

Single-crystal-to-single-crystal $E \rightarrow Z$ and $Z \rightarrow E$ isomerizations of 3-chloroacrylic acid within the nanocavities of a supramolecular framework†

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Single-crystal-to-single-crystal $E \rightarrow Z$ and $Z \rightarrow E$ photoisomerizations of 3-chloroacrylic acid (HCIA) take place with full retention of the crystal lattice in the framework cavities of the supramolecular crystals $\text{CECR} \cdot \text{HCIA} \cdot 2\text{MeOH} \cdot 1.5\text{H}_2\text{O}$ ($\text{CECR} = C\text{-ethylcalix[4] resorcinarene}$); their progress has been monitored as the reaction proceeds.

Since the pioneering work by Cohen and Schmidt¹ on the solid-state photodimerization of cinnamic acid and its derivatives, many solid-state reactions have been studied. Of particular interest are topotactic, single-crystal-to-single-crystal reactions which proceed with retention of the crystal lattice, making it possible to infer the displacement of the individual atoms from the structures before and after the reaction.² Topotactic reactions are rare in neat crystals of photo-reacting species.^{2–4} They occur for intramolecular cyclizations,^{5,6} in which molecular migration is minimal, and for a limited number of intermolecular reactions, including $[2 + 2]$,⁷ and $[4 + 4]$ ⁸ photodimerizations. Such reactions can be controlled by co-crystallization⁹ with a judiciously chosen template molecule that, through hydrogen bonding or other interactions, orients the target molecules in a geometry conducive for the occurrence of the addition reaction.^{10–12}

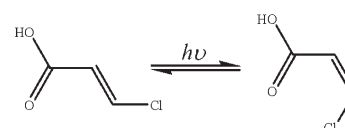
It has been argued that for solid-state reactions requiring significant molecular motions or involving changes in molecular shape, the initiation occurs at defects or surface sites in the crystal and the crystal lattice is destroyed when conversion percentages exceed 5–10%, even though the external shape of the crystals may be perfectly retained.^{4,13} However, recent advances in supramolecular host–guest crystal chemistry offer an alternative by allowing reactions to proceed within nanocavities of framework solids.^{2,14} An example is provided by the recently reported photo-reactions of *cis*- and *trans*-stilbene embedded in the nanocapsules formed by *p*-hexanoylcalix[4]arene.¹⁵ However, in that case photodimerization also occurs and the reactants are disordered in the cavities. Similarly, in the solid-state isomerization of stilbene embedded in a framework of tris-*o*-thymotide the stilbene molecules could not be located in the cavities,¹⁶ thus pre-empting the possible monitoring of the reaction. In the current report we describe a *trans*–*cis* ($E \rightarrow Z$) and the corresponding *cis*–*trans* ($Z \rightarrow E$) reaction that proceed in supramolecular solids without side reactions under full retention of the crystal lattice. In both cases the structures of

product and reactant molecules are fully determined for several conversion percentages.

Photochemical E/Z -isomerizations are of major interest in modern photochemistry as important physiological reactions are triggered by *cis*–*trans* and *trans*–*cis* isomerizations of molecules.^{17,18} Furthermore, such reactions are likely candidates for application in optoelectrical and optomechanical switching and storage devices.¹⁹ We find that fully ordered *trans*- as well as *cis*-3-chloroacrylic acid (HCIA, Scheme 1) molecules can be embedded in a framework formed by CECR ($\text{CECR} = C\text{-ethylcalix[4] resorcinarene}$, Scheme 2) to give supramolecular solids of composition $\text{CECR} \cdot \text{HCIA} \cdot 2\text{MeOH} \cdot 1.5\text{H}_2\text{O}$ (**1-E** and **1-Z**).[‡] They undergo photoisomerizations within the supramolecular nanocavities without distortion of the host framework, even though significant changes in molecular shape occur.

