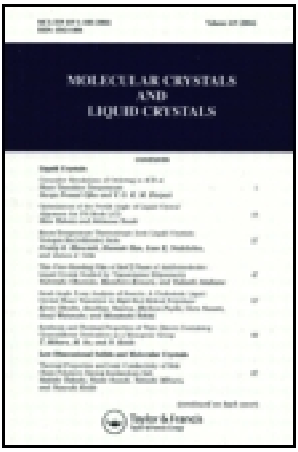

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Topochemical Solid State [2+2] Cyclodimerisations of Enones: Theoretical Considerations

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TOPOCHEMICAL SOLID STATE [2+2] CYCLODIMERISATIONS OF ENONES: THEORETICAL CONSIDERATIONS

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Abstract Molecular orbital calculations using the MNDO computer program were used to study the solid state [2+2] cycloaddition of conjugated enones. Benzylidene methyl ketone was used as a model molecule. The reactive species was identified as a triplet excited state. These calculations were used to clarify the mechanism of this reaction, and to interpret cases of apparent breakdown of the topochemical principle.

INTRODUCTION

Since Schmidt, Cohen, et al first rationalised the behaviour of crystalline trans-cinnamic acid under photoirradiation, in photochemical (ie geometric) terms[1], a number of solid state reactions have been found to occur with what appeared to be minimum atomic or molecular movement[2,3]. The apparent exception to the topochemical rule represented by the solid state behaviour of anthracenes was rationalised in terms of defect controlled reactivity[2].

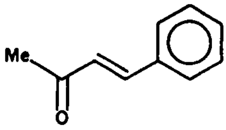
In recent years, however, several reactions were described which would appear to be forbidden under this rule. For example, the [2+2] photocycloaddition of conjugated double bonds should only occur between parallel moieties, and for bond centre to bond centre distances between 0.36 and 0.42nm. 2,5-Dibenzylidene cyclopentanone, however, undergoes topochemical reaction[4] involving double bonds subtending between them an angle of 56°.

Most theoretical investigations have hitherto made use of atom-atom pairwise potentials or have carried out rationalisations in terms of packing coefficients, or molecular dynamics[5-8]. Valuable as this approach may be, it is only applicable to ground state molecules, whereas many topochemical reactions are light induced and therefore involve excited species. Very little use has been made so far of the quantum mechanical approach, mainly for historical reasons. In the present paper we make use of such an approach, in order to understand better the solid state reactivity of the benzylidene cyclopentanone family of compounds.

DISCUSSION

Molecular orbital calculations within the MNDO approximation[9] were performed on benzylidene methyl ketone (I). This compound corresponds to the photochemically active portion of 2-benzyl-5-benzylidenecyclopentanone (II) and is closely related to that for 2,5-dibenzylidene cyclopentanone (III). It can be therefore considered as an adequate model for the solid state photodimerisation of these compounds or their analogues, as the nature of the excited state should be the same, whether the reaction takes place in a fluid or solid environment. This is justified since it has been shown by other workers, that the conformation adopted by BBCP in its crystals is the lowest energy one. It has hitherto been considered that the theoretical study of solid state phenomena should involve consideration of the band structure. However, it is nowadays generally accepted that this is not necessary for molecular crystals since,although electrons would not be localised in the lattice, they can at any given time be treated at a molecular level[10].

The ground state of I was found to have a heat of formation of 10.86 kcal mol^{-1}. The maximum electron density for the HOMO was on C(5) (for numbering scheme, see Figure 1), and for the LUMO on C(13). The geometry, including bond lengths, angles and torsional angles, was close to those found for the benzylidene moieties in the crystal structures of II (Figure 1) or III[9,11]. The lowest excited singlet state was found to have a heat of formation of 42.60 kcal mol^{-1}, with a similar disposition of the HOMO and LUMO as the ground state. The lowest excited state was found to be a triplet state with heat of formation 42.30 kcal mol^{-1}. Maximum electron density for the HOMO was located on C(5), and for the LUMO on C(13).



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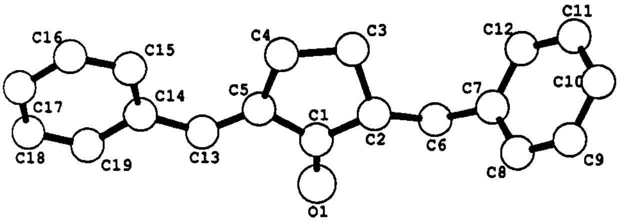

Figure 1 Molecule of 2-benzyl-5-benzylidene cyclopentanone (II), from its crystal structure. The numbering scheme shown here is used for all structures discussed in this paper, both theoretical and experimental.

The very similar energies of the lowest excited singlet and triplet states, mean that transition from the former to the latter is extremely facile. The excited triplet state thus formed, will be vibrationally excited. This can be correlated with the so-called phonon[12] assistance of solid state [2+2] cycloaddition reactions previously reported. The molecular orbital symmetry is such that reaction between two ground state molecules or between one ground state molecule and one in the singlet state is not allowed. On the other hand, reaction between a ground state molecule and one in the triplet excited state is allowed. Thus, the facility of energy transfer between states is crucial to the reaction occurring under topochemical control.

