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THERMAL REARRANGEMENT OF CYANURATES IN THE SOLID STATE

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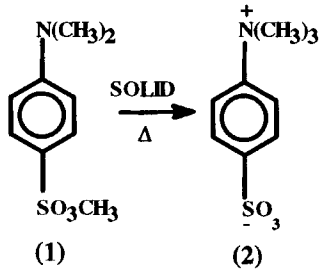
Abstract 2,4,6-trimethoxy-1,3,5-triazine undergoes methyl transfer in few stages, some in the melt and some in the solid-state, to the end product, 2,4,6-trioxo-1,3,5-trimethylazine. The three possible intermediates have been prepared and their methyl transfer reaction was investigated. The mechanism and the dependence of the reactivity on the packing of the molecules in the crystal lattice have been studied by high temperature X-ray diffraction (HTXRD), by thermal analysis (DSC) and by crystal structure determination.

INTRODUCTION

Most of the chemical reactions that are found to take place in the solid-state are either photochemically or thermally induced reactions. One of the most interesting type of thermally induced reactions is that involved with the migration of large groups. There are three known solid-state reactions that undergo rearrangement by the migration of a methyl group from one position in one molecule to another position in another molecule. Two of these cases have been thoroughly studied and the third one will be discussed here. The first example is the conversion of methyl-p-dimethylaminobenzenesulfonate (1) to the zwitterionic product p-trimethylammoniobenzenesulfonate (2), first discuvered by Kuhn & Ruelius[1].



(1) (2)

Sukenik, Bonapace, Mandel, Lau, Wood & Bergman[2] showed that the reaction is intermolecular and proceeds much faster in the crystal than it does either in the melt or in solution. The crystal structure of (1) (shown schematically in Figure 1) consists of stacked molecules nearly ideally oriented for intermolecular methyl transfer.

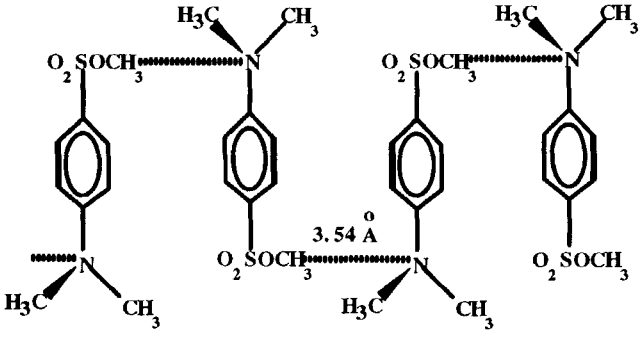
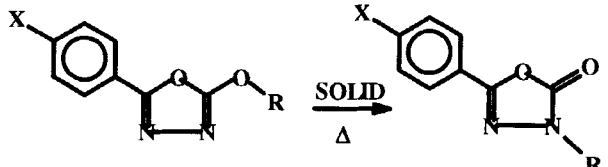


FIGURE 1 Schematic drawing of the crystal structure of (1).

Gavezzotti & Simonetta[3] proposed a two-step mechanism, involving molecular ion-pair intermediate as calculated by extended Huckel theory. Sarma & Dunitz[4] repeated the crystal structure refinement based on diffraction intensity data taken at two different temperatures (193 and 255K, because the crystal decomposes slowly at room temperature), and calculated the packing potential energy. It was also shown that the crystal structure of the product (2) is quite different than that of (1), and that the product undergoes a series of phase transitions.

The second example of methyl transfer in the solid state is the Chapman-like rearrangement of Imino-ethers to N-alkylamides. Dessolin & Golfier[5] have found that in some derivatives of 5-methoxy-2-aryl-1,3,4-oxadiazoles (3) the rearrangement is unusually fast in the solid state.