1-E and **1-Z** crystallize in the triclinic space group $P\bar{1}$, with a 1 : 1 host–guest ratio (Tables 1 and S1, ESI†). The CECR molecules in **1-E** adopt the bowl-shaped (*r-cis-cis-cis*) conformation with four intramolecular hydrogen bonds along their upper rim [90 K: $\text{O} \cdots \text{O}$ 2.730(2)–2.934(2) Å, Table S2, ESI†]. Adjacent CECRs are connected in an up-and-down fashion by intermolecular hydrogen bonds [$\text{O} \cdots \text{O}$ 2.678(2)–2.877(2) Å] to form wavelike layers parallel to the (010) plane (Fig. 1 and S1, ESI†). Adjacent hydrogen-bonded layers are juxtaposed along the *b* axis and form channels along the *a* axis with a 3.4×4.6 Å effective cross-section, which account for 33.6% of the crystal volume (Table S3, ESI†).²⁰ A fully ordered *E*-HCIA molecule (Fig. S2a, ESI†) is entrapped as a monomer in each cavity within the channels, which also contain methanol molecules. The cavity volume per *E*-HCIA molecule is 150.6 Å³. Two fully ordered methanol molecules are hydrogen-bonded to the hydroxyl oxygen atoms of a CECR [$\text{O} \cdots \text{O}$ 2.539(3) Å] and the carboxylic oxygen atoms of adjacent HCIA [$\text{O} \cdots \text{O}$ 2.539(3) Å]. The disordered water molecules fill the remaining void.

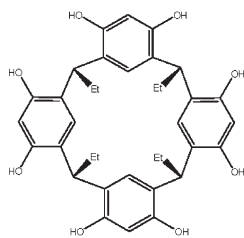
Replacement of *E*-HCIA by *Z*-HCIA gives **1-Z**, which is isomorphous with **1-E**. The HCIA guests (Fig. S2b, ESI†) are located in a 147.4 Å³ cavity within the channels (Fig. S3 and Table S3, ESI†), which account for 33.0% of the crystal volume.



Scheme 1 The E/Z -photoisomerizations of 3-chloroacrylic acid.

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† Electronic supplementary information (ESI) available: Scheme S1, Fig. S1–8 and Tables S1–4. See DOI: 10.1039/b703378h



Scheme 2 Diagram of CECR.

Table 1 Calculated excited state energy separations of HCIA

Energy separation	Z-HCIA <i>E</i> /eV (<i>f</i>)	<i>E</i> -HCIA <i>E</i> /eV (<i>f</i>)
S ₀ -S ₁	4.560 (0.001)	4.660 (0.001)
S ₀ -S ₂	5.820 (0.343)	5.847 (0.373)
S ₀ -S ₃	5.822 (0.001)	6.112 (0.001)
S ₀ -T ₁	3.358 (0.000)	3.373 (0.000)
S ₀ -T ₂	4.151 (0.000)	4.215 (0.000)

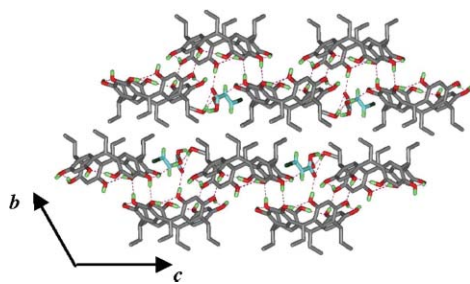


Fig. 1 Three-dimensional supramolecular architecture of **1-E** viewed along the *a*-axis direction.

