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Accessing New Charge-Transfer Complexes by Mechanochemistry: A Tetrathiafulvalene Chloranilic Acid Polymorph Containing Segregated Tetrathiafulvalene Stacks

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Supporting Information

ABSTRACT: Two polymorphs of tetrathiafulvalene chloranilic acid (TTF-CAH₂) have been synthesized by mechanochemistry. The previously known "ionic" polymorph (form I) was prepared by liquid-assisted grinding (LAG) using various highly polar solvents as well as protic but moderately polar solvents, such as alcohols of one to four carbon atoms. A new TTF-CAH₂ polymorph (form II) was obtained by LAG and slurry mechanochemistry using aprotic, low-polarity solvents, as well as nonpolar solvents and neat grinding. The crystal structure of the new TTF-CAH₂ polymorph was determined from the combined analysis of synchrotron



powder X-ray diffraction and neutron powder diffraction data at room temperature. The material displays segregated stacks of TTF and CAH₂ molecules. Fourier transform infrared spectroscopy as a function of the temperature (10-300 K) indicates that TTF-CAH₂ form II is an electrical semiconductor with a small band gap of ~0.115 eV (versus ~0.146 eV for the "ionic" form I), and there is no indication of phase transitions in that temperature interval. The examination of the frequency regions wherein the absorption bands of TTF and TTF^{+•} species occur suggests that TTF-CAH₂ form II is most likely a neutral phase.

INTRODUCTION

Organic cocrystallization is an effective crystal engineering approach^{1,2} to modify the physicochemical properties of organic substances, tailoring them to expected applications,³ such as electronics, pharmaceutical, energy materials,⁴ etc. Modern developments in organic electronics include organic ferroelectrics,^{5,6} multiferroics,³ conducting and superconducting charge-transfer complexes,7 liquid crystals, light-driven actuators, etc.³ In the pharmaceutical research field, cocrystal screening is routinely performed to optimize the properties of solid drug delivery forms and active pharmaceutical ingredient (API) performance.^{3,8,9} Several synthetic methods have been

utilized for the preparation of organic cocrystals,¹⁰ such as solvent evaporation and solution chemistry,¹⁰ melting,⁹ cosublimation, sonication,¹¹ and mechanochemistry.^{12–14} The latter has been increasingly used during recent years,¹⁵ offering advantages beyond reduced use of reaction solvents, economic costs, and reduced environmental impact,¹⁶ such as bypassing reactant solubility issues, shorter reaction times, high selectivity, and good stoichiometry control.¹⁵ Moreover,

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mechanochemical reactions occasionally yield products (crystal structures or stoichiometries) not obtainable from other synthetic routes.^{15,16} However, the mechanochemical reaction mechanisms are poorly understood, and their main characteristics are only starting to be unravelled. Recent significant developments include new methods to measure mechanochemical reaction kinetics in situ using synchrotron powder X-ray diffraction and Raman spectroscopy.¹⁷

"Green" mechanochemical syntheses using small quantities of liquids while grinding the reactants as powders, called liquid-assisted grinding (LAG),^{18–20} are an effective approach to obtain materials of improved crystallinity compared with the products of neat grinding.¹⁸ The powder diffraction data of the former show generally less peak broadening effects and are often treatable toward crystal structure solution from powders,^{21,22} avoiding the need for preparing single crystals by seeding.⁷ The small volumes of liquid added in mechanochemical reactions by LAG facilitate mass transport within the reaction mixtures. LAG can induce mechanochemical reactivity in otherwise unreactive chemical systems and increases the reaction rates, and it can lead to the selective formation of particular product polymorphs.^{16,19,20} A unique explanation for the liquid phase role in LAG reactions does not exist, and most likely it changes from reaction to reaction. However, in some studies solvent polarity has been regarded as a control parameter toward selectively preparing or screening product polymorphs.^{15,23-20}

LAG has been used to obtain pure polymorphic phases of charge-transfer complexes (CTC) of tetrathiafulvalene (TTF), such as the green and black TTF-CA (tetrathiafulvalene chloranil),²³ and the ionic form of TTF-DDQ (tetrathiafulvalene 2,3-dichloro-5,6-dicyano-*p*-benzoquinone).²⁴ The crystal structures of the ionic, diamagnetic TTF-CA (black form) and TTF-DDQ (also ionic) were determined from synchrotron powder X-ray diffraction,^{23,24} while Fourier transform infrared spectroscopy was used to investigate absorption edges, showing that both materials are small band gap semiconductors, and they lack phase transitions while the temperature is decreased from 300 to 10 K. The ionic, black TTF-CA is thermodynamically more stable than the green, pseudoneutral TTF-CA form, which shows a neutral to ionic transition at around 81 K and atmospheric pressure, giving rise to an organic ferroelectric material extensively studied.^{27,28}

As a continuation of the above studies, this work summarizes the mechanochemical synthesis and solid-state characterization of CTC polymorphs of tetrathiafulvalene and chloranilic acid (CAH₂). Tetrathiafulvalene is an extensively studied electron donor,²⁹ with rather facile oxidation forming the stable cation radical TTF^{+•}. Its tendency to pack in columns in the solid state with a consequent overlap of π orbitals, as well as the formation of mixed-valence compounds containing neutral and ionized molecules, often gives rise to exotic properties such as metallic electrical conductivity in organic materials.^{30,31}