(3)

The crystal structure of a derivative of (3) ($R=CD_3$, $X=OCD_3$)[6] is shown schematically in Figure 2. The geometry found to be ideal for the methyl transfer, namely the three O, C, and N atoms involved in the transfer of a methyl group from a given molecule to its

neighbour, are clinearly alligned with a distance of 2.9Å , shorter than the sum of the corresponding van der Waals radii (3.55Å). Also, it was found that the O-Me distance

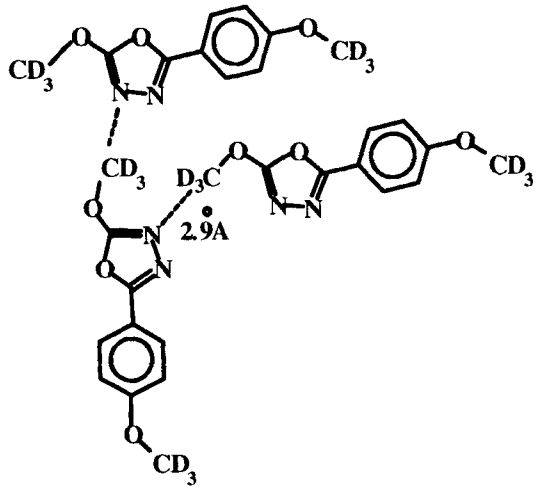
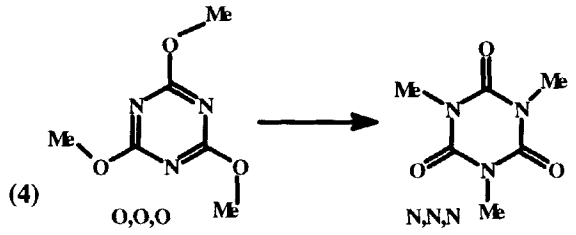


FIGURE 2 Schematic drawing of the crystal structure of (3).

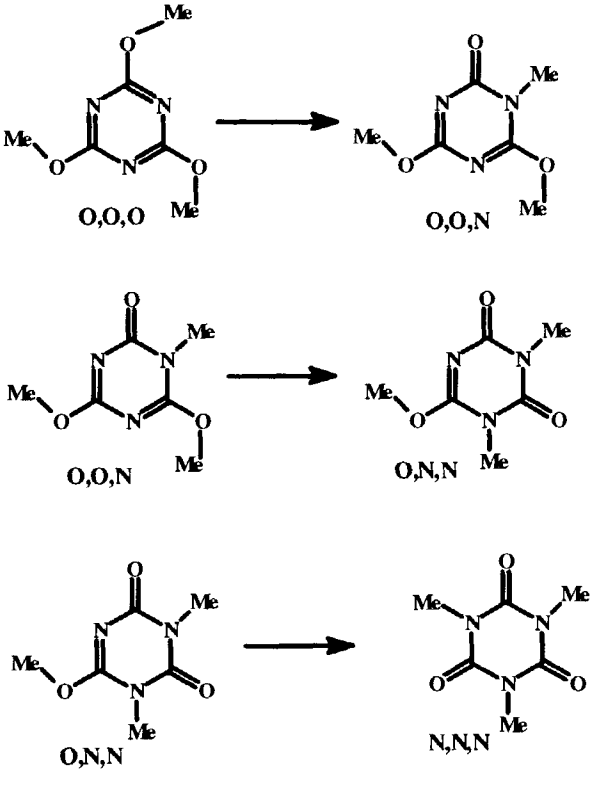
is much longer than normal (1.60Å). A theoretical study have led to the conclusion that the substitutions are domino-like propagated in chains, and that the initial stage is the formation of an anion and a cation followed by the transfer of a methyl group between the ion and an adjacent molecule in the same plane. It was also shown, by kinetic study using NMR measurements, that the activation energy of the reaction in the solid is much lower than for the uncatalyzed reaction in the melt and of the same order (and even slightly lower) than for the catalyzed reaction in the melt.

