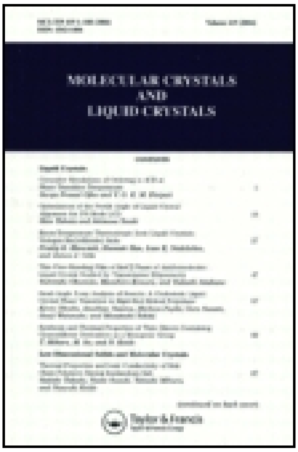

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Solid-Aminolysis of 4-Ethoxy-2-Phenyl-1,3-Thiazin-6-One

Claude Decoret [a], Francois Bayard [a], Francois Baert [b], Mustapha Chenha [c], Jean-Pierre Pradere [c] & Jacques Vicens [d]

[a] Université Claude Bernard, Lyon I., F-69622, Villeurbanne, cédex, France

[b] Université de Lille., F-59650, Villeneuve, d'Ascq. France

[c] Université de Nantes, F-44072, Nantes, cédex, France

[d] Université de Strasbourg, F-67000, Strasbourg, France

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SOLID-AMINOLYSIS OF 4-ETHOXY-2-PHENYL-1,3-THIAZIN-6-ONE

CLAUDE DECORET, FRANCOIS BAYARD
Université Claude Bernard, Lyon I. F-69622. Villeurbanne cédex. France.

FRANCOIS BAERT
Université de Lille. F-59650. Villeneuve d'Ascq. France

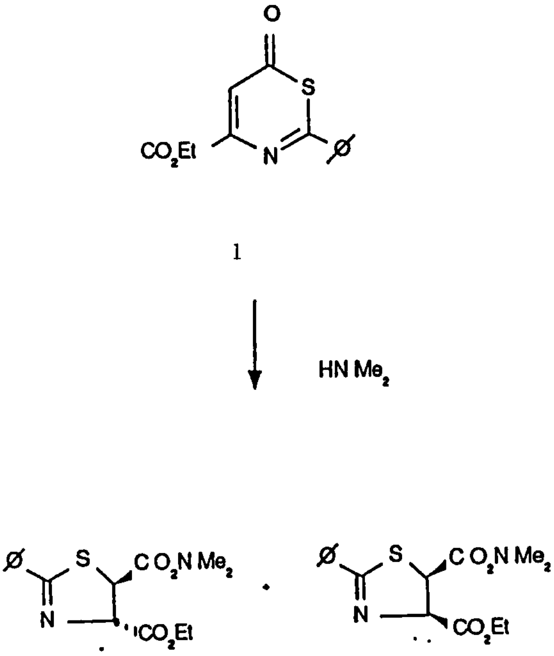
MUSTAPHA CHENHA, JEAN-PIERRE PRADERE
Université de Nantes. F-44072. Nantes cédex. France.

JACQUES VICENS
Université de Strasbourg. F-67000. Strasbourg. France.

Abstract This communication reports our studies on the solid state reactivity of 4-ethoxy-2-phenyl-1,3-thiazin-6-one 1 with vapor of N,N-dimethylamine. The anisotropic behaviour of the reaction process is rationalized by atom-atom potential energy calculations.

INTRODUCTION

In a preceeding communication[1] we described the gaseous aminolysis by N,N-dimethylamine of single crystals of 4-ethoxy-2-phenyl-1,3-thiazin-6-one 1 to yield diastereoisomers 2. The solid state reaction was observed to be anisotropic, the reaction starting at both ends of single crystals of 1 and proceeding along the long axis of 1. This process was rationalized, based on molecular packing, by a solid state mechanism involving a nucleophilic attack of N,N-dimethylamine perpendicular to carbonyl functions of 1 in the crystals.



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In this communication we present our results from investigating the molecular packing of 1 by theoretical means . Such investigation has been proved to be useful in showing evidence of relationships between the molecular forces maintaining the crystal lattice and the observed reaction events[2,3] .

RESULTS AND DISCUSSION

Before stating the main point of the communication we mention that the X-Ray crystal structure of 1 has been re-determined at low temperature. 1 is monoclinic with a =

8.760(4), *b* = 19.553(5), *c* = 7.081(4)A , = 97.18°, Z = 4 and d = 1.44 $g.cm^{3}$, R = 0.035[4] . This crystalline structure slightly resembles the one already published at room temperature[1] and the conclusions remain the same with respect to the geometry of the isolated molecule and the molecular packing[4] .