Chloranilic acid is a versatile organic ligand with redox and acidic properties, which has been used as cocrystal former and a chelation agent in varied organic and metal–organic^{32,33} materials. Many of those are hydrogen-bonded cocrystals or salts with amines,^{34,35} since chloranilic acid is a proton donor, with $pK_{a1} = 0.76$ and $pK_{a2} = 3.08$,³⁶ and thus it yields the CAH⁻ and CA²⁻ species by deprotonation with bases. Chloranilic acid has given rise to another extensively studied organic ferroelectric, CAH₂-phenazine,^{6,37} as well as CTC with pharmaceutical drugs such as cefpodoxime proxetil³⁸ and

methyldopa,³³ among others. One TTF-CAH₂ "ionic" polymorph was found in the literature.³⁹ The previous study reports that "black single crystals began to form at RT after a week of pouring a MeCN solution of CAH₂ into a TTF solution in the same solvent".³⁹ We also obtained this material by LAG (herein it will be called "form I"), as well as in attempts to grow single crystals of a new TTF-CAH₂ polymorph obtained by LAG and neat grinding, called "form I". As in our previous studies,^{23,24} the crystal structure and properties of this new material were determined using room temperature (RT) synchrotron powder X-ray diffraction (PXRD) and FT-IR spectroscopy as a function of the temperature. RT neutron powder diffraction was used to determine CAH₂ hydrogen positions and additional molecular geometry details.

Most commonly, charge-transfer complexes have been synthesized by slow diffusion of solutions or by electro-crystallization,⁴⁰ since the anisotropic measurement of physical properties in single crystals is ultimately sought. However, one of the objectives of the present work has been to gather information about the liquid role in a series of related mechanochemical reactions using LAG, such as those of TTF and benzoquinone derivatives, with the goal of formulating explanations that could ultimately be used in the elucidation of mechanistic aspects or in the correlation of LAG liquid properties with properties of the products (e.g., ionicity, TTF packing motifs). Thus, the synthetic methodology was studied toward gathering observations about the physicochemical conditions yielding forms I or II as pure phases. Understanding those may be of importance not only for the synthesis of organic metals and mixed-valence organic CTC, but for other types of technologically important materials, such as pharmaceutical cocrystals or salts, and nonionized or zwitterionic organic cocrystals in general. The formation of TTF-CAH₂ forms I and II from the orange (monoclinic) TTF reactant is discussed taking into account likely relevant physicochemical properties of the solvents used in LAG (e.g., protic or aprotic character, dielectric constant, vapor pressure), as well as the quantity of solvent in the reaction mixture, expressed as η (μ L of solvent per mg of reactants). Moreover, a few vapor digestion (VD) and solution syntheses were carried out toward determining whether TTF-CAH₂ form II may be only obtainable by mechanochemistry or not.

EXPERIMENTAL SECTION

Synthetic Procedures and Materials. TTF (99% purity) was obtained from Sigma-Aldrich (brown, triclinic polymorph) and Acros Organics (orange, monoclinic polymorph). CAH₂ (99% purity), and solvent reagents were obtained from commercial suppliers and used as received.⁴¹

The sample of TTF-CAH₂ form II used for synchrotron PXRD was synthesized by manually grinding 0.0454 g (2.22×10^{-4} mol) of TTF (orange, monoclinic form) and 0.0464 g (2.22×10^{-4} mol) of CAH₂ in an agate mortar with pestle, with 184 μ L of ethyl acetate immediately before the start of grinding and again 184 μ L of the same solvent after 15 min. The reactants were ground for a total of 30 min.

Samples of form I and II used for FT-IR analysis as a function of the temperature were synthesized by manually grinding in an agate mortar with pestle 0.0454 g (2.22×10^{-4} mol) of TTF (orange form) and 0.0464 g (2.22×10^{-4} mol) of CAH₂ for a total of 30 min. To obtain form I, the reactants were ground with 20 μ L of DMSO added immediately before starting grinding, while TTF-CAH₂ form II was prepared adding to the reactants 92 μ L of MeCN immediately before the start of grinding and again 92 μ L of the same solvent after 15 min of reaction.

Scheme 1. (a) The CAH₂ Neutral Molecule, (b) the Acid Dissociation Product, CAH⁻, (c) the Chloranilate Ion (CA²⁻), and (d) the Reduced Form of Chloranilic Acid, CAH₄



A few attempts to prepare 1 batch of ca. 1 g of TTF-CAH₂ form II (necessary for neutron powder diffraction) using 2 μ L/mg of ethyl acetate or MeCN failed, giving mixtures of both polymorphs. Thus, six batches of TTF-CAH₂ form II, whose purity was previously checked by laboratory PXRD, were mixed to give ~1 g of that material. Each batch was prepared by grinding 0.0800 g (3.915 × 10⁻⁴ mol) of TTF (orange form) and 0.0818 g (3.915 × 10⁻⁴ moles) of CAH₂ for 45 min total, with small aliquots (around 81 μ L) of ethyl acetate added at the start of the reaction, after 20 min, and again after 30 min of reaction. Finally, the six batches were ground together in a glass mortar with three 161.8 μ L aliquots of ethyl acetate for around 15 min.

