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*Published Version:*
D'Agostino, S., Spinelli, F., Boanini, E., Braga, D., Grepioni, F. (2016). Single crystal to single crystal [2+2] photoreactions in chloride and sulphate salts of 4-amino-cinnamic acid via solid-solution formation: A structural and kinetic study. CHEMICAL COMMUNICATIONS, 52(9), 1899-1902 [10.1039/c5cc09412g].

*Availability:*
This version is available at: https://hdl.handle.net/11585/551667 since: 2020-02-04

*Published:*

DOI: http://doi.org/10.1039/c5cc09412g

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This is the final peer-reviewed accepted manuscript of:

**Simone d'Agostino, Floriana Spinelli, Elisa Boanini, Dario Braga and Fabrizia Grepioni, *Chem. Commun.***, 2016,**52**, 1899-1902

The final published version is available online at: **https://doi.org/10.1039/C5CC09412G**

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COMMUNICATION

# Single crystal to single crystal [2+2] photoreactions in chloride and sulphate salts of 4-amino-cinnamic acid *via* solid-solution formation: a structural and kinetic study.

Simone d'Agostino,[a,*] Floriana Spinelli,[a] Elisa Boanini,[a] Dario Braga,[a] and Fabrizia Grepioni[a,*]

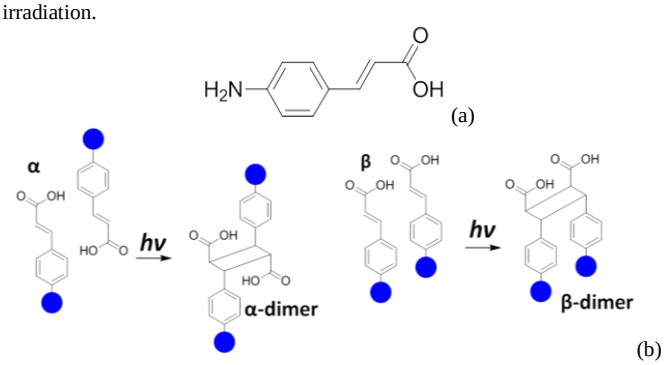
**A set of molecular salts with general formula $[1H]_nA{\cdot}xH_2O$ (1= 4-amino-cinnamic acid, $A^{n-}$=$NO_3^-$, $BF_4^-$, $PF_6^-$, $SO_4^{2-}$, x = 0, 1) was prepared and structurally characterized. [1H]Cl and $[1H]_2SO_4{\cdot}H_2O$ (II) were found to undergo an SCSC stepwise [2+2] photodimerization, which was followed *via* X-ray diffraction; a kinetic analysis was performed on single crystals of both salts. In the case of [1H]Cl the photoreaction was studied also on polycrystalline material.**

Cinnamic acid derivatives became paradigmatic in the field of solid state organic chemistry and crystal engineering[1] after the pioneering work of Schmidt and co-workers who, after studying photoreactivity of this class of compounds, formulated the well known topochemical postulate which states that a maximum centre-to-centre bond separation of 4.2 Å is a necessary condition for [2+2] photoreactions to occur.[2] Nevertheless, either positive or negative exceptions to this rule have been reported in the literature[3] and additional geometrical criteria[4] and alternative mechanisms have been proposed, such as the phase rebuilding mechanism by Kaupp.[5]

This class of reactions has attracted the curiosity of the scientific community, and has been the object of intense investigations over the last decades, aimed at controlling the reactivity in the solid state by using templating units to preorganize double bonds-containing molecules *via* non covalent interactions such as hydrogen bond,[6] metal-coordination,[7] and also halogen bond.[8] Beside this, there is also an emerging interest in the conversion of light energy into mechanical work,[9] and to this end systems able to undergo single crystal to single crystal (SCSC) transformations are particularly sought.[10] Such reactions involve relatively small movements of atoms: in [2+2] reactions the $C_{C=C}$ atoms have to move of *ca*. 0.70 Å to form the cyclobutane ring, and their substituents need to slightly move and reorient themselves accordingly. These movements are unavoidably accompanied by generation and/or accumulation of stress and strain, which can, and most often do, cause single crystals to decompose into microcrystalline or even into amorphous materials in response to the tremendous pressures arising from the chemical reaction.[11]

