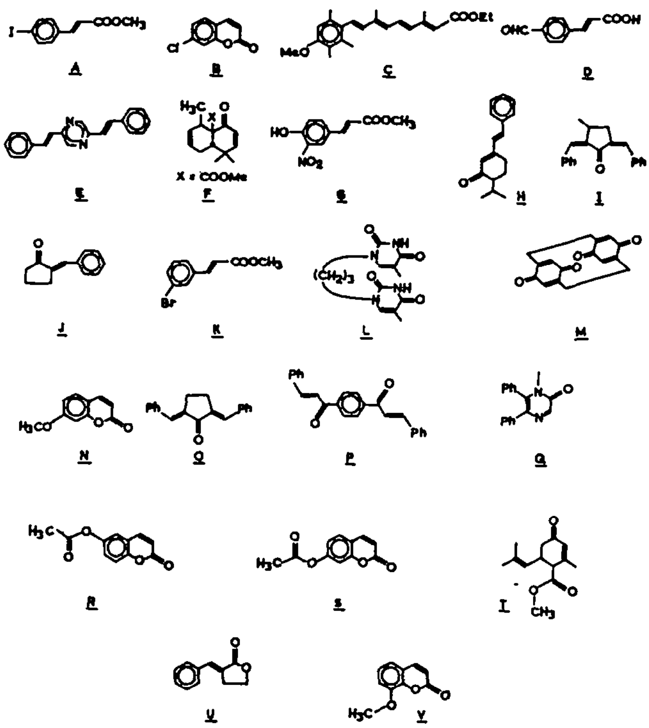


Chart 1

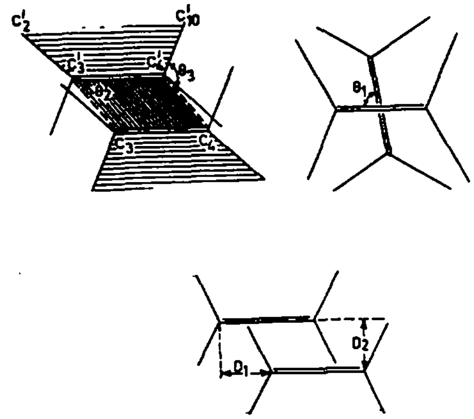


Fig.1

The geometrical parameters used in the relative representation of the double bonds.

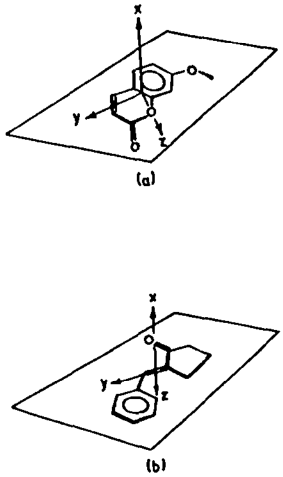


Fig.2

Choice of the origin of the right handed coordinate system for rotations and translations (a)at the centre of mass (b)at the midpoint of the reactive double bond.

Table 1

Examples of Exceptions to Original Topochemical Principles regarding Distance[a]

Compound	Distance between reactive double bonds		Reactivity	Nature of Dimer	Ref.
Methyl-p-iodo cinnamate (A)	β-type	4.3 Å	Yes	minor symmetric	1
7-Chlorocoumarin (B)	β-type	4.45 Å	Yes	Syn head-head	4
Eteretinate (C)		4.4 Å	Yes	-	5
p-Formyl cinnamic acid (D)	β-type	4.825 Å	Yes	minor symmetric	6
Distyryl pyrazine (E)		4.19 Å	No	-	7
Enone (F)		3.79 Å	No	-	8
4-Hydroxy-3-nitrocinnamate (G)		3.78 Å	No	-	9
Benzylidene-dl-pipertone (H)		4.0 Å	No	-	10
(+) 2,5-Dibenzylidene-3-methyl cyclopentanone (I)		3.87 Å	No	-	11
2-Benzylidene cyclopentanone (J)		4.14 Å	No	-	12

[a] For structures of compounds see Chart 1.

Table 2

Examples of Exceptions to Original Topochemical Principles regarding Parallelism of Double Bonds[a]

Compound	Rotational angle of one double bond with respect to the other	Reactivity Dimerization	Ref.
Methyl m-bromocinnamate (K)[b]	38.2°	No	13
1,1'-Trimethylene-bis-thymine (L)	6°	Yes	14
2,2 (2,5)-Benzoquinophane (M)	3°	Yes	15
7-Methoxycoumarin (N)	67.5°	Yes	16
2,5-Dibenzylidene cyclopentanone (O)	56°	Yes	11
1,4-Dicinnamoyl benzene (P)	28.5°	Yes	17
1-Methyl-5,6-diphenyl pyrazine-2-one (Q)	24°	Yes	18

[a] For structures of compounds see Chart 1.

[b] The postulate was formulated on the basis of this compound.