The synthesis conditions to investigate the solvent effect in LAG at increasing η , in VD reactions, and from solutions are detailed in the Supporting Information. In general, 0.0123 g (6.0×10^{-5} mol) of TTF (orange form) was ground in an agate mortar with pestle under air together with 0.0125 g (6.0×10^{-5} moles) of CAH₂. Immediately before start grinding, the reactants were mixed with a spatula to homogenize the powder mixture, and half of the solvent volume corresponding to the reported η was added with a micropipette. The remaining solvent was added after 15 min of reaction. Only for all samples with $\eta = 36$ mL/mg, the total solvent volume was added in three equal aliquots every 10 min. The reactants were manually ground for a total of 30 min in all cases.

FT-IR Measurements. Temperature-dependent FT-IR and midinfrared (MIR) measurements were collected in a Bruker 66 V interferometer with 2 cm⁻¹ resolution at 300, 250, 200, 150, 100, 50, and 10 K. Pellets made of TTF-CAH₂ powders diluted in KBr (for MIR) or polyethylene (for FIR) were mounted on the coldfinger of a He-closed cycle cryostat. Additional FT-IR spectroscopy measurements at RT to identify possible amorphous products (see Supporting Information) were carried out in a Bruker Alpha System with ATR diamond single channel attachment, from 400 to 4000 cm⁻¹ and 4 cm⁻¹ resolution.

X-ray Single-Crystal Diffraction. The diffraction data of TTF-CAH₂ ("ionic" form I) was collected at RT with a Bruker Smart APEX II single-crystal diffractometer equipped with a 4K CCD detector and an Oxford Cryostream Plus variable temperature system. Single crystals were obtained by slow solvent evaporation of a MeCN solution of TTF and CAH₂ seeded with the TTF-CAH₂ mechanochemical product (form II) obtained by LAG with MeCN (2 μ L/mg).

Powder X-ray Diffraction. For initial crystal phase identification, laboratory PXRD data in Bragg–Brentano geometry were collected in a Rigaku Miniflex II powder diffractometer, using Cu K α radiation (λ = 1.5418 Å), in the 2 θ interval 5–65°, with a 0.02° step size and 1°/min scan speed. The samples were loaded on quartz, low-background sample holders. Additional measurements were collected in a Bruker D2 Phaser powder diffractometer, using Cu K α radiation (λ = 1.5418 Å) and a low-background silicon flat-plate sample holder.

For crystal structure determination using direct-space methods, the synchrotron PXRD pattern of TTF-CAH₂ (form II) was collected at RT and $\lambda = 0.699711$ Å, in transmission geometry from a glass capillary, at the beamline X16C, N.S.L.S.-I, Brookhaven National Laboratory, USA. The wavelength was selected with a Si (111) double monochromator, and the incident parallel beam was monitored with an ion chamber. A Ge(111) analyzer crystal was placed after the sample and before the detector to obtain good angular resolution,

whereas the out-of-plane resolution was given by slits. A NaI(Tl) scintillation detector was used to measure the diffracted radiation. The synchrotron PXRD data were indexed with the program McMaille.⁴² A preliminary crystallographic model was obtained with the program PSSP²¹ and later refined and checked with WinPSSP.² The Rietveld refinement was carried out with the program GSAS,⁴³ using soft bond length, angle, and planarity restraints, which target values were those of the orange TTF and CAH₂. The RT neutron powder diffraction data of TTF-CAH₂ (form II) was collected in the BT-1 high resolution neutron powder diffractometer, National Institute of Standards, Center for Neutron Research (NCNR). Around 1 g of sample was placed in a vanadium can. A Ge(311) monochromator was used to select the 2.079 Å wavelength. The joint refinement of the synchrotron and neutron powder diffraction data afforded the independent refinement of C, S, Cl, and O isotropic thermal displacement parameters for the TTF and CAH₂ molecules, whereas those of the H atoms were constrained to 1.2 times the value refined for the non-H atoms bonded to each H. The crystal structures were represented with the program Mercury version 3.10.1.4

RESULTS AND DISCUSSION

Crystal Structure Analysis from Synchrotron X-ray and Neutron Powder Diffraction. The crystal structure of TTF-CAH₂ ("ionic" form I) has been previously reported at 295(2) K.³⁹ In this work, we also obtained single crystals of this polymorph by slow solvent evaporation of a MeCN solution, while we were trying to obtain a single crystal of form II by seeding the solution with the mechanochemical product prepared by LAG with MeCN (2 μ L/mg). The crystal structure of form I was solved and refined again to check the space group symmetry C2/*m*, since it can be also solved in *P*I (the unit cell in that space group was found during the analysis of the PXRD pattern). Because of the redox and acid–base properties of chloranilic acid, a few combinations of charge, π bond delocalization, and H content have been reported, and those are shown in Scheme 1.

