



Experiment title:
Supramolecular crystal devices as containers for new dynamic chemical processes

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CH-1748

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12

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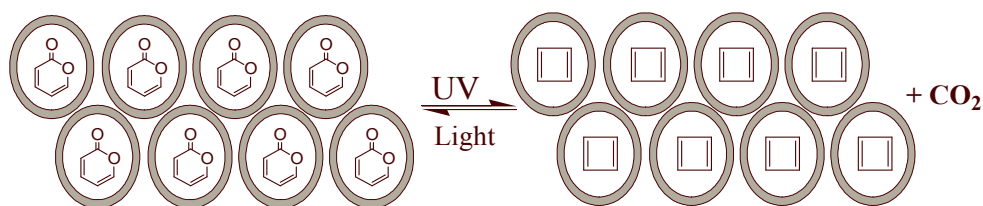
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Report:

Dynamic combinatorial processes generating shape adapted molecules inside the crystalline frameworks.

Generally, guest interconversions involve specific single-crystal to single-crystal phase transformations or a directed crystal-dynamic generation (amplification) of shape-adapted molecules. Recently, several groups have exploited the protective environment of similar molecular cage complexes to stabilise reaction intermediates of otherwise highly volatile molecules. In a few cases, it was possible to subsequently crystallise the host/guest system in order to determine the structure of the guest compound. Generally, however, the stabilised guest could only be studied in solution.

We proposed to study processes such as described above, including carrying out the photochemical synthesis of metastable short-lived molecules within already formed cyclodextrin-pyrone complex monocrystals. In this way we aim to measure the reaction pathway, rate and products during and after the reactions. As an ultimate goal, we aim to photosynthesise, in situ, cyclobutadiene, C₄H₄.



This elusive species, due to its reactivity, has never been stabilised in a crystal structure. Thus the structure of this molecule, of enormous theoretical importance, remains unknown, although

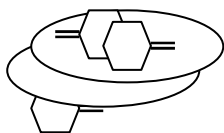
substantial calculations, indirect experimental evidence and studies on substituted cyclobutadienes suggest that it deviates largely from square symmetry. Cram et al showed that cyclobutadiene could be produced photochemically from a commercially available starting product encapsulated in a hemicarcerand cage.

Results:

In total 30 dataset have been collected between 80K and 293K.

The inclusion of alpha-pyrone in cyclodextrin was successfully achieved; very good crystallographic data was obtained.

The study has revealed the stoichiometry (3:2 guest:host) and the orientation of included a-pyrone molecules in dimeric β -cyclodextrin host molecules. Crystal packing is that of channels giving rise to supramolecular nano-tubes in which alternating a-pyrone are stacked.



Upon UV-irradiation, the CD structure stays unchanged while the positions of the a-pyrone atoms become disordered and dimers seem to form. Upon more UV-irradiation, although “squares” are forming among other geometrical shapes, it is difficult to ascertain for sure that the required cyclobutadiene structure was present, due to high thermal factors.

Those results are very encouraging: in terms of (i) reactivity, we have the proof that the two molecules of a-pyrone react together to form by-products (as seen in solution); (ii) synthetic formation, we can observe an evolution in function of (irradiation) time; (iii) result as we believe we made the required product, although it was not resolved well enough to claim we did.

Several problems were identified:

-if using conventional acquisition methods, it is extremely difficult to optimise the conditions of irradiation (intensity, duration) in order to bring enough energy for the reaction to take place, without bringing too much to avoid the destruction of the target product.

-once a radical forms, it probably reacts fairly rapidly even at 80K, therefore lengthy acquisition times probably decrease the chances to observe transition state species.

In order to improve this achievement, we have to make

- many
- rapid
- intense

measurements in order to isolate for sure the required crystalline form, as well as to identify the reaction mechanism for the formation of one very reactive but precious compound.