Table 3

Non-bonded Interaction Parameters used for the Lattice Energy Calculations

Atom type	$A_i\ A_j$ (kcal mol^{-1} Å^{-6})	$D_i\ D_j \times 10^{-3}$ (kcal mol^{-1} Å^{-12})
Cl...Cl	2979.96	8178.66
O...O	259.53	152.84
C...C	421.07	633.80
H...H	29.05	6.91
Cl...O	876.21	1118.05
Cl...C	1120.07	2276.76
Cl...H	293.97	239.10
O...C	330.51	314.32
O...H	86.68	33.90
C...H	110.46	70.07

Table 4

Initial Geometrical Parameters, Initial and Final Energies and the Total Increase in Energy for the Systems Investigated

Sl. No.	Compound*	Distance between the double bonds (Å)	Initial Values						Final Energy	Total increase in energy
			θ_1	θ_2	θ_3	D_1 (Å)	D_2 (Å)	E_o (kcal mol^{-1})	E_f (kcal mol^{-1})	$E = (E_f - E_o)$ (kcal mol^{-1})
			(degrees)							
1.	R	3.900	0.0	94.1	118.3	0.28	1.92	-21.2	-12.9	8.3
2.	S	3.833	0.0	106.4	110.3	1.08	1.32	-20.1	147.6	167.6
3.	T	3.860	0.0	102.2	108.1	0.82	1.23	-19.7	10.00	29.7
4.	U	3.666	0.0	109.3	77.0	1.21	0.72	-18.5	-13.6	4.9
5.	V									
	Pair I	4.070	0.0	122.4	63.8	2.18	1.56	-37.2	7.8	45.0
	Pair II	3.870	0.0	117.4	67.7	1.78	1.33	-37.2	- 9.1	28.1
6.	F	3.790	0.0	81.6	63.5	0.55	1.60	-21.5	1482.9	1504.4
7.	N	3.830	67.5	109.9	66.5	-	-	-37.3	162.8	200.1
8.	P									
	Pair I	4.03	28.5	101.2	99.2	-	-	-36.0	2.8	38.8
	Pair II	3.93	28.5	101.2	99.2	-	-	-36.0	4.8	40.8
9.	K	3.93	38.2	65.2	104.8	-	-	-20.4	6705.6	6726.0
10.	B									
	Translated	4.454	0.0	131.8	85.3	2.97	0.29	-17.9	159.1	177.0
	Centrosymmetric	4.120	0.0	127.9	73.0	2.53	0.94	-17.9	18064.9	18082.8
11.	J	4.143	0.0	119.1	75.4	2.01	1.00	-18.5	- 5.3	13.2
12.	H	3.915	0.0	105.2	86.4	1.07	0.17	-25.4	-24.6	0.8

* For structures of the compounds see Chart 1 and Table 5.

6-Acetoxycoumarin: The reactive double bonds are related by a translational symmetry. Only rotations were performed to obtain the final orientations. Origin was chosen at the midpoint of the double bond as shown in Fig. 2(b). Rotations were performed along the Y-axis at 4° interval from 0° to -28° followed by 5° along the Z-axis. The total rise in energy is 8.3 kcal mol^{-1}. The packing diagrams of the initial and final orientations are shown in Fig. 3.

7-Acetoxycoumarin: Here too the reactive molecules are related by a translational symmetry. Origin was chosen as shown in Fig. 2(b). Only rotations were performed at an interval of 2° along the Y and the Z-axes upto -19° and 17.2° respectively. The total increase in energy is 167.5 kcal mol^{-1}.

Methyl-6-isobutyl-2-methyl-4-oxocyclohex-2-ene-carboxylate: The reactive double bonds are related by an inversion centre. With the origin as in Fig. 2(b), translation motions at intervals of 0.02, 0.04 and 0.06 Å upto 0.20, 0.409, 0.614 Å along the X, Y and Z-axes respectively were performed to achieve the final orientations. The total rise in energy is 29.7 kcal mol^{-1}.

α -Benzylidene-γ-butyrolactone: The reactive double bonds are related by a centre of inversion. The origin was chosen at the double bonds as in Fig. 2(b). Only translations upto -0.15, 0.606 and 0.36 Å along the X, Y and Z-axes respectively were performed at intervals of 0.025, 0.101 and 0.06 Å. The total increase in energy is 4.9 kcal mol^{-1}.

8-Methoxycoumarin: There are two independent molecules in the asymmetric unit (Table 4). Both the molecules react with their centrosymmetrically related partners. One pair was translated at a time, keeping the other pair at the original position in the lattice. The origin was chosen as shown in Fig. 2(b). For the molecular pair (I) (Table 4) translations were performed at intervals of 0.05, 0.11 and 0.08 Å upto -0.45, -1.09 and 0.782 Å along X, Y and Z-axes respectively. As for the molecular pair (II) the total motions given were 0.40, -0.89 and 0.665 Å along the X, Y and Z-axes respectively. The final rise in energies for molecular pairs (I) and (II) are 45.0 and 28.1 kcal mol^{-1} respectively.

(II) Improperly juxtaposed and photostable compounds:-

In order to confirm the generality of the method adopted here, a system which is photoinert because of unfavourable geometry in the crystalline state was chosen for analysis. A well known case in this context is methyl-m-bromocinnamate.