In P1, two crystallographically independent C–O distances (corresponding to $C-O^-$ and C=O) could be refined in the CA^{2-} anion, whereas all four C–O distances are equivalent by symmetry in C2/m (see Scheme 1). We found that the refinement in C2/m is as good as that in $P\overline{1}$ with a slightly better agreement factor of R = 4.30%, compared with R =4.71% for $P\overline{1}$. This points to delocalized C–O bonds in the chloranilate anion (CA^{2-}) as previously reported.^{32,39} This is, in TTF-CAH₂ (ionic, form I), the reduction of CAH₂ leads to charge and hydrogen disproportionation generating two species, the chloranilate ion CA2- (without hydrogen), and the electrically neutral reduced form, CAH₄ (see Scheme 1). This implies proton transfer among pairs of CAH₂ reactant molecules. Moreover, for ionic CTC of tetrathiafulvalene, a strong σ type, two-electron bond is formed in the eclipsed (and ionic) dimeric radical cation units $(TTF^{+\bullet})_2$, which give rise to diamagnetic and insulating properties. This bonding is observed in the "ionic" TTF-CAH₂ form.³⁹

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Figure 1. Rietveld refinement graphs for TTF-CAH₂ at RT. (a) Synchrotron X-ray powder diffraction data ($\lambda = 0.699711$ Å), and (b) neutron powder diffraction data ($\lambda = 2.079$ Å). Experimental data are shown as blue dots, the calculated profiles as red lines, and the difference plots as black lines (at the bottom). Small angular regions (corresponding to flat lines on the difference plots) were excluded due to impurity peaks. Vertical black symbols represent allowed peak positions.



Figure 2. Crystal structure of TTF-CAH₂ form II at RT, calculated from the combined Rietveld refinement of synchrotron and neutron powder diffraction data shown in Figure 1. (a) View approximately from the *b*-axis showing TTF and CAH₂ stacks made of equally spaced molecules (C: gray, S: yellow, Cl: green, O: red and H: light gray, small spheres). Classical hydrogen-bonding distances between CAH₂ molecules of adjacent columns (as determined by PLATON) are shown with dashed blue lines. (b) The interplanar TTF…TTF and CAH₂…CAH₂ distances within stacks (indicated as dashed gray lines), viewed approximately along the *c*-axis. Hydrogens are not shown for clarity. Standard uncertainties are indicated between parentheses.

Form II of TTF-CAH₂ has not been easy to obtain as a single phase. Often, a few impurity peaks are still observed in the PXRD patterns of the mechanochemical products. The crystal structure of TTF-CAH₂ form II was solved from the synchrotron powder X-ray diffraction data at RT. Neutron powder diffraction data confirmed the structural model, and it was used to determine the hydrogen positions in CAH₂. It is worth noting that the hydrogen atoms do contribute incoherent scattering, and therefore the background is large and sloping, but they also have a negative coherent scattering length and hence contribute to the Bragg peaks. The Rietveld refinement graphs are shown in Figure 1.

The crystal structure of TTF-CAH₂ is represented in Figure 2. Perhaps the most interesting aspect of it is the presence of segregated TTF and CAH₂ in π -stacked columns made of

equally spaced molecules, as the main packing motif. Further crystal cohesion is achieved by classical hydrogen-bonding among CAH₂, with distances 2.784(7) Å and 2.676(7) Å as shown in Figure 2a, and weak (nonclassical) hydrogen bonds between the C–H groups of TTF and the –Cl and –O atoms of CAH₂ in adjacent columns (see Figure S1, Supporting Information).

The π -stacks of TTF in form II are remarkable similar to the typical segregated columnar stacks observed in TTF-based organic conductors. However, in TTF-CAH₂ form II the interplanar distance among TTF units, 3.58(1) Å, is closer to that in the neutral, orange TTF reactant (3.62(1) Å) than to the corresponding value in the organic metal prototype TTF-TCNQ⁴⁵ ($\rho = 0.59 \text{ e}^-$), for which this distance is 3.473(2) Å at 295 K. This structural feature suggests a reduced π orbital



Figure 3. Overlay of the FT-IR absorption spectra of TTF-CAH₂ at 300 K (dark red), 250 K (light red), 200 K (orange), 150 K (brown), 100 K (green), 50 K (light blue), and 10 K (dark blue), for (a) TTF-CAH₂ form I, and (b) TTF-CAH₂ form II. The band gaps shown in the figure correspond to the absorption edges, estimated as the extrapolation of the dashed lines on the frequency axes at 1175 cm⁻¹ for form I and 925 cm⁻¹ for form II, respectively.

overlap between adjacent TTF molecules of $TTF-CAH_2$ form II in comparison with TTF-TCNQ.

The unit cell volumes determined from single crystal diffraction for form I are 729.91(3) Å³ in $P\overline{1}$ (Z = 2) and 1459.75(5) Å³ in C2/m (Z = 4), whereas for the mechanochemical product from synchrotron PXRD this is 1458.53(8) Å³ in C2/m (Z = 4). For form II, the unit cell volume from Rietveld analysis of the combined synchrotron and neutron powder diffraction data is 731.30(4) Å³ (for Z = 2). Thus, ionic form I is slightly more dense than form II, suggesting (based solely on density) that form I is thermodynamically more stable than form II.

