Anomalous mechanical behavior of the deltic, squaric and croconic cyclic oxocarbon acids

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Abstract

The structural and mechanical properties of the deltic, squaric and croconic cyclic oxocarbon acids were obtained using theoretical solid-state methods based in Density Functional Theory employing very demanding calculation parameters in order to yield realistic theoretical descriptions of these materials. The computed lattice parameters, bond distances, angles, and X-ray powder diffraction patterns of these materials were in excellent agreement with their experimental counterparts. The crystal structures of these materials were found to be mechanically stable since the calculated stiffness tensors satisfy the Born mechanical stability conditions. Furthermore, the values of the bulk modulus and their pressure derivatives, shear and Young moduli, Poisson ratio, ductility and hardness indices, as well as mechanical anisotropy measures of these materials were reported. A complete review of the literature concerning the negative Poisson ratio and negative linear compressibility phenomena is given together with the theoretical study of the mechanical behavior of cyclic oxocarbon acid materials. The deltic, squaric, and croconic acids in the solid state are highly anisotropic materials characterized by low hardness and relatively low bulk moduli. The three materials display small negative Poisson ratios. The croconic acid displays the phenomenon of negative linear compressibility for applied pressures larger than ~0.4 GPa directed along the direction of minimum Poisson ratio and undergoes a pressure induced phase transition at applied pressures larger than ~1.0 GPa.

Keywords: cyclic oxocarbon acids, deltic acid, squaric acid, croconic acid, mechanical properties, mechanical stability, DFT, negative Poisson ratio, negative linear compressibility

1. Introduction

The cyclic oxocarbon acids ($C_nO_nH_2$, $n = 3, 4, 5, 6$) and their conjugated bases [1-5], the oxocarbon dianions ($C_nO_n^{2-}$), have been studied in great detail both experimentally [6-25] and theoretically [25-39] because they possess very interesting cyclic structures, and exhibit very attractive physical and chemical properties leading to a large amount of applications of these materials [19,38,40-73]. The smallest members of the series, the deltic ($n = 3$) and squaric ($n = 4$) acids, are surprisingly stable despite of the large bond-angle strain

associated with three and four-membered rings. However, there are still several significant pieces of knowledge concerning these materials which remain unsolved and are waiting for their study. Among them, one important gap is the solid-state structure of the highest member of the series ($n = 6$), the rhodizonic acid, which remains unknown nowadays [21]. Other one is the mechanical behavior of these compounds, which has never been studied using the experimental or theoretical methodologies. This work is aimed to unveil the mechanical characteristics of three of these materials in the solid-state, the deltic, squaric, and croconic

acids ($n = 5$), which have been found to be extremely interesting.

The synthesis of these compounds is well-known [12]. The highest members of the oxocarbon acid series, the croconic and rhodizonic acids, were synthesized by the first time by Gmelin [6] and Heller [7], respectively, in the nineteenth century. The synthesis of the lowest members, the deltac and squaric acids, was achieved in the twentieth century by Eggerding and West [8-9] and Park, Cohen and Lacher [10-11], respectively. The solid-state structures of the deltac [13], squaric [14-18], and croconic [19-20] acids have been accurately determined.

One of the most attractive features of these acids is their cyclic structure, which reminds that of the cyclic hydrocarbon compounds, such as cyclopropane, cyclobutadiene, cyclopentadiene, and benzene. In 1960, West *et al.* [2] classified cyclic oxocarbon dianions as aromatic systems which are stabilized by π -electron delocalization. This general classification was questioned by Aihara [74], although the aromaticity of the two smallest members of the oxocarbon acid family, the deltac and squaric acids, and of the corresponding dianions has been confirmed using several criteria for aromaticity [4,13,26]. Among these criteria, the most convincing one is the one obtained from the analysis of the nucleus-independent chemical shifts (NICS) [75], leading to the conclusion that the croconic and rhodizonic acids are clearly non-aromatic [26]. In fact, rhodizonic acid is not even planar [26]. Chemically, the cyclic oxocarbon acids behave as true acids due to the great stability of the corresponding mono and dianions resulting from their increased aromaticity [9,28,76-78].