The third example is the multiple methyl transfer in 2,4,6-trimethoxy-1,3,5-triazine (methyl cyanurate) and 2,4,6-trimethylthio-1,3,5-triazine (thio cyanurate)[7]. 2,4,6-trimethoxy-1,3,5-triazine (4) includes three methyl groups that may be transfered and reveal the end product (2,4,6-trioxo-1,3,5-trimethylazine). Kinetic study[7] have shown that the methyl transfer proceeds faster in the melt or in the solid and labeling experiments have shown that the reaction is intermolecular. We have studied the topochemistry of this reaction and the partial results are presented here.



RESULTS AND DISCUSSION

In principle (4) can undergo three stages of methyl transfer according to scheme 1. The crystal structure of all four compounds (O,O,O; O,O,N; O,N,N; N,N,N) have been determined, their high temperature X-ray diffraction patterns (HTXRD) have been taken and a thermal sudy have been done using differential scanning calorimetry (DSC). The results are briefly summarized below.



SCHEME 1 Possible Intermediates.

The Structure and Thermal Behavior of O,O,O

The crystal packing of O,O,O is shown in Figure 3. The planar molecules are packed in the **ac** plane with the reacting centers (N...C(Me)-O) arranged in infinit trimers with geometry (N....C(Me) distances and N....C(Me)-O angles) that might suggest that the compound will undergo methyl transfer in the solid-state. However, DSC shows two endotherms (the first one is very small) followed by an exotherm. The product (after cooling) found to be N,N,N by NMR spectra. HTXRD shows clearly that the powder pattern has been change at 343K and then disappeared at 403K (due to the formation of melt). Upon cooling the powder pattern is identical with that of N,N,N.

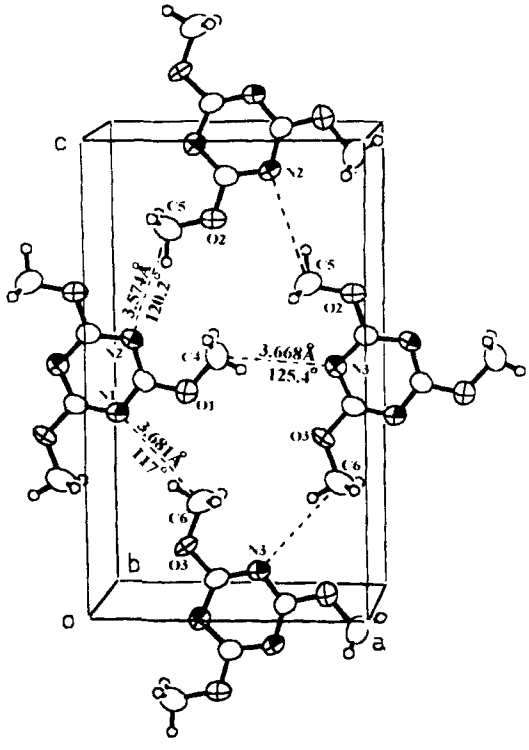


FIGURE 3 Crystal structure of O,O,O

The explanation is that O,O,O undergoes phase transition at relatively low temperature. The new phase, loosing the relative geometry that was almost ideal for methyl transfer, melts before methyl transfer can take place. This assumption should be examined by

determining the crystal structure of the new phase (yet we had no success in growing single crystals of the high temperature phase).

The Structure and Thermal Behavior of O,O,N

The packing of O,O,N molecules is very similar to of O,O,O (see Figure 4). HTXRD shows a change of the powder diffraction pattern at 383K. There is no sign for melt up to 553K. The DSC curve shows one exotherm and no endotherm up to 573K. The product (checked after cooling) shown to be N,N,N.