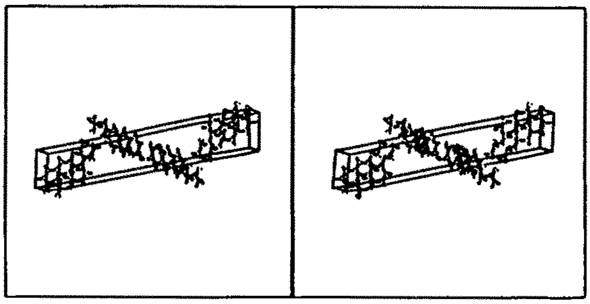
Methyl-m-bromocinnamate: In this compound the reactive double bonds are related by the a-glide plane. The double bonds are in a twisted orientation in the ground state crystal lattice. Origin was chosen at the double bond as shown in Fig. 2(b). Rotations of 16.8°, 10° and 19.5° were performed along the X, Y and Z-axes respectively followed by a translation of -0.23 Å along the Y-axis in 10 increments. The rise in energy to achieve final orientations is as large as 6726.0 kcal mol^{-1}. It is significant that the alternate choice of coordinate system, namely choosing origin at the centre of gravity (Fig. 2(a)) also resulted in a rise in energy by $\sim$ 7,000 kcal mol^{-1}. The packing diagrams of the initial and final orientations are shown in Fig. 4.

(III) Properly juxtaposed but photoinert molecules:-

Prompted by the success of the lattice energy calculations in rationalising the topochemical systems, we decided to carryout calculations on non-topochemical systems results of which are reported in the following sections.

4,4,8 -Trimethyl-8aß-carbomethoxy-4aß,5,8,8a-tetrahydro-1(4H)-naphthalen-1-one: The reactive double bonds are related by an inversion centre. Origin was chosen as in Fig. 2(b) for the translations performed to achieve the final orientations.

6-ACETOXY COUMARIN INITIAL ORIENTATION



6-ACETOXY COUMARIN FINAL ORIENTATION

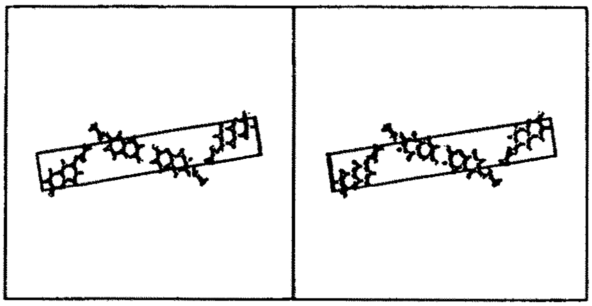
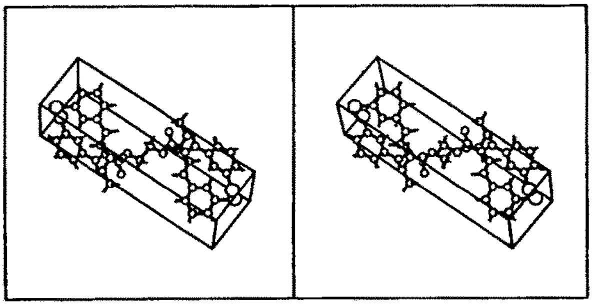


Fig.3

Packing stereo-diagrams of initial(above) and final(below) orientations of 6-acetoxycoumarin.

METHYL M-BROMO CINNAMATE --INITIAL ORIENTATION



METHYL M-BROMO CINNAMATE --FINAL ORIENTATON

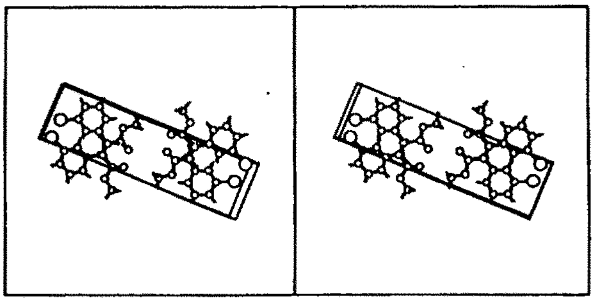


Fig.4

Packing stereo-diagrams of initial(above) and final(below) orientation of methyl-3-bromocinnamate.

Quanta of translations 0.17, 0.267 and -0.55 Å along X, Y and Z-axes respectively in the first step were followed by increments of 0.01 and 0.05 along the X and Z-axes respectively, the total translations along these axes being 0.22, 0.267 and -0.85 Å. The total increase in energy is 1504.4 kcal mol^{-1}. The packing diagrams of the initial and final orientations are shown in Fig. 5.

It is reassuring that the rise in lattice energy is significantly and consistently larger for compounds which are photostable and considerably smaller for the photoreactive ones.