A diffractometer-mounted crystal of **1-E** was exposed to 325 nm light from a 48 mW He/Cd laser at 90 K. After 1 h exposure, the external shape of the crystal and its color were essentially unchanged (Fig. S4, ESI†). Fourier difference maps²¹ clearly show light-induced peaks corresponding to a conversion of part of the molecules to the *Z*-configuration (Fig. 2(a)), and to shifts in the position of the whole molecule. The latter is attributed to repulsion of the Cl atom of the isomerized molecule by the channel wall. The dihedral angle between the plane through the three carbon atoms before and after irradiation is 11.6(1)°, whereas the Cl atom in the product is displaced by 0.460(2) Å from the carbon plane before irradiation. Least squares refinement of the data after 1 h exposure indicates that 29.1(3)% of the *E*-HCIA molecules were converted

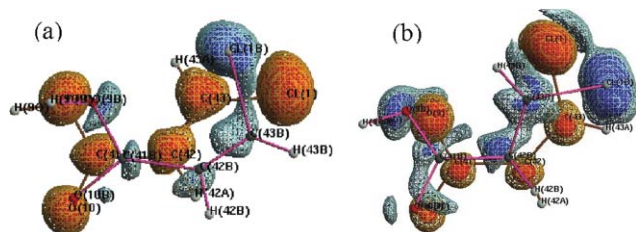


Fig. 2 The Fourier difference map of the HCIA (a) in **1-E** after 1 h exposure (blue: 2.0; light blue: 1.0; orange: -1.0; red: -2.0 e Å⁻³); (b) in **1-Z** after 1 h exposure (blue: 1.5; light blue: 0.7; orange: -1.5; red: -3.0 e Å⁻³).

to the *Z* form (Fig. 3, Table S4, ESI†). The population of *Z*-HCIA increases on further irradiation until a photostationary state with a conversion percentage of 41.1(4)% is reached after 10 h (Fig. 4). Even though the conversion percentage is considerable and both the shape of the guest and its position are affected by the photoisomerization, only small changes (<1%) in the unit cell parameters were observed after exposure (Tables S1 and S4, ESI†), confirming that the host molecules form the dominant structural component of the crystals.

In a second experiment, 39.7(3)% of the *Z*-HCIA molecules in **1-Z** were converted to the *E* form (Fig. 2(b), S5–S7, ESI†) after 1 h irradiation. The dihedral angle between the plane through the three carbon atoms before and after irradiation is 13.5(1)°, whereas the Cl atom in the product is displaced 0.363(2) Å from the carbon plane before irradiation. In the course of the reaction in the **1-Z** cavity the HCIA molecules undergo a reorientation, as do the methanol molecules (Fig. S8, ESI†). The reorientation of the latter provides additional space in the cavity for the product molecules. The rearrangement of guest molecules, which has been observed in other solid-state reactions^{2,22,23} favors the photoisomerization. Only very small expansions of the unit cell (Table S4, ESI†) occur, but the increase in cavity size per HCIA on *cis*–*trans* isomerization in **1-Z** (from 147.4 to 160.5 Å³, Table S3, ESI†) is significant and larger than that for the opposite reaction in **1-E** (from 150.6 to 151.5 Å³).

The percentages of *Z*-HCIA in **1** as a function of irradiation time of **1-E** and **1-Z**, derived from the structure analyses at each intermediate point, are presented in Fig. 4. The curves can be fitted with the exponential functions $y = 0.411(0) - 0.406(27) \exp[-t/0.98(8)]$ ($R = 0.98$) for $E \rightarrow Z$ in **1-E**, and with $y = 0.502(11) + 0.496(24) \exp[-t/0.68(9)]$ ($R = 0.99$) for $Z \rightarrow E$ in **1-Z**, where y is the percentage of *Z*-HCIA in the solids. Using first-order kinetics^{2,24,25} and standard equilibrium expressions,^{2,25} gives the following rate constants: for irradiation of **1-E**, $k(E \rightarrow Z) = 0.42(4) \text{ h}^{-1}$ and $k(Z \rightarrow E) = 0.60(4) \text{ h}^{-1}$; for **1-Z**, $k(E \rightarrow Z) = k(Z \rightarrow E) = 0.74(5) \text{ h}^{-1}$. Thus, the reaction is faster in the *Z* structure, in which the space available to the reactant in the channel shows a larger increase as the reaction proceeds, and the photostationary state contains equal amounts of the two isomers.²⁶ In the *E* structure the reaction cavity is less flexible and the *cis*–*trans* ‘back’ isomerization is favored over the *trans*–*cis*, as a result the equal distribution is not reached. It should be noted that the absolute values of the rate constants given here depend on the incident photon flux, while the relative values for the forward and back reactions in one crystal depend on the relative absorption of the two isomers and the oscillator strength of the photoinduced transition to the reactive (π^*) excited state. However, parallel TDDFT calculations²⁷ show the HOMO– π^* energy gaps and