Oxocarbon acids and the salts of the oxocarbon anions are of much interest in supramolecular chemistry and crystal engineering research because of their potential for π -stacking effects [20-21,40-45]. In these works, the cyclic oxocarbon acids were employed to exploit the robustness and reproducibility of hydrogen-bonding interactions. The relative simplicity of the molecules used as building blocks provided a better insight into the factors which are most important for crystal construction [20,42]. The oxocarbon anions were also utilized for evaluating some fundamental aspects of hydrogen-bonding interactions [45].

Squaric and croconic acid related compounds have been recently used as near-infrared absorbing dyes which may be employed as optical sensors [5,46-51]. Croconic acid-based dyes have been less studied than similar squaraines [5,46-47]. However, croconine dyes appear to have advantages over squaric acid ones. They show stronger absorption, greater photostability, and better yield and absorb up to longer wavelengths [48,51]. Croconic acid is a ferroelectric material at room temperature [19]. Due to its hydrogen-bonded polar structure in the crystalline state [44], the application of an electric field to croconic acid can align coherently the

molecular polarities and produce a well-defined polarization hysteresis. Ferroelectric compounds are very useful materials in practice because they can switch their polarity, may be pyroelectric and piezoelectric (sensible to temperature and pressure variations), and may be used to manipulate light through the electro-optic effect. This material is the organic ferroelectric displaying the highest spontaneous polarization which persists up to 400 K and may be employed in active capacitors and nonlinear optics elements [19]. The use of squarates and croconates as singlet fission sensitizers has been devised [38]. Squaric acid related compounds have achieved many important applications in catalysis, chemical synthesis and crystal engineering and in biomedical and optical applications [52,46-47,53-56]. For example, squaric acid-based compounds have been used as protein inhibitors [53,55] and squaraine dyes have been employed as long-wavelength fluorescent protein labels [46-47]. Lithiated oxocarbon salts have been considered for possible use in rechargeable electrical batteries [57]. Deltate dianions have been employed for carbon monoxide polymerization [58]. The croconic acid may be used in the laboratory to produce hydrated coordination compounds with divalent cations of transition metals as copper, iron, zinc, nickel, manganese, and cobalt [59-62]. Rhodizonic acid and rhodizonate salts have been used in chemical assays for barium, lead and other metals and in the analysis of radium in fresh waters [63-69]. Sodium rhodizonate test is used to detect gunshot residues, which contain lead [70-71]. Rhodizonate materials can be used to produce croconate dianion containing compounds [72-73].

There is a strong symmetry independent correlation between the value of the elastic anisotropy [79] and the values of the maximum and minimum Poisson ratios of a given material [80-81], taking into account all possible longitudinal and transverse directions. Because the considered cyclic oxocarbon acids were observed to be highly anisotropic materials in our preliminary theoretical calculations of these materials, it was considered of interest to reinvestigate their mechanical properties using very accurate theoretical calculations with special emphasis in the study of the associated Poisson ratios. The theoretical solid-state methods used here are based in Density Functional Theory (DFT) using plane waves and pseudopotentials [82]. These methods have already been employed successfully in order to study the mechanical properties of a series of uranyl containing materials [83-90]. There are many recent published works in which the first-principles theoretical methodology has been employed in the research of materials exhibiting negative Poisson ratio (NPR) and negative linear compressibility (NLC) [91-116]. For example, one may cite the works by Keskar and Chelikowsky [91] and Grima *et al.* [92] on crystalline SiO_2 , Grima *et al.* [93] and Coudert *et al.* [94-95] on several zeolitic compounds, Yao *et al.* [96] on crystalline cellulose, Tan *et al.* [97-98] on zeolitic imidazolate frameworks (ZIFs), Sun *et al.*

