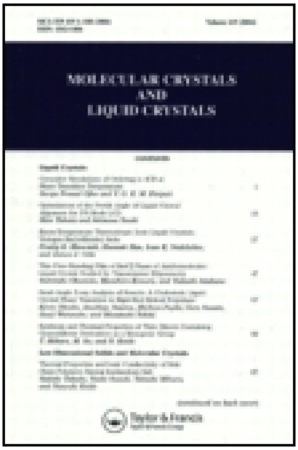

Molecular Crystals and Liquid Crystals

Isomerisation of Molecules in Organic Crystals, A Theoretical Study

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ISOMERISATION OF MOLECULES IN ORGANIC CRYSTALS, A THEORETICAL STUDY

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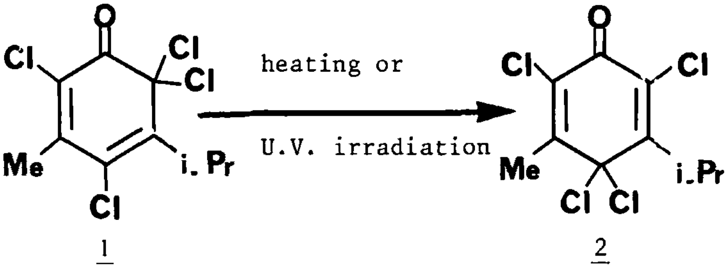
Abstract The effect of the minimization of crystal energy on the rearrangement in the solid state of orthocyclohexadienone 1 into paracyclohexadienone 2 is investigated using a combination of theoretical lattice energy and quantum chemical calculations. Lattice energy calculations show the crystalline structure of para-dienone 2 to be less stable than the crystalline structure of ortho-dienone 1. On the contrary concerning the energies of isolated molecules the para-dienone 2 is more stable than the ortho-dienone 1. Such an approach including crystal energetic calculations and energetic analysis of isolated molecules promises to be useful in the investigation of the chemical pathway for the rearrangement in the solid state.

INTRODUCTION

Few theoretical studies have been devoted to molecular organic reactions or to molecular organic rearrangement in the solid state[1]. We have described[2] the experimental part of the thermal and photochemical rearrangement in the solid state of *ortho* cyclohexadienone 1 into the *para* isomer 2 according to the following scheme.



Crystal I Crystal II

The aim of the present work is to show a theoretical approach to the rearrangement in the solid state. Till now we are unable to calculate the total reaction path but it is possible to suggest the early stage of the energy profile. First we can obtain informations about the thermodynamic view of these reactions. Thus we are able to calculate both stability differences between the crystals I and II and between isolated molecules 1 and 2.

For this study we take into account :

- the lattice energy of solid state for crystals I and II.
- the energy of the isolated molecules 1 and 2 involved in the rearrangement.

A STABILITY OF CRYSTALS

For the calculations of the first type energy we used the theoretical approach proposed by CAILLET and CLAVERIE[3]. Contrary to liquids or gases, the position of the molecules in crystals does not change on the average in time. Therefore a model can be built, involving a molecule surrounded by other molecules. In this model the three dimensions of the crystal are taken into account by calculating the interaction energy in a unit cell then adding successive layers of cells until minimization. The molecules are being permitted to rearrange by displacement and rotation around Eulerian angles in the framework of the crystalline symmetry. The parameters of the cell can also vary. The packing energy can be calculated for the central molecule by summing the contributions that are at work in such a model, that is electrostatic, polarization, dispersion and repulsion forces. This packing energy is the energy needed to bring one molecule to infinity from bulk of the crystal. Here these energies are divided by two to account for lattice energy (to avoid counting each contribution twice). For the evaluation of the different terms we used the following formula.

$$E_{el} = \sum_i^{(a)} \sum_j^{(b)} \frac{Q_i Q_j}{R_{ij}}$$

Q_i, Q_j are the net charges of atoms i and j for molecules (a) and (b) given by a CNDO/2 calculation. R_{ij} is the distance between atoms i and j.