In this paper we report our findings on the solid-state [2+2] photoreactivity in a series of molecular salts with general formula $[\mathbf{1}H]_nA{\cdot}xH_2O$, where **1** is the 4-amino-cinnamic acid, and the inorganic anion $A^{n-}$ is $NO_3^-$, $BF_4^-$, $PF_6^-$, or $SO_4^{2-}$ (x = 1 for the $SO_4^{2-}$ and 0 for all the other anions). By varying the size, shape, and charge of the inorganic anion we expected to obtain different arrangements for the $\mathbf{1}H^+$cations within the crystal structures, that might lead to different photoproducts upon irradiation (see Chart 1).

**Chart 1.**(a) The 4-amino-cinnamic acid **1**; protonation of the amino group leads to the cationic unit $[\mathbf{1}H]^+$ (blue dot = —$NH_3^+$). (b) Depending on the head-to-tail (α) or head-to-head (β) arrangement of the cationic units, truxillic or truxinic acid derivatives, respectively, could in principle be obtained upon irradiation.




To this end we have prepared crystals of the molecular salts containing the cationic unit $[\mathbf{1}H]^+$ and the inorganic anions $Cl^-$, $NO_3^-$, $BF_4^-$, $PF_6^-$, or $SO_4^{2-}$, by first reacting **1** with HCl to obtain the chloride salt [**1**]Cl, followed by anion exchange with the appropriate silver(I) salt (see ESI). All compounds were characterized *via* single-crystal X-ray diffraction, with the exception of $[\mathbf{1}H]NO_3$, whose structure was solved from powder diffraction data. The sulphate $[\mathbf{1}H]_2SO_4{\cdot}H_2O$ and the tetrafluoroborate $[\mathbf{1}H]BF_4$ salts were obtained in two polymorphic modifications, form I and form II (see ESI for full structural descriptions).

A preliminary analysis of the geometrical parameters (d, τ, α)[‡] for the mutual orientation of neighboring $[\mathbf{1}H]^+$ cationic units (see Scheme 1 and Table 1), allowed us to evaluate the feasibility of the [2+2] photoreaction.

Promising values of d, τ, α were found only for [**1**]Cl, $[\mathbf{1}H]_2SO_4{\cdot}H_2O$ (II), $[\mathbf{1}H]NO_3$ and $[\mathbf{1}H]BF_4$ (II). In order to test their reactivity, the same single crystals (with the exception of $[\mathbf{1}H]NO_3$, available only as polycrystalline powder) used for structure determination were

irradiated *ex-situ* for a period of 12 h with a LED source (λ = 365 nm) placed at a distance of 1 cm from the sample.
Subsequent X-ray data collections on the irradiated specimens showed that the cyclization reaction had been successful in the case of [1H]Cl and $[1H]_2SO_4{\cdot}H_2O$ (II), for which only a slight decrease in the quality of the diffraction data crystals was observed, but no crystal destruction (see ESI). $[1H]NO_3$ and $[1H]BF_4$ (II), on the contrary, are photostable, which confirms the observation that the 4.2 Å empirical rule, though a necessary condition, is not sufficient in guaranteeing the outcome of the cycloaddition reaction. The reasons why these reactions do not occur are not fully clear to us. Perhaps, the lack of reactivity may be interpreted in terms of other factors as reaction cavity and lattice energy.[12] *i.e.* the required molecular migration of the reactants within the crystal lattice are hampered by the strongest/different and destabilising electrostatic repulsions, arising from the charge balancing anions, which make the packing "*less plastic*", thus less prone to reaction.

**Scheme 1.** Geometrical parameters used to evaluate the potential photoreactivity of crystalline $[1H]_nA{\cdot}xH_2O$.