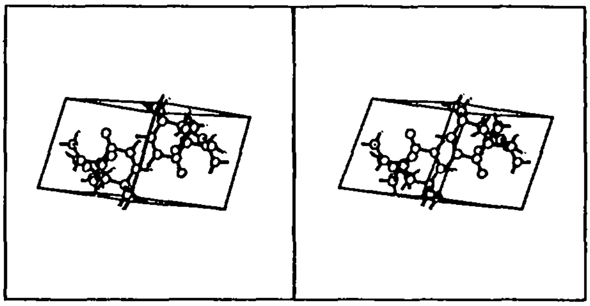
(IV) Improperly juxtaposed and photoreactive molecules:-

7-Methoxycoumarin: The calculations carried out[22] on the monomer of 7-methoxycoumarin showed that a total rotation of 24° of the monomers about the X-axis (Fig. 2(a)) could be realized with an increase in the lattice energy of 24.9 kcal mol^{-1}. More thorough calculations were performed now as detailed below. Origin was chosen at the centre of mass with the X-axis perpendicular to the plane of the molecule, Y-axis in the direction of the double bond and Z-axis perpendicular to the X and Y-axes to make a right handed coordinate system. Rotations of -34° and 9° along the X- and Y-axes respectively were performed at intervals of 5° and 2°. Both the independent molecules in the asymmetric unit were rotated in the opposite sense simultaneously. While the rotation along the X-axis brought θ_1 to zero, rotation along the Y-axis had contributed to avoid intermolecular short contacts. After these operations the origin was shifted to the double bond as in Fig. 2(b) to perform translations so as to reach $\theta_2=\theta_3=90°$. Translations of 0.40, -1.26 and 0.75 Å for the other molecule along the X, Y and Z-axes respectively brought the molecules to ideal juxtaposition. The total rise in energy was 200 kcal mol^{-1}. The packing diagrams for the initial and final orientations are shown in Fig. 6.

1,4-Dicinnamoylbenzene: Molecular centre of symmetry coincides with crystallographic centre of inversion. Thus the asymmetric unit is composed of half of the two molecules occupying different centres of symmetry in the unit cell. Full molecules were generated from symmetry and the energy was calculated in P1 space group. Hence, the energy calculated would be twice that of the real energy and their values are reported in Table 4. It was reported[17] that upon irradiation of the crystals about 90% double dimerized product with a small amount of oligomeric product were obtained. Origin was chosen at the centres of mass of both the molecules and the coordinate system as shown in Fig. 2(a). When the rotation along X-axis was performed to bring the twist angle θ_1 to zero, the increase in energy was very large (>10,000 kcal mol^{-1}). However, when the axis of rotation (X-axis) was chosen as the line joining the centres of the two molecules, the rise in energy to bring θ_1 to zero was very much decreased (60.2 kcal mol^{-1}). A rotation of 16° was given for each molecule in 6 steps to attain $\theta_1=0°$. Now the origin was shifted to one of the double bonds as in Fig. 2(b). As there are two pairs of reactive double bonds, at a time only one pair could be brought into proper juxtaposition. Translations of -0.375, -0.60 Å for one molecule and 0.375, -0.60 Å for the other molecule along the Y and the Z-axes respectively brought the double bond pair (1) into the proper orientation with the total rise in energy of 38.8 kcal mol^{-1}. As for the other pair translations -0.4, -1.644 Å for one molecule and 0.4, -1.644 Å for the other molecule along the Y and the Z axes respectively yielded the final orientation with a net rise in energy of 40.8 kcal mol^{-1}.

It may be noted that after bringing θ_1 to zero, when the translations were performed to set $\theta_2=\theta_3=90°$ to have one pair of double bonds juxtaposed, the other pair of double bonds of the molecule get displaced by as much as 5 Å. Infact this end comes closer to the reactive bond (4.42 Å) of the molecule translated

DERIVATIVE OF NAPHTHALEN-1-ONE



DERIVATIVE OF NAPHTHALEN-1-ONE FINAL ORIENTATION

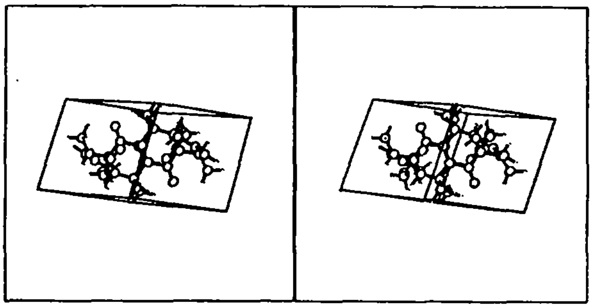
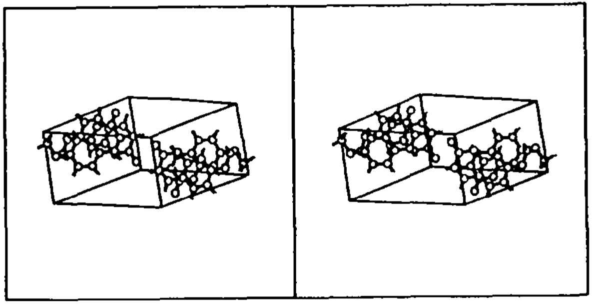


Fig.5

Packing stereo-diagrams of initial(above) and final(below) orientations of naphthalene-1-one derivative.