Furthermore, since form II is a new CTC, it was necessary to estimate its ionicity (charge transferred). Experimental data which could lead to this is the molecular geometry determined from neutron powder diffraction, as previously done for the green form of TTF-CA from neutron single crystal diffraction data.²⁸ Using the formula -15.55 + 20.42 r/s, where *r* and *s* are the C=C distance in TTF and the average of the four adjacent C-S distances, respectively, the calculated ionicity would be 0.19 e⁻. However, we considered that the neutron powder diffraction data did not afford sufficient unambiguous detail to confidently assign a charge transferred value solely from the above analysis, although it does suggest that form II is closer to neutral than to ionic, and the powder data refined well with the bond distance and angle restraint target values based on neutral TTF and CAH₂ molecules. Moreover, the neutron powder diffraction data were used to calculate the hydrogen

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Figure 4. FT-IR absorbance spectra of TTF-CAH₂ forms I and II at 300 and 10 K. (a) $600-850 \text{ cm}^{-1}$, and (b) $1400 \text{ cm}^{-1} - 1600 \text{ cm}^{-1}$ frequency regions. The vertical red dashed lines indicate expected frequencies for neutral TTF.⁴⁷

positions, which unless for exceptional cases, cannot be determined from PXRD patterns. In TTF-CAH₂ form I, there are two crystallographically independent fragments describing CA^{2-} and CAH_4 ; however, in form II all CAH_2 molecules are on inversion centers and have two hydrogen atoms, and only one crystallographically independent fragment describes chloranilic acid in the asymmetric unit. Thus, no hydrogen disproportionation (accompanying charge transfer in the CAH_2 reduction process) is required to form this polymorph from the reactants.

FT-IR Spectroscopy, lonicity, and Band Gap. We carried out FT-IR studies of the TTF-CAH₂ forms I and II as a function of the temperature (300 K to 10 K) to experimentally investigate the presence of band gaps and phase transitions. The spectra are shown in Figure 3. The differences in the FT-IR spectra of both polymorphs (at the same temperature) would make it possible to identify them from FT-IR spectroscopy. In particular, note the broad band in the 2500 cm⁻¹-3400 cm⁻¹ frequency region for form I but absent in form II.

The absorption borders were determined as shown in Figure 3, at around 925 cm⁻¹ (form II) and 1175 cm⁻¹ (form I), and those are associated with band gaps of ~0.115 eV and ~0.146 eV, for TTF-CAH₂ forms II and I, respectively.

Furthermore, for the assumed thermodynamically most stable ionic form I, phase transitions as a function of the temperature are not expected. These are not evident from the rather monotonous changes from 300 K down to 10 K in the FT-IR spectra shown in Figure 3a. On the contrary, it is wellknown that the columnar 1-D stacks of TTF molecules are thermodynamically unstable, and thus phase transitions often occur by varying an order parameter (e.g., reducing the temperature), breaking the lattice symmetry, charge, or spin degrees of freedom,⁴⁶ and one could expect those to occur in TTF-CAH₂ form II. However, one can see from Figure 3b that the FT-IR spectra of form II also change monotonically from 300 K down to 10 K, and phase transitions, detected as a change in the number of vibrational modes, are not observed. On the other hand, we note that when the temperature is reduced, the band gap of form II decreases to \sim 850 cm⁻¹,

while for form I it slightly increases. These changes could be attributed to changes in lattice parameters in both crystal structures. In particular, a reduction of the *b*-axis in form II would increase the overlap of π orbitals in TTF and CAH₂ columns. Reductions in the *a*- and *c*-axes would decrease the distances among hydrogen-bonded atoms, thus increasing the overall strength of hydrogen-bonding interactions and cohesion in the material, rendering the molecular connectivity "less one-dimensional" than that at RT.

Moreover, we also examined in detail two frequency regions of the above spectra (at 300 and 10 K) which could be used to assess the ionicity of TTF-based CTC.⁴⁷ These are shown in Figure 4. Four absorption bands corresponding to the neutral TTF at around 780 cm⁻¹ ($b_{1u} \nu_{16}$), 1518 cm⁻¹ ($a_g \nu_3$), 1530 cm⁻¹ ($b_{1u} \nu_{14}$), and 1555 cm⁻¹ ($a_g \nu_2$) are present in the spectra of form II (at 300 and 10 K) suggesting a neutral character. These observations agree with the refined molecular shape from Rietveld analysis of the neutron powder diffraction pattern, the hydrogen atoms equally distributed on CAH₂ molecules, and the interplanar separation between TTF molecules in the one-dimensional π -stacks, of value comparable with that in the neutral TTF (orange polymorph).

Solvent Effect in Mechanochemical Syntheses. Toward understanding the LAG solvent effect in TTF-CAH₂ mechanochemical syntheses, a series of reactions were carried out from the orange, monoclinic TTF polymorph by neat grinding and by LAG using a series of solvents: water, DMSO, dimethylformamide (DMF), acetonitrile (MeCN), methanol (MeOH), ethanol (EtOH), acetone, isopropanol, 1-butanol, ethyl acetate, chloroform, toluene, hexane, and heptane. The laboratory PXRD patterns of the mechanochemical products were used for crystal phase identification, and Figure 5 shows the PXRD data for each LAG solvent and neat grinding as well. Form II was in general more difficult to prepare as a single phase, and occasionally impurity peaks were detected.