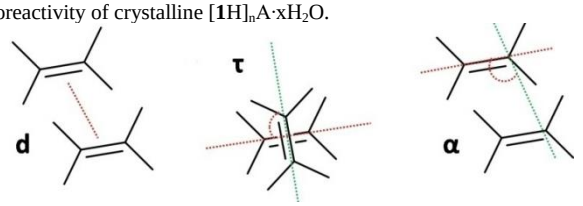



**Table 1.** Types of head-to-tail (α) arrangements observed in crystalline$[1H]_nA{\cdot}xH2O$, together with relevant geometrical parameters.

| | type | d (Å) | τ (°) | α (°) |
|---|---|---|---|---|
| [1H]Cl | α[a] | 3.657(5) | 0 | 86.8(2) |
| $[1H]NO_3$ | α[a] | 4.128(2) | 0 | 86.8(5) |
| $[1H]_2SO_4{\cdot}H_2O$ (II) | α1[a] | 3.542(5) | 0 | 80.2(2) |
| | α2[b] | 4.726(6) | 0 | 56.7(2) |
| $[1H]BF_4$ (II) | α1[a] | 3.681(7) | 0 | 74.4(3) |
| | α2[a] | 3.746(7) | 0 | 88.7(3) |

a) Double bonds related by an inversion center. b) This α arrangement is not expected to be reactive, because of the long d value.

In crystalline [**1**H]Cl the photoreaction proceeds quantitatively (Fig.1a), accompanied by variations in the unit cell parameters and a significant contraction of the cell volume (–5.2 %), while the hydrogen bond distances remain almost unaltered (see ESI).

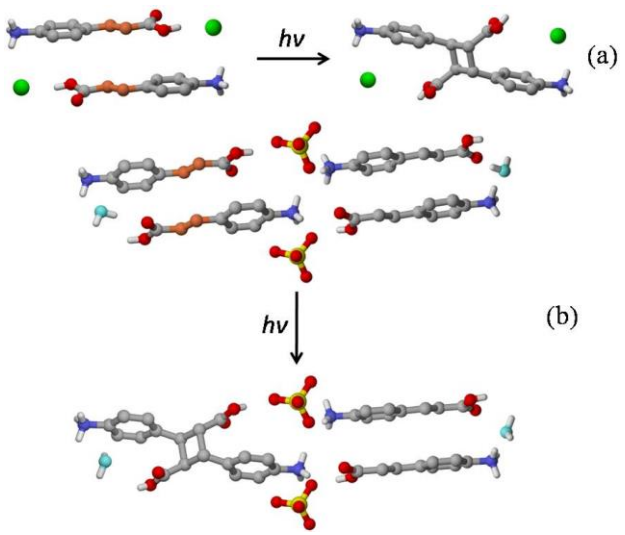
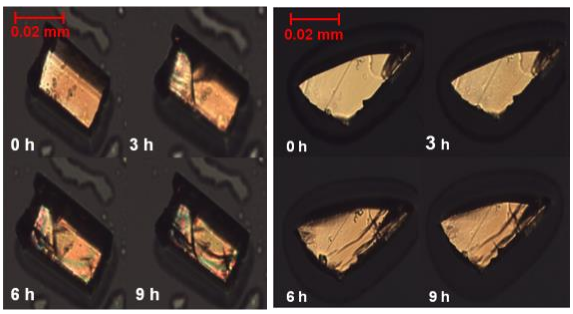



**Fig.1.** Photodimerization of [**1**H]Cl and $[1H_2]SO_4{\cdot}H_2O$ (II) upon UV irradiation. Reactive double bonds in *orange* (arrangement α and α1 for [**1**H]Cl and $[1H_2]SO_4{\cdot}H_2O$ (II), respectively). Water oxygens in cyan, and $H_{CH}$ omitted for clarity.

In the case of $[1H]_2SO_4{\cdot}H_2O$ (II) a less pronounced variation both in the unit cell parameters and volume (–1.6 %) were observed (see ESI). The minor change can be ascribed to the fact that only the α1 dimer (Table 1 and Fig.1b) is photoreactive. As observed in the case of the chloride salt, the hydrogen bonds distances remain almost unaltered (see ESI).[¥]

To further investigate the SCSC reactions, two single crystal specimens of [**1**H]Cl and $[1H]_2SO_4{\cdot}H_2O$ (II) were selected, and the photoreaction under UV irradiation was followed by taking pictures with a cross-polarized optical microscope at time intervals of 3 h (see Fig.2).