[99] on penta-graphene and phagraphene, Du *et al.* [100] on black phosphorus, Li *et al.* [101] on an ammonium-zinc metal-organic framework, Qiao *et al.* [102] on oxammitte mineral, Coates *et al.* [103] on $\text{Cd}(\text{NH}_3)_2[\text{Cd}(\text{CN})_4]$, Marmier *et al.* [104] on cooperite mineral, Kang *et al.* [105] on $\alpha - \text{BiB}_3\text{O}_6$. The description of solid-state crystalline compounds using computational modelling techniques, appears to be sufficiently advanced nowadays to predict their mechanical properties in good agreement with experimental values. For example, the NLC effect in $[\text{NH}_4][\text{Zn}(\text{HCOO})_3]$ was anticipated theoretically in 2012 [101]. The research of the structural response of several polymorphs of Te and Se to applied pressures, performed by means of Raman spectroscopy, was complemented with DFT calculations [115], and very good agreement was obtained. Therefore, the theoretical methodology confirmed the NLC mechanisms responsible of the mechanical behavior of these elements. Since the NLC phenomenon has rarely being studied in organic materials, this work represents one of the first studies dealing with the anomalous mechanical behavior of organic materials, pointing out the need of performing systematic studies of the mechanical properties of this kind of materials.

This paper is organized as follows. In Section 2, the concepts of negative Poisson ratio and negative linear compressibility are explained and a complete review of the literature concerning these phenomena is provided. This review gives a broad outlook on these research fields and covers the most important aspects which must be known by a non-specialized reader to understand this paper and may be used as a guide to begin his or her own research. The computational methodology used in this work is described in Section 3. Then, in Section 4, the main results of this work are given and discussed. This section contains three main Subsections, 4.1 4.2 and 4.3. In the first one the structural properties of the considered materials in the solid state are studied and, in the second one, the corresponding X-ray diffraction patterns are reported. In the last subsection, the mechanical properties of these materials and the mechanical stability of the corresponding crystal structures are studied. In this same subsection the anomalous mechanical behavior of the deltic, squaric and croconic acids is described. Finally, the conclusions of this work are presented in Section 5.

2. Negative Poisson ratio and negative linear compressibility

2.1 Negative Poisson ratio

2.1.1 NPR concept

For a stress directed along a certain direction applied to a solid material, the Poisson ratio [117-119], ν , is defined as the negative value of the ratio of the resulting differential

transverse and longitudinal strains, $\nu = -\delta\epsilon_{trans}/\delta\epsilon_{long}$. In this relationship, the strain ϵ_i is the variation of the solid size ΔL_i along direction i divided by the original size L_i , $\epsilon_i = \Delta L_i / L_i$. The term Poisson ratio, was coined after Siméon Denis Poisson, a scientist of the 19th century, who made very significant contributions to the theory of elasticity [120]. A positive sign is expected for the Poisson ratio because when a positive pressure applied along a certain direction to the solid a contraction along the longitudinal direction and an extension along all the transverse directions is usually found. However, negative values of Poisson ratio are theoretically possible, and some materials exhibit anomalous NPRs [117-118] for certain longitudinal and transverse directions. These solids laterally expand when they are stretched or laterally shrink when compressed. These materials are known as auxetic from 1991 [121], although they are also referred to as dilational [122]. The Poisson ratio is a fundamental material parameter because it controls the associated material deformation field. A large amount of important material properties like concentration of strain, toughness and wave speed propagation depends on Poisson ratio [117].

Several scientists of the 19th century as Voigt [123] already found materials displaying the auxetic or NPR effect. A negative Poisson ratio for iron pyrites was reported in 1944 by Love [124] although a positive ν was later found [125] for these materials. Two and three-dimensional NPR structures were discovered in the earlier years of the eighties [126-127]. The first man-made NPR material was reported by Lakes [128] in 1987, who produced an auxetic polymeric foam structure by applying compression and heating processes to a commercial foam used as precursor. This research was the starting point of a fruitful search of natural auxetic compounds and of manufacturing processes of new materials displaying NPR, which has found a wide range of applications and continues today [117-118]. The understanding of the NPR effect at atomistic level and the discovery of new mechanisms [129] leading to negative Poisson ratios are, therefore, very important because they may lead to new useful auxetic materials and ways to produce them.