$$E_{pol.}(a) = -\frac{1}{2} \sum_i \alpha_i (\varepsilon_i)^2$$

ε_i is the electric field created at the atom i of molecule (a) by all other molecules. α_i is the atomic polarizability. It is calculated from bond polarizability and it is specific for each atom i of the molecule.

$$E_{disp.-rep.} = \sum_i^{(a)} \sum_j^{(b)} k_i k_j \left[-\frac{0.214}{z6} + 47\ 10^3 \exp(-12.35 z) \right]$$

$$z = R_{ij} / R_{ij}^0 \qquad R_{ij}^0 = \sqrt{(2R_i^W)(2R_j^W)}$$

R_i^W and R_j^W are the VAN der WAALS radii of atoms i and j.

The results of the lattice energy calculations are summarized in table I.

TABLE I Summary of lattice energy calculations (kcal/mole)

	E (I) monoclinic	E (II) monoclinic	ΔE(II-I)
Electrostatic energy	- 1.46	- 1.10	+ 0.36
Polarization energy	- 1.50	- 0.81	+ 0.69
Dispersion and repulsion energy	-23.91	-16.26	+ 7.65
Total energy	-26.87	-18.17	+ 8.7

From these calculations we notice :

1) The largest energy contribution comes from the dispersion repulsion term. All terms favour the monoclinic form I.

2) These total interaction energies are not in agreement with a spontaneous rearrangement of crystal I into crystal II.

3) The parameters a, b, c and β for the unit cell were permitted to vary but slightly did so. The space group symmetry was retained for the calculation. One shell of 26 cells surrounding the central one appears to be sufficient and displacement and rotation of molecules are very short. (Table II) .

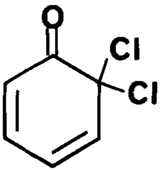
A combination of analysis of the lattice energy with molecular orbital calculations is needed to analyse the relative stabilities of the two systems.

TABLE II Calculated and experimental parameters a, b, c and β.

	I		II	
	Calculated	Experimental	Calculated	Experimental
a	8.387	8.398	18.736	18.736
b	11.443	11.457	9.892	9.892
c	13.264	13.274	13.758	13.758
β	108.9	108.2	105.7	105.1

B ENERGY OF THE ISOLATED MOLECULES

*Ortho*cyclohexadienones are known to be less stable than *para*cyclohexadienones[4] and we decided to deal with the model molecules 3 and 4.



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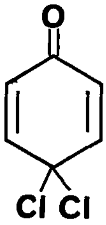

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This energy was studied by MNDO method with geometry optimization[5]. We calculate the difference in energy between 3 and 4. The minimized heats of formation obtained are −16.93 kcal/mole for 3 and −18.36 kcal/mole for 4. Molecule 2 should be more stable than molecule 1. Because the difference in nature of the lattice energy and molecular orbital energy calculations only a qualitative comparison of the two kinds of results can be drawn.

From the approach employed including lattice and isolated molecular energies it seems that the rearrangement of the *ortho*cyclohexadienone 1 into the *para*cyclohexadienone 2 in the solid state is due to the greater stability of the isolated molecule 2.

C APPROACH OR THE FIRST STAGE OF REACTION PATH.

Another interesting problem is the evolution of the relative positions of molecules and energies in the crystal at the beginning of the reaction. The reaction is assumed to occur by a chlorine migration from the *ortho* position in molecule 1 to the *para* position of a neighbouring molecule 1'. This feature was modelled by minimizing the lattice energy of I build from molecules 1 in which the reactive C - Cl bond is lengthened from 1.78 Å to 1.9 Å. We have observed a rearrangement of molecules 1 such that the chlorine atom in *ortho* position comes nearer to the *para* position of another molecule d = 4.64 Å (1.78 Å), d = 4.08 Å (1.9 Å) we note a slight stabilization of the packing energy (-28.82 kcal/mole). This calculation is thought to represent an approach of the reaction path. Theoretical and experimental works are in progress to elucidate the mechanism of the rearrangement.

In conclusion isomerisation in solid state can be studied by balance of packing energy and quantum chemical energy analysis. The most interesting aspect is the fact that our calculations can give an approach of the beginning of the chemical path in solid state.

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