7-METHOXY COUMARIN --INITIAL ORIENTATION



7-METHOXY COUMARIN --FINAL ORIENTATION

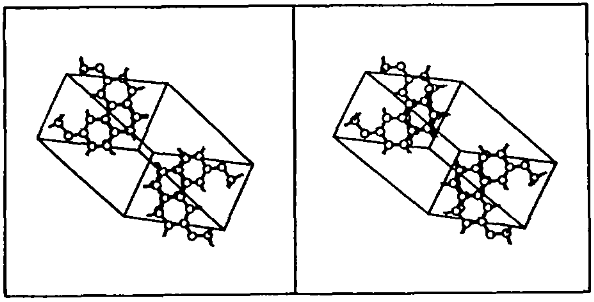


Fig. 6

Packing stereo-diagrams of initial(above) and final(below) orientation of 7-methoxycoumarin.

along a-axis but with θ_2=130° and θ_3=98°. Thus using the methodology adopted here it was not possible to bring simultaneously both the double bond pairs into proper juxtaposition. Perhaps the situation encountered here has relevance to the proposal of Hasagawa and co-workers[17] that the double dimerization is a step-wise process.

But the approximation arising from treating this essentially non-rigid molecule as a rigid body as well as not taking into account the significant changes in the topology of the molecule when the reactive carbons change from sp^2 to sp^3 state should be kept in mind. As discussed later these factors are likely to be crucial in systems such as this.

(V) More than one topochemically permitted dimers, yet only one of them is preferred:-

7-Chlorocoumarin: In this crystal an interesting situation is encountered. The double bonds related by a centre of symmetry as well as the translated pair (along the a-axis) are both well placed for reaction. When the translated molecular pair geometries were brought to ideal values, the unit cell was doubled along the a-axis to accommodate two translationally related molecules in the asymmetric unit. Thus the lattice energy obtained for this calculation would be twice the real value in its magnitude. Hence, the values recorded in Table 4 are half of the calculated values. Origin was chosen as defined in Fig. 2(b). Translations in opposite directions with increments 0.05, 0.15 and 0.015 Å along the X, Y and Z-axes were performed to reach the final values of 0.45, 1.485 and 0.144 Å along these axes. The net increase in energy was 176.9 kcal mol^{-1}. For centrosymmetric pair of double bonds, no doubling in unit cell was done. Choosing the same origin translations of 0.5, 1.267 and 0.468 Å were performed at intervals of 0.05, 0.125 and 0.05 Å along the X, Y and Z-axes respectively. Interestingly in this case the rise in energy was very large (18,082.8 kcal mol^{-1}). This explains the experimental observation of syn H-H dimer in this crystal.

(VI) Miscellaneous:-

Results arrived at via lattice energy calculations on two unusual examples presented below probably brings to light the limitations of the method.

Benzylidenecyclopentanone: Potentially reactive double bonds are related by a crystallographic centre of symmetry. Origin was chosen as in Fig. 2(b). Translations were performed in increments of 0.1 and 0.05 Å upto the final values of 1.0 and -0.475 Å along Y and Z-axes respectively. The net rise in energy was 13.2 kcal mol^{-1}. It was noticed that after bringing the molecules to the final orientation, the energy decreased as the distance between the double bonds decreased. At a distance as low as 3.08 Å the lattice energy was -5.3 kcal mol^{-1} compared to the crystal minimum of -18.5 kcal mol^{-1}. When the distance was increased to 3.80 Å, the lattice energy increased to 2,477.3 kcal mol^{-1}. The situation encountered here is quite opposite to that in other cases analyzed earlier. For example in compound (6) (Table 4) when θ_2 and θ_3 were brought to 90°, without translating along the X-axis, the distance between the double bonds reduces from 3.790 Å to 3.396 Å with the energy increasing to 10,902.5 kcal mol^{-1}. Whereas when the distance was increased to 3.821 Å, the energy value was 1482.9 kcal mol^{-1}.

α-Benzylidene-dl-piperitone: The potentially reactive double bonds are related by an inversion centre. Choosing the origin as in Fig. 2(b), translation of 0.54 Å along Y-axis was provided to bring the double bonds into the ideal orientation. The total rise in energy was 0.8 kcal mol^{-1}. But surprisingly the molecule is photostable.

DISCUSSION

The lattice energy calculations (E) approach described here show that in general the variation in E as the molecules are given necessary movements from the original positions in the lattice such that the π-orbitals are properly oriented, is considerably smaller in photoreactive systems than in the photostable cases. The notable exceptions are cases (11) and (12) (Table 4) which are discussed in detail later.

It must be stressed that the values calculated for E as such have no absolute significance in view of the various approximations used in obtaining the constants and the form of the expression chosen for calculating E. Also in the calculations performed by us, the contributions due to Coulombic terms are not taken into account. It has been verified in one example namely 7-methoxycoumarin that the omission of this contribution did not alter the conclusions reached. However, it must be cautioned that the omission of this term may lead to erroneous conclusions in highly polar molecules. Yet another very important factor to be kept in mind in discussing the results is that all the calculations have been carried out for the ground state geometry with the dispersion constants applicable for the ground state. We have no knowledge whatsoever regarding the polarizability α of the atoms in the excited state of the molecules discussed in this paper. The value of α is dependent upon the distortion of the electron clouds from the normal shapes. For example, in the first excited singlet state of naphthalene α has a measured value of ~ 27 $Å^3$ which is more than for the ground state (~ 17 $Å^3$) and this has a profound influence on the attractive terms of the van der Waal's energy[20]. With all these approximations it is heartening to note that the reactive molecules (1-5, 7, 8 and 10 in Table 4) do not require a large energy to attain the suitable geometry for dimerization from their initial positions in the lattice. The above eight examples definitely provide support to this lattice energy calculations approach in predicting reactivity of molecules in the solid state. Even more remarkable is the fact that in the photostable ones the variation in E is very much larger (cases 6 and 9; Table 4).