(a) (b)

**Fig.2.** Optical microscope pictures showing single crystals of [**1**H]Cl (a) and $[1H]_2[SO_4]{\cdot}H_2O$(II) (b)after UV irradiation at time intervals of 3h.

In both cases the crystals outer shapes were preserved, but the unit cell volumes, determined by X-ray diffraction at t=0 and 6h, corresponded to the starting and reacted crystals, respectively [945.962(1) $Å^3$ and 896.799(5) $Å^3$ for [**1**H]Cl, and 988.758(2) $Å^3$ and 977.415(1) $Å^3$ for $[1H]_2SO_4{\cdot}H_2O$ (II). The larger volume contraction, *i.e.* the greater stress, experienced upon photodimerization by [**1**H]Cl, with respect to $[1H]_2[SO_4]{\cdot}H_2O$ (II), is probably at the origin of the damaged aspect of the chloride single crystal surface when compared to the sulphate analogous after only 3h of exposure to UV radiation. This was confirmed by SEM microscopy. In Fig.3. are shown the micrographs of single crystals of[**1**H]Cl and $[1H]_2SO_4{\cdot}H_2O$ (II) taken before and after overnight irradiation. Even though both crystals retain their overall integrity, it is clearly visible how the crystal surface of [**1**H]Cl is more cracked, compared the one of$[1H]_2SO_4{\cdot}H_2O$ (II), as a result of the UV irradiation and structural change.

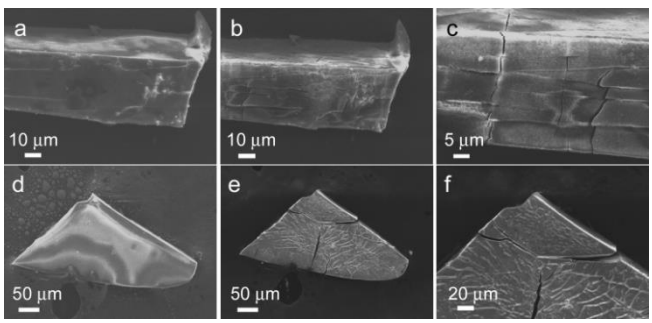



**Fig.3.**SEM micrographs of single crystals of (top) [**1**H]Cl before (a) and after (b, c) overnight irradiation at 365 nm; and of (bottom) $[1H]_2[SO_4]{\cdot}H_2O$ (II) before (d) and after (e, f) overnight irradiationat 365 nm.

The SCSC photodimerization process was then followed stepwise: a fresh single crystal was selected for each of the two salts, and it was exposed to UV radiation for subsequent short time intervals (30 min or 1h); the UV lamp was kept at a distance of 1cm. *After each*

*exposure* single crystal data were collected and the structure re-determined. Upon irradiation, the presence in the crystals of the cyclobutane ring was detected, and its percentage increased linearly with the irradiation time up to complete conversion (see ESI for details), in a zero-order process, for both compounds (Fig.4), and with rate constants of 12.26 $h^{-1}$ and 17.10 $h^{-1}$ for [**1**H]Cl and [**1**H]$_2SO_4 \cdot H_2O$ (II), respectively.[§] These findings are in contrast with what previously detected on similar system by Abrahams et al. or Turowska-Tyrk, who found a first order behaviour,[13] or by Hayes et al. who found a sigmoidal dependence of the dimer content *vs* time that could be described by the AVRAMI model.[14] Concerning the difference in the rate constant, we can only assume that is due to the presence of water in the crystal lattice of [**1**H]$_2SO_4 \cdot H_2O$ (II). An effect of crystallization water on the photoreactivity in other cinnamic acid derivatives or acridizinium salts was previously reported.[15]

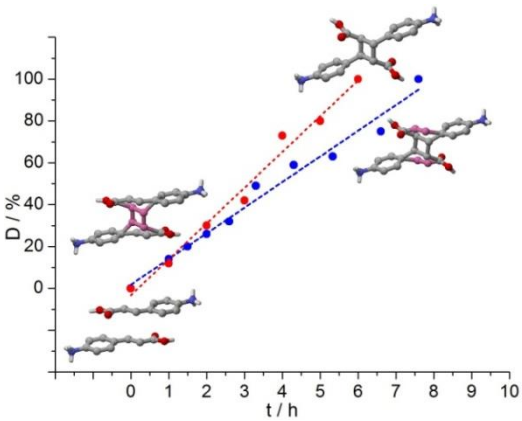



**Fig.4**. (a) Dependence of dimer content (D, %) on the irradiation time for [**1**H]Cl (in blue) and [**1**H]$_2SO_4 \cdot H_2O$ (II) (in red), and qualitative representation of the photodimerization over the course of UV irradiation: pink atoms represent the lower occupancy sites. $H_{CH}$ omitted for clarity.