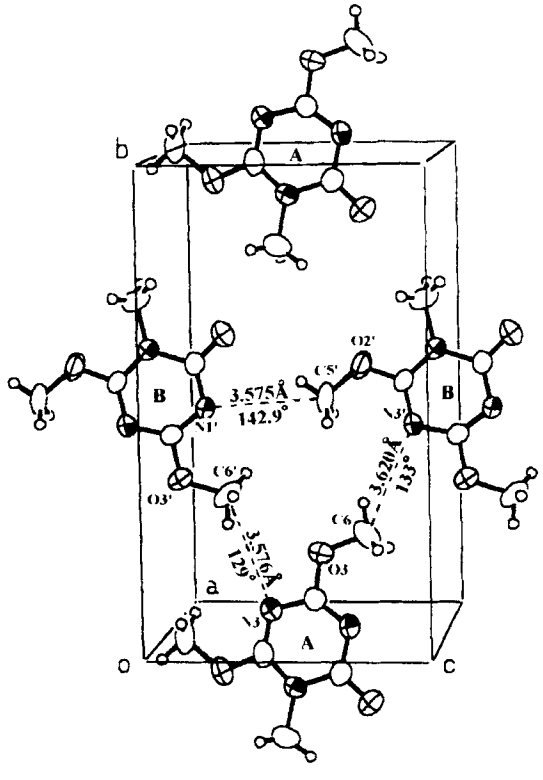


FIGURE 4 Crystal structure of O,O,N

All these experiments suggest that O,O,N undergoes methyl transfer in the solid-state. The obvious question is what is the product and what is the mechanism. There are two crystallographically independent molecules (A, and B in Fig. 4) in the unit cell. The two different molecules are coplanar and they form a ribbon. The reacting centers are

arranged in trimers within the ribbon. The different ribbons are separated by N-methyl:N-methyl intermolecular interactions. there are two possible mechanisms for the methyl transfer: (1) "Homo-Chain mechanism" (HC) (see Figure 5 left) and (2) "Hetero-Chain Ribbon mechanism" (HCR) (see Figure 5 right). The first one will lead to the formation of O,N,N and the second to the formation of the end product, N,N,N.

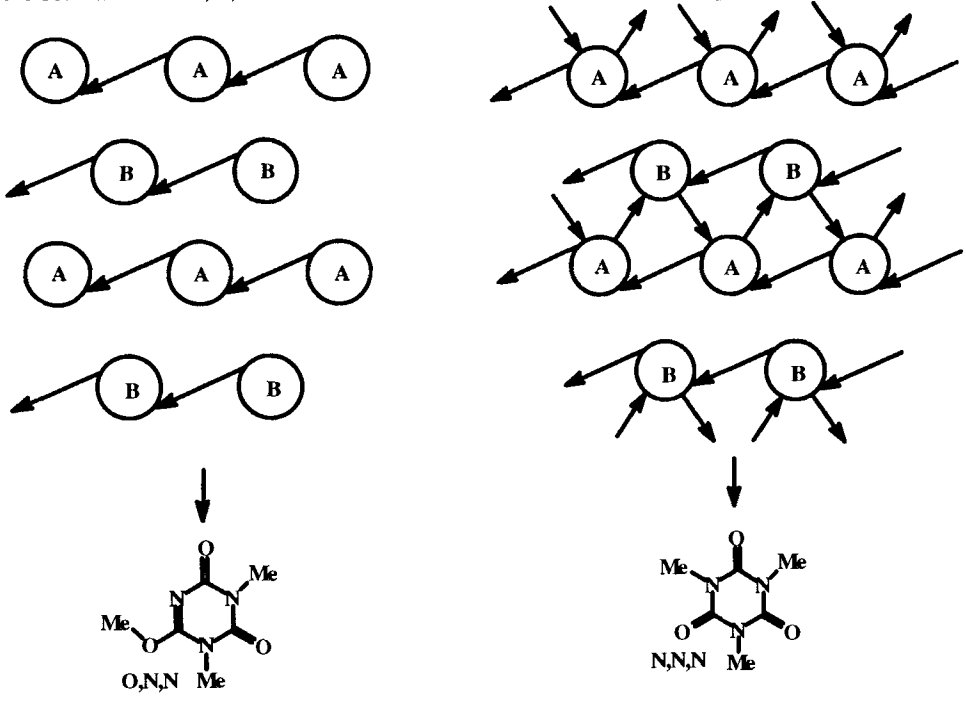


FIGURE 5 Left: Homo-Chain methyl transfer mechanism, Right: Hetero Ribbon methyl transfer mechanism.