An interesting observation was made in the case of 7-chlorocoumarin[4]. Irradiation of crystalline 7-chlorocoumarin yielded a single dimer (70% yield) assigned to have a syn head-head configuration. The packing arrangement reveals that there are two potentially reactive pairs of 7-chlorocoumarin. One pair being translationally related has a centre-centre distance of 4.54 Å. Further, the centrosymmetrically related double bonds are closer, the centre-centre distance being 4.12 Å. The translationally related coumarins are expected to yield, upon excitation, syn head-head dimer whereas the centrosymmetrically related coumarins would give anti head-tail dimer. However, the only dimer obtained on excitation corresponds to the syn head-head dimer. The reason for the absence of reaction between centrosymmetrically related monomers inspite of closer distance is not immediately obvious. However, the lattice energy calculations provide a convincing answer. The rise in energy to achieve the ideal geometry in the crystal lattice for the translated pair was 177 kcal/mole whereas for centrosymmetric pair the energy increase was much larger (18082.8 kcal/mole). It is evident then why the dimerization is preferred between translated pair although the distance criteria alone would lead us to predict the reaction between the centrosymmetric pair.

This approach is also helpful in understanding the non-reactivity of a few molecules inspite of favourable topochemical arrangement. Compound 6 (Table 4), although crystallizes in a lattice arrangement which is ideal for intermolecular [2+2] photodimerization, surprisingly exhibits a complete lack of photoreactivity

Table 5

Crystal Data, Solid State Reactivity and the Nature of the Dimer if formed for the Systems Investigated

Sl. No.	Compound*	Crystal data	Solid State reactivity	Ref.
1.	6-Acetoxycoumarin (R)	$P2_1/n$; a=3.90; b=37.53; c=6.46 Å; β=103.7°; Z=4; d_c=1.475 gm cm^{-3}	Yes Syn H-H	26
2.	7-Acetoxycoumarin (S)	$P2_1/c$; a=3.833; b=22.665; c=10.975 Å; β=96.3°; Z=4; d_c=1.43 gm cm^{-3}	Yes Syn H-H	27
3.	Methyl-6-isobutyl-2-methyl-4-oxo-cyclohex-2-ene carboxylate (T)	$P2_1/c$; a=14.96; b=8.20; c=11.00 Å; β=109.4°; Z=4; d_c=1.16 gm cm^{-3}	Yes Anti H-T	28
4.	α-Benzylidene-γ-butyrolactone (U)	$P2_1/n$; a=11.01; b=5.96; c=14.29 Å; β=108.1°; Z=4; d_c=1.38 gm cm^{-3}	Yes Anti H-T	13
5.	8-Methoxycoumarin (V)	$P2_1/a$; a=7.53; b=13.80; c=16.18 Å; β=102.1°; Z=8; d_c=1.422 gm cm^{-3}	Yes Anti H-T	5
6.	4,4,8α-Trimethyl-8aβ-carbomethoxy-4aβ,5,8,8a-tetrahydro-1(4H)-naphthalen-1-one (F)	$P\bar{1}$; a=8.31; b=11.65; c=8.23 Å; α=98.2°; β=111.6°; γ=106.4°; Z=2; d_c=1.205 gm cm^{-3}	Nonreactive	9
7.	7-Methoxycoumarin (N)	$P\bar{1}$; a=6.83; b=10.67; c=12.60 Å; α=108.2°; β=95.23°; γ=95.22°; Z=4; d_c=1.38 gm cm^{-3}	Yes Syn H-T	17
8.	1,4-Dicinnamoylbenzene (P)	$P\bar{1}$; a=5.80; b=7.92; c=19.31 Å; α=89.1°; β=82.1°; γ=88.7°; Z=2; d_c=1.28 gm cm^{-3}	Yes Double dimerization major product	19
9.	Methyl-3-bromocinnamate (K)	$P2_1/a$; a=7.83; b=5.98; c=21.21 Å; β=99.3°; Z=4; d_c=1.63 gm cm^{-3}	Nonreactive	14
10.	7-Chlorocoumarin (B)	$P2_1/n$; a=4.45; b=30.49; c=5.68 Å; β=91.2°; Z=4; d_c=1.55 gm cm^{-3}	Yes Syn H-H	5
11.	2-Benzylidene cyclopentanone (J)	$P2_1/n$; a=7.47; b=6.82; c=19.00 Å; β=94.1°; Z=4; d_c=1.18 gm cm^{-3}	Nonreactive	13
12.	α-Benzylidene-dl-piperitone (H)	$P2_1/n$; a=6.116; b=16.127; c=14.417 Å; β=96.62°; Z=4; d_c=1.131 gm cm^{-3}	Nonreactive	10

*For structures of the compounds see Chart 1.

when irradiated in the solid state. Scheffer and co-workers[8] have attributed the lack of reactivity to the steric compression developed between the reactive molecules and the nearest neighbours when reactive molecules start to move towards each other. It is indeed remarkable that the photo-inertness of this compound can also be understood on the basis of lattice energy calculations. The rise in energy is as high as 1504.4 kcal/mole for bringing the two molecules to the total π-orbital overlap.