Solvent polarity, at a molecular scale, is quantitatively indicated by the electrical dipole moment and higher moments (e.g., for nonpolar molecules such as CO_2 , quadrupole moments can exert short-term effects).⁴⁸ The *dielectric constant* (or *relative permittivity*), ε_v , the ratio of the permittivity of the



Figure 5. Laboratory PXRD data of the TTF-CAH₂ mechanochemical reaction products of the orange TTF and CAH₂ with a series of solvents of decreasing polarity (from top to bottom) and neat grinding. The patterns shown with a solid blue line correspond to the products ground with water (2 μ L/mg), DMSO (0.2 μ L/mg), and DMF (2 μ L/mg) and belong to TTF-CAH₂ form I (ionic). Those represented with a black line correspond to MeOH (2 μ L/mg), EtOH (2 μ L/mg), isopropanol (2 μ L/mg), and 1-butanol (2 μ L/mg) and belong to TTF-CAH₂ form I. The patterns shown in red correspond to MeCN (2 μ L/mg), acetone (2 μ L/mg), ethyl acetate (2 μ L/mg), chloroform (2 μ L/mg), toluene (2 μ L/mg), hexane (2 μ L/mg), heptane (2 μ L/mg), and neat grinding, and belong to TTF-CAH₂ form II.

medium, ε , to the permittivity of free space, ε_0 , determines the strengths of interactions between charged species in the medium, and it will be used in this work as a scale of solvent polarity. The liquids used for LAG and their dielectric constants are summarized in Table 1, together with the corresponding TTF-CAH₂ polymorphs synthesized using $\eta = 2 \mu$ L/mg (except for DMSO, $\eta = 0.2 \mu$ L/mg, since in previous studies large DMSO volumes do not easily evaporate and lead to reaction byproducts²³). By definition, η is the volume of LAG liquid (in μ L) per mg of the total mass of reactants ground.^{11,19}

The results shown in Figure 5 and Table 1 point to the following trend: the highly polar solvents (e.g., water, DMSO, DMF) yield the "ionic" form I, whereas low-polarity, aprotic solvents (e.g., ethyl acetate, chloroform, toluene) and nonpolar solvents (e.g., hexane and heptane) yield form II, most likely a neutral compound or pseudo-neutral at most.

We must note that a comparable trend was observed for TTF-CA (the ionic form was obtained from the highly polar water and DMSO; and from the orange TTF using MeCN,

Table 1. TTF-CAH₂ Mechanochemical Product Polymorphs for Various Liquids Used in LAG Mechanochemical Synthesis ($\eta = 2 \ \mu L/mg$), and Their Dielectric Constants (ε_r)

liquid	LAG reactions $(2 \ \mu L/mg)^a$	\mathcal{E}_{r}
water	I	78.30
DMSO	I ^b	47.6
DMF	I	36.7
MeCN	II	36.2
MeOH	I and II	32
EtOH	I and II	24
acetone	II	20.7
isopropanol	I and II	18.3
1-butanol	I and II	17.8
ethyl acetate	II	6.02
chloroform	II	4.7
toluene	II	2.4
hexane	II	1.9
heptane	II	1.92
neat	II	

^{*a*}Calculated as the total volume of solvent added during reaction in a mortar and pestle (the solvent is able to evaporate), for a total grinding time of 30 min. Additional details are in Table SI (Supporting Information). ^{*b*}Only for DMSO, $\eta = 0.2 \ \mu L/mg$.

while less polar solvents yielded the pseudo-neutral green form).²³ A similar trend was observed also for TTF-DDQ, the ionic form was obtained from DMSO by LAG and from MeCN by vapor digestion²⁴ (water was not used due to DDQ decomposition). Regarding neat grinding (without solvent), this yields TTF-CAH₂ form II (most likely neutral), as well as the pseudo-neutral (green) TTF-CA²³ rather than the respective ionic polymorphs. Hence, the analogous trend for the TTF-CAH₂ syntheses inferred from Figure 5 and Table 1 seems reasonable, since in all three cases TTF and a *p*benzoquinone derivative must be partially or fully ionized to form CTC, and the presence of a polar solvent is deemed necessary for full ionization of molecules to occur and the crystallization of the ionic polymorphs during LAG reactions.