In the HC mechanism the methyl transfer proceeds in a chain of the same type of molecules (A or B), and each molecule looses and gains one methyl group. In the HCR mechanism the two different molecules participate in the methyl transfer and each molecule looses and gains two methyl groups. All the methods used so far can not provide direct evident for the true mechanism, because of the time scale of these methods. However, it was noticed that the powder diffraction pattern of the product obtained by the solid-state reaction of O,O,N is different from that of the N,N,N product obtained by recrystallization from solvent, but the NMR analysis show that this product is N,N,N. A possible explanation is that a different modification of N,N,N molecules are formed during the solid-state reaction.

The Structure and Thermal Behavior of O,N,N

O,N,N molecules are packed in the lattice in parallel planes with the reacting centers arranged in dimers (see Figure 6). Both, HTXRD and DSC suggest that the methyl transfer occurs in the melt and not in the solid.

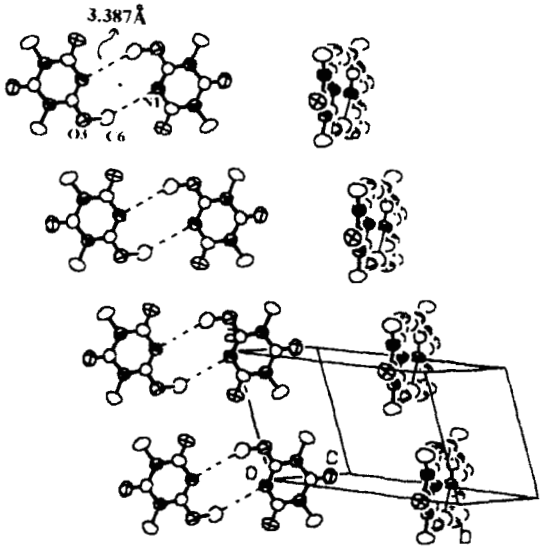


FIGURE 6 Crystal structure of O,N,N

There is no methyl transfer in the solid because of severe steric repultions between the methyl cations to be transferred..

The Crystal Structure of N,N,N

The crystal structure of N,N,N is shown in Figure 7. The structure consisits of two non-crystallographically independent molecules. The packing is no longer described by stacked planar and parallel molecules. It is a three dimensional structure made up of pairs of parallel molecules. The structure is very different from the other intermediates. Such a structure can be obtained either from the melt, from a solution or by a nucleation and growth process.

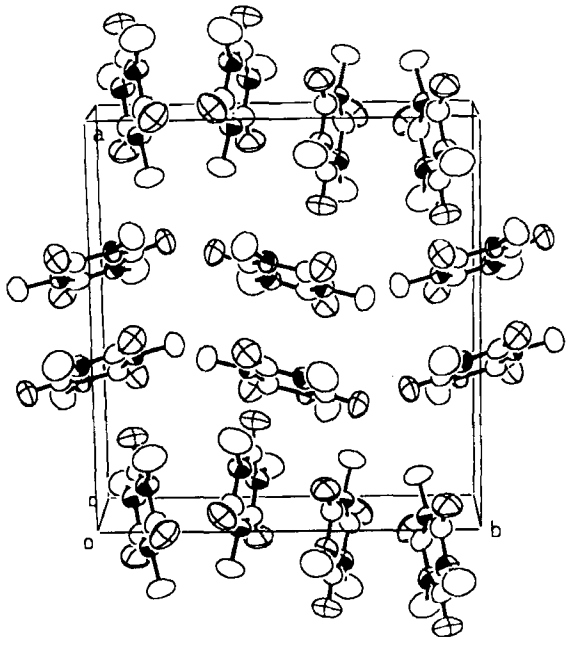


FIGURE 7. Crystal structure of N,N,N

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