The most noteworthy case discussed in this paper pertains to the situation obtained in 7-methoxycoumarin. X-ray crystal structure analysis of 7-methoxycoumarin[16] reveals that the reactive double bonds, although within the reactive distance are not suitably juxtaposed for dimerization (Fig. 6). We believe that the possible presence of a certain degree of inherent orientational flexibility of the molecule in the crystal lattice is responsible for the unusual behaviour of 7-methoxycoumarin. Lattice energy calculations show that the energy increase to bring the two reactant molecules to proper orientation is only 200 kcal/mole, which is close to the value obtained in many ideally oriented pairs (Table 4). This example when compared with the photoinertness of methyl-m-bromocinnamate[13] is revealing. In this case, similar to 7-methoxycoumarin, the double bonds are not topochemically oriented for dimerization (Fig. 4). The distance between the centres of adjacent double bonds is 3.93 Å but the double bonds are not parallel. The bonds make an angle of 38.2° when projected down the line defined in connection with θ_1 in the methodology and results section. Based on the behaviour of 7-methoxycoumarin one would expect this molecule to undergo dimerization in the solid state. But it is photostable. The reason becomes obvious when one looks at the results of lattice energy calculations. The energy increase to align the moelcules parallel to each other in a geometry suitable for dimerization is quite high (6726 kcal/mole). Such an increase is not expected to favour dimerization. Thus "dynamic preorganization" although could favour dimerization, it is resisted by the nearest neighbours. The photobehaviour of dicinnamoyl benzene[17] (case 8, Table 4) can also be readily rationalized on the basis of lattice energy calculations described in detail in the results section.

The thermal motion of the rigid molecules can be analyzed for their librational motion about the molecular axes. In the case of 7-methoxycoumarin such an analysis has been carried out using the program THMB developed by Trueblood[24]. The major librational axes L_1 and L_2 are nearly in the plane of the coumarin ring (L_1=34.1, 30.4 deg^2, L_2=17.8, 14.4 deg^2 for the two independent molecules respectively) and the minor one L_3 (10.4 and 11.1 deg^2) perpendicular to the ring. Upon irradiation one may expect the librational motion to increase, as part of the energy would be utilized in increasing the thermal energy of the system and thus increasing orientational flexibility. It is quite possible that the two crystallographically independent molecules in 7-methoxycoumarin having extra freedom of motions undergo rotations in the opposite direction which tends to bring the reacting bonds into a favourable position.

It seems relevant to record here an experimental observation made by us on 7-methoxycoumarin and this is concerned with the variation of dimer yield with temperature. The sample of 7-methoxycoumarin was kept at different temperatures and irradiated. It was found that for temperatures 30°, 50° and 70° C the percentage yields of dimer were 17.9%, 23.9% and 17.3% respectively (irradiation time 1 hour and sample amount 10 mg). Far more detailed results of this kind have been recently reported by Hasagawa et al.[25] in the case of 4-(3-oxo-3--phenyl-1-propenyl)benzoic acid and its derivatives. From these results it follows that there is a critical temperature for each compound at which the thermal vibrations of the reacting molecules are most efficient for photodimerization. It seems reasonable to attribute part of the observed variation in yield to changes in the mosaic character of the crystalline sample when changing the temperature.

While the lattice energy calculations allow us to gain an insight into the dynamic aspects of the topochemical correlations, the application of the method has in the same breath raised some questions. For example, cases (11) and (12), according to the calculation of variations in E (Table 4) should be reactive whereas experimentally they are known to be photostable. Infact, both the crystalline compounds have low m.p. ($\sim$60°C) and following irradiation the crystals become sticky. Irradiation at 0°C leaves the crystals intact with no photoreaction. It may be mentioned that the lattice energies calculated in the cases of photoreactive 2,5-dibenzylidenecyclopentanone (Table 2) as well as the photostable (+)2,5--dibenzylidene-3-methylcyclopentanone (Table 1) show very large increase in energy ($>$10,000 kcal/mole) even for small rotations ($\sim$20°) in the lattice. All these cases bring into focus the limitations in our approach. Firstly, in all the calculations the molecule is treated as a rigid-body when carrying out the required rotations and translations in the lattice. This assumption is reasonable in general for molecules without molecular conformational flexibility. But it is too severe an assumption when there are a large number of single bonds about which rotations can occur and indeed it would be necessary to take into account the conformational variations when we calculate lattice energy as the molecules are rotated and translated in the lattice. Secondly, in its reaction pathway involving changes in hybridization of the reacting atoms from sp^2 to sp^3, the lengthy side group attached to a reacting atom would be expected to undergo large scale changes in the molecular topography and hence positional changes in the lattice. The reaction cavity must be of sufficient size to allow for such perturbations. It seems that these changes are very important in cases (11) and (12). Also these factors appear to be very important in understanding the photobehaviour of case (8) (Table 4).