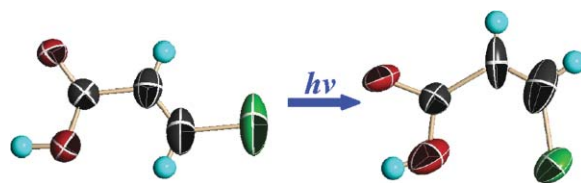


Fig. 3 Perspective views showing 50% probability displacement ellipsoids of *E*-HCIA in **1-E** before exposure and *Z*-HCIA in **1-E** after 1 h exposure.

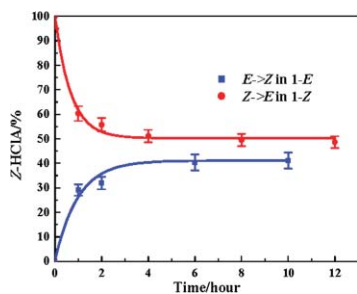


Fig. 4 Percentage of Z-HClA in the CECR host-guest complexes as a function of irradiation time.

oscillator strengths (Fig. S9, ESI† and Table 1) to be practically identical for the *E* and *Z* isomers.

In summary, $E \rightarrow Z$ and $Z \rightarrow E$ photoisomerizations in the supramolecular solid state have been monitored directly by experimental structural methods. Isolation of the photoactive molecule in the supramolecular framework prevents [2 + 2] dimerization or polymerization, which occur when C=C bonds are oriented parallel in sufficiently close proximity.^{1,13,15} Even though the conversion percentage is quite large and both the shape of the photo-active guest and its position are affected by the photoisomerization, the hydrogen-bonded framework is sufficiently robust to preserve the crystal structure in both cases.

The ability to monitor chemical reactions of molecules confined within an inert periodic framework is of particular importance in the developing field of time-resolved diffraction,²⁸ as it points the way to methods for elucidating the mechanism of chemical reactions with pump-probe techniques. The time-resolution that can be achieved in such studies is limited by the width of both the laser-pump and the X-ray probe-pulse. New X-ray sources now under construction promise to greatly reduce such limitations and thus add to the importance of exploratory studies like the one described here.²⁹

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Notes and references

† *Synthesis*: **1-E**: A methanol solution (3 mL) of *E*-HClA (0.05 mmol) was added dropwise to a stirred methanol solution (5 mL) of CECR (0.05 mmol) at 50 °C for 30 min. Slow evaporation at room temperature produced pale yellow crystals after two weeks (yield 82%).

1-Z: As for **1-E**, with Z-HClA replaced by *E*-HClA (yield 68%).

Photocrystallography: A crystal of **1** mounted on a diffractometer was used for data collection at 200 and 90 K and subsequently exposed at 90 K to 325 nm light from a 48 mW He/Cd laser for different lengths of time (Table S4, ESI†). The crystal was rotated around the ϕ axis during irradiation. X-Ray data were collected at 90 K starting 1 h after each irradiation. All the non-hydrogen product atoms were found in the 90 K Fourier photodifference maps, with coefficients $F_o(t) - F_o(0)$. The percentages of the reactant and product in the crystal were determined in the data refinement. CCDC 629568–629580. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b703378h.

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