Poisson ratio values are between 0.25 and 0.35 for common materials and become 0.5 for soft rubber. The Poisson ratios of polycrystalline materials, averaged over all possible directions, are usually within the same range of 0.25 to 0.35. Soft polycrystalline metals, such as lead and indium, have Poisson ratios as high as 0.44 to 0.45 as a result of the low shear modulus [117]. For isotropic solids, the range of values for the Poisson ratio is rigorously from -1 to 0.5 [130]. For anisotropic materials, Poisson ratio may have any value from minus infinity to plus infinity [131].

2.1.2 NPR materials

After the work by Lakes [128] it has been observed that many other materials exhibit NPR. Microstructures leading to

isotropic materials with ν close to -1 were predicted by Rothemburg *et al.* [132], Milton [122], and Sigmund [133]. Negative Poisson ratio naturally occurs in extreme states of the matter [134-135] as inside the high-density neutron stars or in very low-density crystals [134]. In 1998, Baughman *et al.* [136] showed that around two thirds of cubic metals (and alloys) do have negative Poisson ratios in the [110] direction. For some metallic materials [131,137] as AuCd alloy [81], the [111] direction is the one of minimum Poisson ratio, instead of [110]. Other metallic single crystal compounds showing auxetic behavior are the transversely isotropic zinc [138] and an orthorhombic CuAlNi alloy [139]. Some non-metallic single crystal elements like arsenic, antimony and bismuth are highly anisotropic and display negative Poisson ratios in some directions [140]. TmSe crystals also exhibit NPR behavior in the {001} plane [141].

A systematic study of auxetic monoclinic crystals was presented in 2004 by Rovati [142]. Monoclinic lanthanum niobate, LaNbO_4 , is one of the materials showing the most extreme values of the Poisson ratio, $\nu_{\min} = -3.01$ and $\nu_{\max} = 3.96$ [142,81]. For α -cristobalite, a SiO_2 polymorph [91-92,143-144], the magnitudes of the minimum and maximum values of the Poisson ratio are much smaller, 0.10 and -0.5 , respectively, but this case is extreme in the sense that if a stretch is made in almost any direction, the area of the section perpendicular to the stretch increases. NPRs have been also found in zeolites [93-95,145-147], framework silicates [148,142], crystalline cellulose I_β [96,149], zeolitic imidazolate frameworks (ZIFs) [97-98] and ceramic materials as $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$ [150]. Skin is an anisotropic natural composite material and some skin tissues exhibit negative Poisson ratios [151-152]. The nuclei of embryonic stem cells extracted from a mouse were recently found to be auxetic during a metastable transition state [153].

Polycrystalline materials frequently show negative Poisson ratios in the proximity of solid-to-solid phase transformations [117]. In these cases, extreme NPR values are not observed due to the directional averaging. For example, NPR values have been observed to arise in the vicinity of the α - β transition in polycrystalline quartz [154], within a narrow range of temperature near the volume transition in a polymer gel [155-157], in the proximity of the Curie temperature of the ferroelastic cubic-to-tetragonal transition in barium titanate ceramic [158-159] or in the phase boundary of morphotropic phase changes as in polycrystalline In-Sn alloys [160].

Negative Poisson ratio in single crystals and polycrystalline materials can be also obtained under the effect of applied pressures and deformations. As an example, structures made with silicone rubber exhibited NPRs by applying large compressive stresses [161]. A change of the sign of Poisson ratio appears for deformed highly aligned carbon nanotube sheets [162-163]. Graphene sheets [164,99] exhibit a highly strain-dependent Poisson ratio that is slightly positive at near

zero strain but becomes negative at a few percent strain. Similarly, single-atomic-layer black phosphorus has a puckered structure that straightens under tension, giving rise to a negative Poisson ratio [165,100]. Isotropic molecular compounds under large enough isotropic pressures should display NPR values [166].