The approach adopted by us in this paper is clearly only a beginning although it has thrown much valuable light on the importance of orientational flexibility and the influence of environments in crystals with rigid molecular systems and their photobehaviour. It remains to be seen whether this lattice energy calculations approach could be of some use in understanding a large number of uni and bi molecular solid state transformations.

REFERENCES

1 (a) M.D. Cohen and G.M.J. Schmidt, J. Chem. Soc. 1966 (1964).
(b) M.D. Cohen, G.M.J. Schmidt and F.I. Sonntag, J. Chem. Soc. 2000 (1964).
(c) G.M.J. Schmidt, J. Chem. Soc. 2014 (1964).
2 G.M.J. Schmidt, Pure Appl. Chem. 27, 647 (1971).
3 V. Ramamurthy and K. Venkatesan, Chem. Rev. In Press.
4 K. Gnanaguru, N. Ramasubbu, K. Venkatesan and V. Ramamurthy, J. Org. Chem. 50, 2337 (1985).
5 K.H. Pfoertner, G. Englert and P. Schoenholzer, "Abstracts of Papers", 12th International Conference on Photochemistry, Tokyo, Japan, 487 (1985).
6 (a) F. Nakanishi, H. Nakanishi, M. Tsuchiya and M. Hasegawa, Bull. Chem. Soc. Jpn. 49, 3096 (1976).
(b) H. Nakanishi, M. Hasegawa and T. Mori, Acta Crystallogr. Sect. C, 41, 70 (1985).
7 H. Nakanishi, G.M. Parkinson, W. Jones, J.M. Thomas and M. Hasegawa, Isr. J. Chem. 18, 261 (1979).
8 S. Ariel, S. Askari, J.R. Scheffer, J. Trotter and L. Walsh, J. Am. Chem. Soc. 106, 5726 (1984).
9 A.W. Hanson, Acta Crystallogr. Sect. B, 31, 1963 (1975).
10 D. Kanagapushpam, V. Ramamurthy and K. Venkatesan, J. Chem. Soc. Perkin Trans. 2, Submitted.
11 C.R. Theocharis, W. Jones, J.M.Thomas, M. Motevalli and M.B. Hrusthouse, J. Chem. Soc. Perkin Trans. 2, 71 (1984).
12 S.K. Kearsley and G.R. Desiraju, Proc. Roy. Soc. London, Ser. A, 397, 157 (1985).

13 L. Leiserowitz and G.M.J. Schmidt, Acta Crystallogr. 18, 1058 (1965).

14 (a) N.J. Leonard, R.S. McCredie, M.W. Loyue and R.L. Cundall, J. Am. Chem. Soc. 95, 2320 (1973).
(b) J.K. Frank and I.C. Paul, J. Am. Chem. Soc. 95, 2324 (1973).

15 H. Irngartinger, R.D. Aekes, W. Rebufka and H.A. Stabb, Angew Chem. Int. Ed. Engl., 13, 674 (1974).

16 N. Ramasubbu, T.N. Guru Row, K. Venkatesan, V. Ramamurthy and C.N.R. Rao, J. Chem. Soc. Chem. Commun. 178 (1982).

17 M. Hasegawa, K. Saigo, T. Mori, H. Uno, M. Nohara and H. Nakanishi, J. Am. Chem. Soc. 107, 2788 (1985).

18 M. Kaftory, J. Chem. Soc., Perkin Trans-II, 2757 (1984).

19 (a) M.D. Cohen, Angew Chem. Int. Ed. Engl., 14, 386 (1975).
(b) M.D. Cohen, Mol. Cryst. Liq. Cryst., 50, 1 (1979).

20 (a) M.A. Collins and D.P. Craig, Chem. Phys. 54, 305 (1980).
(b) D.P. Craig and C.P. Mallet, Chem. Phys. 65, 129 (1982).
(c) D.P. Craig, R.N. Lindsay and C.P. Mallet, Chem. Phys. 89, 187 (1984).
(d) K. Norris, P. Gray, D.P. Craig, C.P. Mallet and B.R. Markey, Chem. Phys. 79, 9 (1983).

21 M.M. Bhadbhade, G.S. Murthy, K. Venkatesan and V. Ramamurthy, Chem. Phy. Letts. 109, 259 (1984).

22 K. Mirsky in Proceedings of an "International Summer School in Crystallographic Computing", H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld and G.C. Bassi (Eds.), Twente (Delft Univ. Press, Delft), 169 (1978).

23 W.R. Busing, WMIN, a Computing Program to Model Molecules and Crystals in Terms of Potential Energy Function, Oak Ridge National Laboratory, Oak Ridge (1981).

24 K.N. Trueblood, THMB, Zurich (1982).

25 M. Hasegawa, H. Arioka, H. Harshina, M. Nohara, M. Kubo and T. Nishikubo, Isr. J. Chem. 25, 302 (1985).

26 G.S. Murthy, V. Ramamurthy and K. Venkatesan, Unpublished Results.

27 N. Ramasubbu, K. Gnanaguru, K. Venkatesan and V. Ramamurthy, Can. J. Chem. 60, 2159 (1982).

28 M.J. Begley, L. Crombie and T.F.W.B. Knapp, J. Chem. Soc. Perkin Trans. I, 976 (1979).