Furthermore, additional features of TTF-CAH₂ mechanochemical synthesis must be noted for medium-polarity solvents. Because mixtures of forms I and II were obtained using 2 μ L/mg of the alcohols, a series of syntheses at increasing η values were carried out to further investigate the solvent effect. The results are summarized in Table SII (Supporting Information). The observed trend is that all medium-polarity solvents (protic and aprotic) produce mixtures of forms I and II by LAG and slurry reactions if η is below a threshold value (different for each liquid), while form I is produced when η is above such threshold. These results are graphically represented in Figure 6, indicating the threshold η values for medium-polarity solvents that lead to form I as a single phase. Since the aprotic MeCN and acetone, with dielectric constants comparable with those of the alcohols, yield only form II at 2 μ L/mg (see Table 1 and Figure 5) and particularly MeCN requires larger η to produce form I from slurries than the alcohols (see Table SII and Figure 6), it seems that the protic character facilitates the formation of the ionic form I, even at moderate η . It is interesting to point out that H⁺ ions are very mobile in water and MeOH due to the Grotthuss mechanism, by which H⁺ can jump from molecule to molecule without movement of the larger ion.⁴⁸ Thus, the



Figure 6. Laboratory PXRD patterns of the slurry mechanochemical reaction products using protic and aprotic, medium-polarity solvents, corresponding to the threshold η for which form I is obtained (indicated next to each solvent) as a single phase, as well those corresponding to low-polarity and nonpolar solvents for $\eta = 36 \,\mu\text{L/}$ mg. The PXRD patterns of TTF-CAH₂ form I (ionic) are shown in blue, whereas those of TTF-CAH₂ form II are shown in red.

presence of these medium-polarity but protic solvents around CAH_2 facilitates the formation of form I (ionic), likely aiding proton transfer among molecules.

Since the protic character of the solvent is deemed to have also an effect toward determining the formation of TTF-CAH₂ forms I or II, solvent polarity, though probably the most important property in this regard, is not solely determining the polymorphic outcome of mechanochemical syntheses of TTF-CAH₂. Moreover, functional groups such as alcohols and possibly others (e.g., ketone, nitrile) that may have a different ability to support hydrogen exchange among molecules could play a role. Since the reactions were carried out in a mortar with pestle (and the liquids are allowed to evaporate during solid-state grinding), other LAG solvent properties such as vapor pressures and solubilities of reactants and/or products may also play a role, since less volatile liquids will remain with the powders ground for longer (e.g., DMSO) than liquids which rapidly evaporate and poorly dissolve the reactants and/ or products (e.g., hexane). Overall, these observations suggest that the LAG liquids not only facilitate the diffusion of species^{49,50} needed to increase the reaction rates, or afford a solid-state reaction at all,¹⁸⁻²⁰ but also can provide a chemical environment or a physicochemical property needed in the reaction mechanism leading to particular product polymorphs (e.g., to afford full ionization or proton transfer among molecules); otherwise, other products are obtained instead (e.g., neutral or pseudo-neutral polymorphs of this type of CTC), or the reactions may not proceed at all. However, we point out that these results are applicable to reactions of TTF (one reacting polymorph) and similar substituted *p*-benzoquinones since it has been reported (e.g., for the synthesis of three forms of anthranilic acid:caffeine cocrystals) that one LAG

liquid used at increasing η can lead to several polymorphs in rather complex fashion.⁵¹

Moreover, a good understanding of the solid-state grinding conditions leading to TTF-CAH₂ forms I and II is necessary to gain control over the polymorphic forms obtained by mechanochemistry and to relate those to solution products. Thus, we carried out a few more syntheses using large volumes (36 μ L/mg) of the low-polarity solvents (e.g., ethyl acetate, chloroform, and toluene), and nonpolar solvents (hexane and heptane), since was interesting to determine whether form I (ionic) could be obtained from them at all by mechanochemistry. As a result, only form II was obtained in all cases (as a crystalline phase) confirmed by laboratory PXRD. These results are shown also in Figure 6.

Moreover, because the mechanochemical reaction mechanisms are different than those of solutions, mechanochemical reactions occasionally lead to unique structures or stoichiometries. 15,16 To further investigate whether $\mathrm{TTF}\text{-}\mathrm{CAH}_2$ form II may be only obtainable by mechanochemistry, we carried out a few vapor digestion (VD) reactions from the orange TTF polymorph, as well as a few solution syntheses (when feasible) from the previously indicated low-polarity and nonpolar solvents. The synthesis conditions and results are summarized in sections III and IV of the Supporting Information, and as it follows. Interestingly, ethyl acetate yields a black powder corresponding to TTF-CAH₂ form I (ionic) from a solution as well as by VD synthesis. These results suggest that the solvent role in VD reactions may be more similar to that in solutions than to mechanochemistry (which for ethyl acetate yields form II at $\eta = 36 \ \mu L/mg$), probably mainly involving the partial dissolution of the reactants in small quantities of the solvents, which reach the solid reactants as vapors.

VD with hexane and no solvent did not afford a chemical reaction, and dissolution of the reactants in hexane was not possible. These results are reasonable (note CAH₂ is a hydrogen-bonded solid). TTF-CAH₂ form II was not identified by PXRD as a crystalline phase by VD with chloroform or from a chloroform solution. However, a color change from orange (reactants) to red-purple was observed in both cases, suggesting a chemical reaction had occurred, although the presence of decomposition products was not ruled out. Moreover, for the VD reaction, the reactants (plus one unidentified peak) were identified from PXRD, and the FT-IR spectrum also mostly resembles that of the reactant mixture, suggesting a small amount of reaction, often observed in VD syntheses. The FT-IR spectrum of the chloroform solution products is more similar to that of TTF-CAH₂ form II than to the spectrum of the reactant mixture; however, it cannot be concluded from these data only that form II was obtained (as an amorphous phase).