The lifetime of the triplet state for III as measured from the phosphorescence in emission spectra at 77K was 200 µs (C. Bräuchle and C.R. Theocharis, unpublished results). This relatively short lifetime means that the excited molecule cannot transfer its energy to a neighbouring ground state one. This process is called energy hopping, and where it occurs the solid state reaction is not homogeneous, as it is no longer random. Defects in the lattice act as energy traps and therefore such a reaction is more likely to occur at defects. The shapes of the two excited states are very similar to that of the monomeric residues in the dimer, except for the dihedral angle between the mean planes of the 5-membered and benzene rings. The other bond lengths and angles as determined from MNDO for the two excited states of I, correspond well with those found crystallographically for the dimer of II (compare Figures 2 and 3).

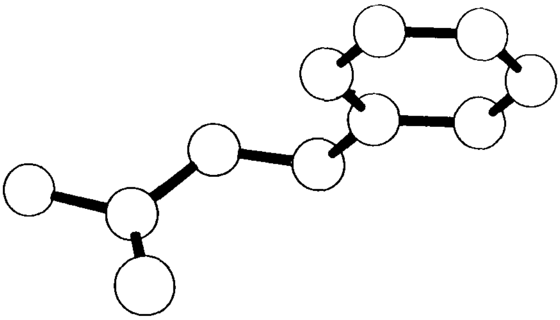

Figure 2 Excited molecule of I, as calculated by MNDO.

The change in shape which accompanies excitation has two consequences: first, it makes energy hopping less likely, since this process is more probable between molecules closely related in structure. Second, this movement probably causes the reactive centres to move closer together, compared to the position they occupy when in the ground state. The rate of reaction is also related to the fact that the transition state is closer in structure to the product than the reactant. The symmetry of the orbitals in the triplet and ground states indicates that both the head to head and head to tail reactions are intrinsically feasible. Further, the cycloaddition has to be a non-concerted process, since only one pair of orbitals of the two involved are initially of the correct symmetry.

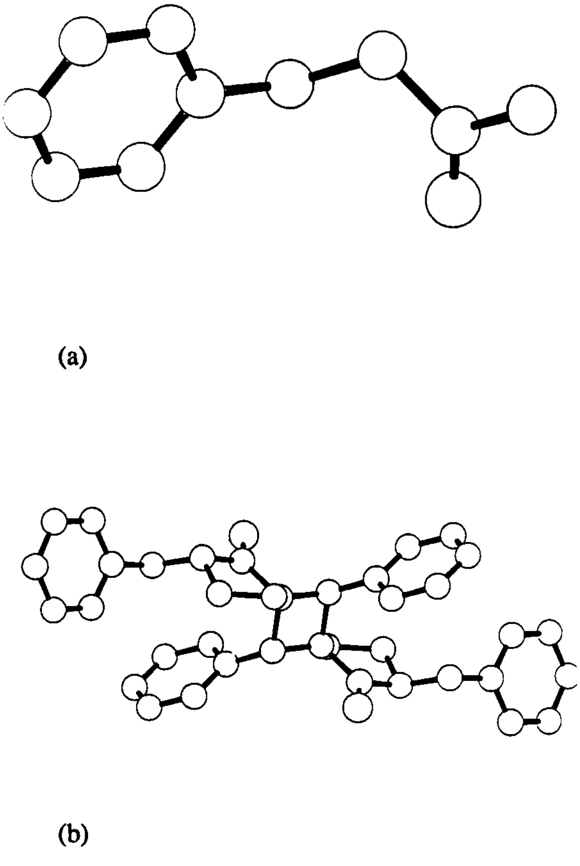

Figure 3 Structure of (a) the residue corresponding to I in the dimer of II, and (b) dimer molecule of II, obtained from the crystal structure of the dimer.

A number of reactions appear to occur under topochemical control, in so far as the geometry (nature) of the product can be rationalised in terms of the crystal structure of the reactant, yet they occur between double bonds either too far apart, or not totally parallel. A possible explanation for these discrepancies may be that parallel double bonds represent the ideal geometry to enable a lobe of an orbital with correct phase in the ground state molecule to overlap with one in the excited state molecule. This overlap is clearly possible for orientations other than parallel bonds. Furthermore, since in the present example the phases of the lobes are such that the reaction cannot be concerted, it may be that, at the start of the reaction, contact has to be favourable for only one atom on each molecule in order for reaction to be possible, and not for both atoms simultaneously. The term "minimum movement" probably should only refer to the initial movement of the reacting atoms, and after that the consequent movement for the rest of the molecule may be larger. This movement will probably cause strain and the breakdown of the mechanical integrity of the crystal, and therefore stop any further reaction, as topochemical control would be lost.

The topochemical principle is a very useful tool for the solid state chemist, and is capable of application in a variety of situations. It does suffer, however, from the disadvantage that crystallography provides the structure of ground state molecules when in the case of photochemical reactions excited states are involved.

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