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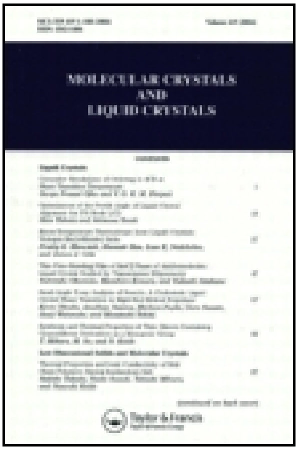

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cis-trans Photoisomerization in Tri-Ortho-Thymotide Inclusion Complexes: Crystal Structures of cis- and trans- Stilbene TOT Clathrates

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cis-trans Photoisomerization in Tri-Ortho-Thymotide Inclusion Complexes

Crystal Structures of *cis*- and *trans*- Stilbene TOT Clathrates

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New clathrate inclusion complexes of tri-*ortho*-thymotide (TOT) with *cis*-stilbene, *trans*-stilbene, methyl *cis*-cinnamate, methyl *trans*-cinnamate, and with other ethylene derivatives, have been prepared and characterized. In the triclinic crystal structure of the TOT-*trans*-stilbene inclusion complex (space group $P\bar{1}$), each unit cell contains four TOT and two *trans*-stilbene molecules. Two pairs of TOT molecules are related to each other by a center of symmetry and both stilbene molecules are located in special positions on these centers. The stilbene guests occupy two different channels which are perpendicular to one another (see Figure 1).

Contours of the free space available show that in each channel void pockets are present which allow *cis*-stilbene molecules to be accommodated in the same (or slightly modified) channels as these of the *trans*-stilbene clathrate. This accounts for the observation that the *cis*-stilbene-TOT clathrate is isomorphous with the *trans*-stilbene-TOT clathrate. However, since the *cis*-stilbene molecular symmetry cannot coincide with the symmetry of the cavity, the *cis*-stilbenes are disordered. Thus the guest occupancy of the *cis*-stilbene clathrate is less than that of the *trans*-stilbene complex, and the refinement

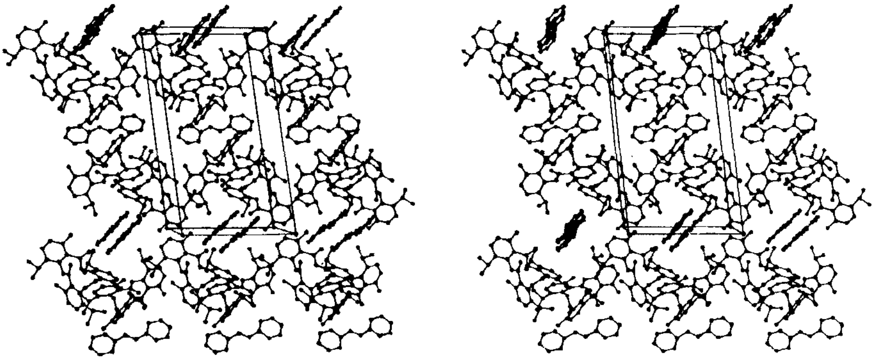

FIGURE 1 Stereoscopic view of the *trans*-stilbene-TOT clathrate structure viewed along the x-axis. The axial directions are **a** up out of the plane of the paper, **b**→ and **c**↑. Pairs of stilbene molecules are seen edge-on in the channels parallel to the x-axis (there are six such channels in the figure). The channel which is parallel to the y-axis is more clearly seen; three stilbene molecules in such channels are illustrated in the upper half and at the bottom of the figure.

does not reveal *cis*-stilbene molecules as such on the Fourier maps. There is a marked preference for the *trans*- over the *cis*-isomer during TOT inclusion; crystallization of TOT from a methanolic solution containing a 1 : 1 ratio of *cis*- and *trans*-stilbenes affords only the *trans*-stilbene-TOT inclusion complex.

The methyl esters of *cis*- and *trans*-cinnamic acid also afforded triclinic TOT clathrates which are isomorphous with those of stilbene. Full structure analyses were not performed on these crystals but we note that here both isomers, as in the case of *cis* stilbene, lack centers of symmetry and can only be accommodated with disorder in the centrosymmetric cavities shown in the Figure.

The two pairs of clathrates show a striking difference when irradiated through Pyrex under identical conditions. The *trans*-stilbene-TOT clathrate is completely light-stable but the *cis*-stilbene TOT clathrate, on irradiation, is converted entirely (i.e., no *cis*-stilbene remains) to the *trans*-stilbene-TOT clathrate; a small amount of phenanthrene is also formed. By contrast, irradiation of the TOT clathrates of the *cis*- or *trans*-isomers of methyl cinnamate gave a "photoequilibrium" containing approximately equal amounts of each isomer.

In order to better understand the nature of the lattice control upon these reactions, we sought information about the locus of the photoreaction: does photoisomerization occur within the (perhaps deformed) cavities or do guest molecules diffuse out of the cavities into unencumbered positions and react there? Although we cannot rigorously exclude the latter route we favor a

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"reaction-in-cavity" pathway. Thus, powder diffraction spectra taken before and after the conversion of *cis*-stilbene-TOT to *trans*-stilbene-TOT show that clathrate, and not individual crystallites of TOT and *trans*-stilbene, is formed. In addition, under conditions where iodine vapor-catalyzed *cis* → *trans* isomerization of the TOT enclathrated *cis*-stilbene does not take place (but where unclathrated *cis*-stilbene is rapidly isomerized by this method), the photoisomerization of *cis*-stilbene-TOT clathrate to *trans*-stilbene clathrate proceeds smoothly.

We tentatively ascribe the reactivity patterns in these systems as being subject to control by the symmetry of the reaction locus. The centrosymmetric cavity stabilizes centrosymmetric molecules and favors pathways which lead to centrosymmetric products, as in the case of the stilbenes. When neither reactant nor product can achieve the symmetry of the cavity, neither isomer is strongly favored and a "photoequilibrium" results, as in the case of the methyl cinnamates.