In summary, the combined mechanochemical, VD, and solution results so far indicate that TTF-CAH₂ form II may be only obtainable by mechanochemistry, at least as a crystalline solid. We must note also that the mechanical treatment and mechanical activation of the reactants, absent in VD or solution reactions, leads to changes in chemical reactivity^{15,18,52} unique to mechanochemistry and probably in that arena one should look for the physicochemical conditions yielding TTF-CAH₂ form II. Considering the results herein reported, one could speculate that mechanical energy could be necessary for TTF-CAH₂ form II to crystallize during solid-state grinding, perhaps through specific molecular/lattice vibrational modes, which would stabilize the crystal lattice of

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TTF-CAH₂ form II and their new bonding intermolecular interactions. An interesting observation is that the crystal structure of TTF-CAH₂ form II can be thought as made of intercalated TTF columns and hydrogen-bonded CAH₂ columns, essentially already found in the crystal structures of the reactants, plus weak hydrogen bonds (see Figure S1, Supporting Information). This is schematically shown in Figure S44 (Supporting Information). Thus, mechanical treatment of the crystalline reactants may provide a unique reaction path of low activation energy leading to form II, in the absence of a polar liquid medium over a threshold η leading to form I, however necessarily disrupting the hydrogen-bonding motif found in the CAH₂ reactant. The mechanochemical preparation of TTF-CAH₂ form II might mostly involve concerted small molecular movements within the columnar stacks of the reactants and the formation of weak (nonclassical) hydrogen bonds among already existing CAH₂ and TTF columns (in the orange polymorph), which become in contact at the molecular scale through shearing and other mechanical treatment. However, form II is also obtained from the brown TTF polymorph (see Table Supporting Information) which lacks TTF columns, although this could be explained considering that the reuse of the CAH₂ hydrogenbonded stacks is energetically very favorable. The latter agrees with the observed lack of reaction by vapor digestion with hexane and without a solvent, since the molecular mobility of CAH₂ from the hydrogen-bonded stacks would be largely reduced, which seems also reasonable considering the experimental CAH₂ melting point of ~284 °C. However, currently these are only hypotheses and tentative explanations and must be further studied in other mechanochemical reactions of CAH₂ and/or hydrogen-bonded reactants.

CONCLUSIONS

This work used mechanochemistry as a suitable method for polymorph screening of CTC and to discover new materials not accessible from solution. We report the mechanochemical synthesis of two TTF-CAH₂ polymorphs, form I (ionic) and form II (a new material). The molecular and crystal structures of form II were determined from the combined analysis of RT synchrotron and neutron powder diffraction data. FT-IR spectroscopy as a function of the temperature led to the estimation of small band gaps (~0.146 eV and ~0.115 eV for forms I and II, respectively) corresponding to semiconductors, while the ionicity of form II was estimated as close to zero. Phase transitions were not observed in our FT-IR spectra in the 300 to 10 K temperature range.

Moreover, the solvent effect in the mechanochemical syntheses (LAG and slurry) was further studied toward determining the conditions leading to single polymorphic phases of forms I and II, and they were compared with those of a few vapor digestion syntheses and solution chemistry. The results agree with a hypothesis stating that a sufficiently large dielectric constant of the medium in which the mechanochemical reaction is conducted is required to afford full ionization of all molecules and the formation of ionic polymorphs of this type; however, if a polar medium provided by the liquid (with η above a threshold value for that particular liquid) is absent, the mechanochemical reactions yield neutral or pseudo-neutral polymorphs. This particular reaction involves hydrogen disproportionation in CAH₂, and it was also observed that protic solvents of medium polarity (alcohols) yield also ionic CTC at moderate η values. In this regard, the small quantities

of liquids used for LAG behave as catalysts for the synthesis of the ionic forms, pointing to solvent polarity as a good "control parameter" to synthesize ionic CTC of tetrathiafulvalene. This could be of overall interest for the preparation of other types of organic CTC and organic cocrystals significant in varied research fields, although additional studies are needed to confirm it. The vapor digestion and solution products suggest that vapor digestions (at least in the absence of solids with noticeable vapor pressure) may resemble more solution reactions than mechanochemical processes, which involve mechanical treatment, changes in the reactivity of substances, and mechanisms which are not yet well understood.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.9b00182.

Additional experimental details of the syntheses, Rietveld refinement details of the neutron and synchrotron PXRD data, additional FT-IR spectroscopy data, optical micrographs (PDF)

Accession Codes

CCDC 1889584 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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ABBREVIATIONS

CA, chloranil; CAH₂, chloranilic acid; CTC, charge-transfer complex; DDQ, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone;

DMF, dimethylformamide; DMSO, dimethyl sulfoxide; FT-IR, Fourier transform infrared spectroscopy; LAG, liquid-assisted grinding; MeCN, acetonitrile; RT, room temperature; TTF, tetrathiafulvalene; VD, vapor digestion; PXRD, powder X-ray diffraction

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