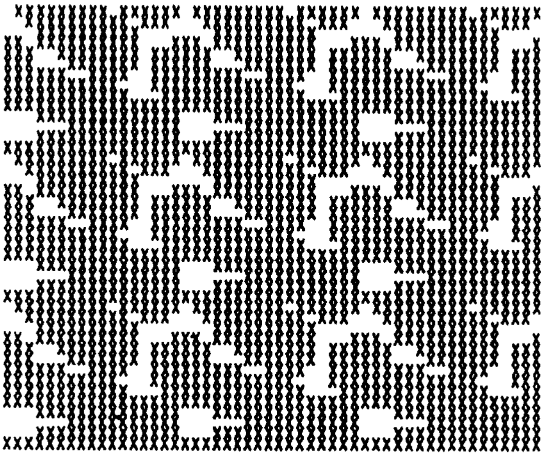
In order to understand the anisotropic destruction of crystal 1 we have studied the molecular arrangement and the crystal morphology with Gavezzotti's program[5] and by analyzing the molecular interactions at the surface of the unit cell by an atom-atom potential method developed by Caillet and Claverie[6]

Free Space Calculation with Gavezzotti's Program

The results of the calculation for 1 are shown in Figure 1 . From these representations we concluded that pockets and gaps do not communicate with each other in an anisotropic way. This observation was almost general for any section of crystal 1 . This is in contrast with previous studies on crystals of benzoxazinones and naphtoxazinones by the same means[2,3] . We therefore decided to use atom-atom potential energy calculations to evaluate energies needed to extract molecules from the surfaces of crystal 1 .

Atom-atom Potential Energy Calculations.

Using Caillet and Claverie's program we calculated the interaction energies of a molecule of 1, situated at the surface of unit cell A, with all other molecules



SECTION 0.1154 CUT AT 50% a=horiz c=vert

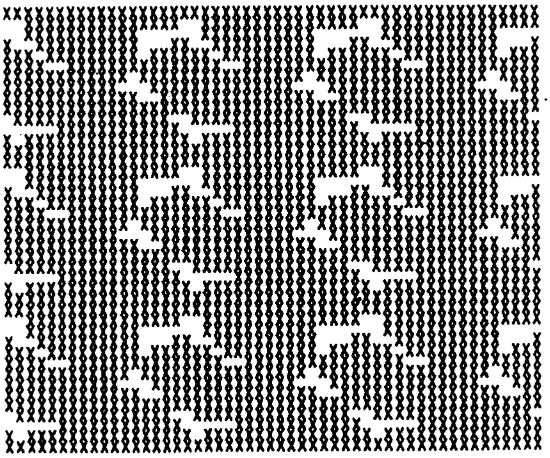


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FIGURE I Density maps of crystal 1 according to the Gavezzotti'program. For details of calculations and analysis see references 3 and 5.

belonging to the unit cells surrounding A. This method has already been described by us[3]. These calculations were run for each surface perpendicular to [100], [010] and [001] directions. They are presented in Table 1. Underlined are the energies for the concerned molecules which lie closest to the surface perpendicular to the chosen direction. The values show that molecules numbered 1 and 4 present the lowest energy of interaction with other molecules in crystal 1. They are on the surface perpendicular to [001], **which is the direction of the reaction**. Similar findings have been made for benzoxazinones and naphtoxazinones[3].

CONCLUSION

Theoretical calculations seem to be, up to now, one of the more reliable means to evaluate and characterize specific energies involved in chemical process occuring in the solid state or in crystalline assemblies[7]. The results presented here with, others already published[3], indicate that the molecular forces steering the molecular arrangement of molecules in a crystal have to be taken into account for explaining observable phenomena characteristic of the solid state processes. In our examples **the molecular forces inducing the crystal to grow in one preferred direction also induce the anisotropic destruction of the crystals along the same direction** during the solid-gas reactions.

TABLE I Calculated energies of extraction of molecules from the surface of unit cell A (in kcal/ mole)

Direction	1	2	3	4
[100]	-23.809	-20.939	-24.449	-19.535
[010]	-24.227	-27.437	-23.180	-27.208
[001]	-16.818	-26.333	-26.298	-16.513

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