UV irradiation experiments were carried out in polycrystalline materials, with the exception of [**1**H]$_2SO_4 \cdot H_2O$ (II), which could only be obtained as a mixture of forms I and II (see ESI). ATR-FTIR spectra were run before and after irradiation of the powder samples (see ESI), and only for compound [**1**H]Cl the characteristic band of the conjugated C=O stretching at 1690 $cm^{-1}$ shifted to 1710 $cm^{-1}$ due to the deconjugation of the carbonyl group, and disappearance of olefinic C=C stretching (1639 $cm^{-1}$) was observed when dimerization was complete (see Fig.5).[16]

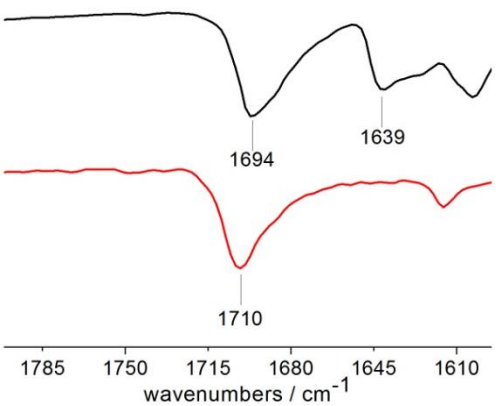



**Fig.5.** Portions of the ATR-FTIR spectra for crystalline [**1**H]Cl run before and after UV irradiation.

Also $^1$HNMR solution spectroscopy showed that, upon irradiation, [**1**H]Cl quantitatively converted in the corresponding α-dimer,as confirmed by the disappearing of the olefinic peaks at 7.5 and 6.4 ppm and the emergence of cyclobutane protons at 4.3 and 3.8 ppm (see Fig 6).

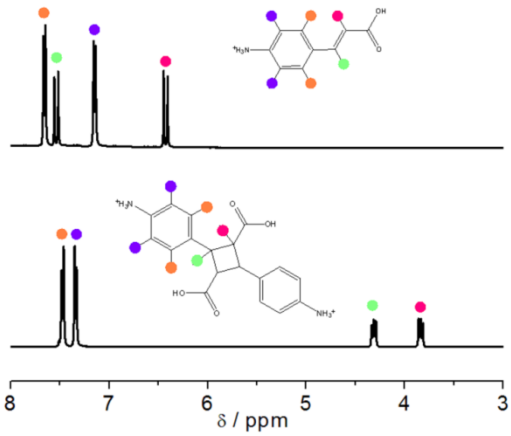



**Fig.6.** $^1$HNMR spectra in DMSD-$d_6$ of [**1**H]Cl run before (top) and after (bottom) overnight irradiation at 365 nm.

One aspect still needed clarification, i.e. if also polycrystalline material would behave as large, single crystals, and proceed through solid solution formation over the full range of composition. To this aim, powder XRD diffraction was monitored on a polycrystalline sample of [**1**H]Cl during steady UV irradiation (see ESI for experimental details).

Fig.8a and 8c show how the starting (0 h) and final (after 12 h) XRD patterns are in good agreement with the simulated ones, thus indicating samples purity and completion of the photoreaction, while peaks broadening was observed after 4h of irradiation (Fig. 8b). This is probably due to the simultaneous presence of solid solutions at different stages of reactivity, with the one at 60% of conversion (black line) being the major component, and the reason for this could either be an effect of inhomogeneous permeation of the UV radiation into the material or of particle size distribution in the polycrystalline sample. To our knowledge, this is the first time that the [2+2] photocycloaddition reaction has been found to proceed *via* solid solution formation also in polycrystalline samples.

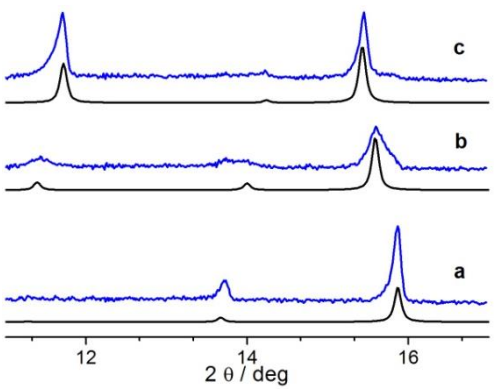



**Fig.8.**Details of the comparisonbetweencalculated (blacklines) and experimental (bluelines)XRPD patterns for [**1**H]Cl recorded during steady UV irradiation: (a) starting material, (b) after 4h (ca. 60% conversion) and (c) after 12h (100% conversion).

In summary, in this paper we reported the synthesis and the structural characterization of a series of molecular salts with general formula [**1**H]$_n$A$\cdot$x$H_2O$, where: **1** = 4-amino-cinnamic acid, $A^{n-}$ = inorganic anion ($NO_3^-$, $BF_4^-$, $PF_6^-$, and $SO_4^{2-}$) x = 1, for the $SO_4^{2-}$, and = 0, for

all the other anions. In crystalline [**1**H]Cl, [**1**H]$_2$SO$_4$·H$_2$O (II), [**1**H]NO$_3$, and [1H]BF$_4$ (II) the mutual arrangement of the double bonds satisfy all the commonly relevant geometrical criterions. Only the chloride and sulphate salts, though, undergo a SCSC [2+2] photodimerization to the corresponding α-dimers, while the nitrate and tetrafluoroborate salts are phototostable under UV irradiation. Interestingly, in crystalline [**1**H]$_2$SO$_4$·H$_2$O (II) only one arrangement for the cationic units [**1**H]$^+$ was found to be reactive.

For [**1**H]Cl and [**1**H]$_2$[SO$_4$]·H$_2$O (II) the photoreactions were followed by single crystal X-ray diffraction (*ex-situ* irradiation), which evidenced a zero-order kinetic behaviour, and visually monitored by cross-polarized optical microscopy and SEM, which showed that upon irradiation single crystals of [**1**H]Cl experience a greater stress than those of [**1**H]$_2$SO$_4$·H$_2$O (II).

The behaviour of polycrystalline samples was also investigated for [**1**H]Cl *via* ATR-FTIR and $^1$HNMR spectroscopy. Powder XRD run during steady UV irradiation indicate that also in polycrystalline specimens the photoreaction proceed *via* formation of solid state solutions, and to the best of our knowledge this is the first evidence of such behaviour.

In order to perform a full and detailed kinetic analysis of the photoreaction in polycrystalline samples, quantitative extraction of the content of reactant and product from each crystal phase would be essential, as well as a careful analysis of the factors causing the inhomogeneous permeation of the UV radiation into the polycrystalline sample. More accurate experiments, such as time-resolved XRPD experiments,[9b,17] and the exploration of different experimental setups are thus necessary. Work in this direction is ongoing.

Financial support from MIUR and the University of Bologna is acknowledged.

## Notes and references

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‡d = centre-to-centre bond separation between carbon atoms of C=C bonds in adjacent molecules (Schmidt's rule). Upper limit is 4.2Å. τ = torsion angle C=C···C=C formed by the adjacent molecules. The ideal value is 0°. α = shift of one C=C bond along the second C=C. The ideal value is 90°.

¥ It is perhaps worth noting that the cyclodimerization process results in the formation of *a dication* from two monocationic units.

§ The plots can be described by the following linear equations: dimer(%)_in_[**1**H]Cl= 1.82 + 12.26·t(h) with $r^2$ = 0.97; and dimer(%)_in_[**1**H]$_2$SO$_4$·H$_2$O (II) = -3.17 + 17.10·t(h) with $r^2$ = 0.98.

†Electronic Supplementary Information (ESI) available:synthesis and crystal growth, single crystal data and measurements details, ORTEP plots, packing features, powder X-ray diffraction patterns. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/


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