Diverse natural and man-made polymeric materials [167-173] composites [174-183,122], ceramics [184,150,158-159], engineered structures [185-189], and networks [190-193] are also auxetic. Some auxetic polymers were designed and manufactured to have a molecular framework that causes auxetic behavior [117]. The synthetic approach based in studies at the atomic level, provides the best possibilities for designing new NPR materials with their own characteristic structures and properties and different deformation mechanisms. Some examples include the design of honeycomb structures [121], the synthesis of liquid-crystal polymers [194] emulating node-fibril micro-structures [195], and the design of new organic molecular networks [191-193] that are auxetic. Some micro-scale auxetic polymers including molecular honeycombs are based on alternative macro-scale auxetic mechanisms [191,195-197]. However, the structural characteristics of auxetic molecular honeycombs [197] make their synthesis very difficult [96]. Polymeric foams [128,198-201], as polyurethane foams [128], have Poisson ratios which vary with strain in a nonlinear way [201]. NPRs occur in anisotropic deformed polyethylene, polytetrafluoro-ethylene and polypropylene polymers [167-173], carbon fibre [174], and in some oriented fibrous composites for certain directions [175-176]. Nano-scale locally auxetic behavior has also been found in elastomeric polypropylene [173]. NPR mechanic meta-materials are manufactured systems that exhibit NPR macroscopically due to the structure of the constituent units instead of their chemical composition [186-187,202-213]. For example, folding of non-auxetic materials as paper (origami) may show NPRs in planes [202-205]. The so-called fixed-connectivity membranes [188-189] display NPRs due to variations in entropy resulting from deformation. Such membranes reduce the undulations due to thermal fluctuations [189].

2.1.3 NPR applications

NPR materials have found an enormous range of applications [185,214,118,129] because they have improved material properties resulting from the auxetic behavior [215-217]. Among these properties we may cite enhanced fracture toughness [129,218-220], double (synclastic) curvature under pure bending [128,185,197], indentation resistance [200,221-225], resilience [128,222,225], crashworthiness [226-227], shear rigidity [201,228-230], vibration damping [231-233,189], and acoustic absorption [234-236]. These properties make the auxetic materials very appropriate in many applications as those involved in textile [237-243] and

automotive industries [244], personnel protection [233], biomedicine [185,245-246], aerospace and defense [247-250], and in many commercial applications requiring filters, sieves, sensors, packaging and insulation [185,239,251]. Natural auxetic materials are very useful and have many potential applications in sensor, molecular sieve and separation technologies. Among these natural materials, one of the most important examples is that of zeolites, which are widely employed as molecular sieves, adsorbents and catalysts [93-95,145-147] and have great availability.

Auxetic honeycombs and lattices may be used in many structural applications as for the construction of sandwich panels for airplane wings that morph or change shape to reduce vibration in many electronic devices [249-250]. Fixed-connectivity membranes are useful to reduce thermal fluctuations [189]. Auxetic lattices and polymers have been designed incorporating sensors and actuators to develop smart structures [252-254] and piezoelectric sensors [254-256]. Smart materials are intelligent systems capable of sensing and actuation and adaptive structures with active control. Shape memory auxetic polymers have been developed [257] as well as smart auxetic structures including piezoelectric actuators to analyze the problem of the shape control [254]. Moisture sensitive auxetic materials have been also obtained [258]. Auxetic materials as auxetic polymers and zeolites offer very specific improvements in filter technology [185,239,251,259] because they permit to create filters with enhanced pore size and shape tuneability. The use of these materials reduces the number of spent filters and the required filter replacements. Metallic auxetic meta-materials inherit several properties of the original metals as localization of plastic strain, strain hardening, and irreversible deformation leading to enhanced strength over standard meta-materials and, therefore, they are suitable for constructing protective structures and materials [260-261]. Auxetic hierarchical meta-materials and structures are a class of meta-materials which are composed of structural elements which themselves have structure [186-187,262]. These natural or manufactured materials exhibit NPR macroscopically due to the material and unit substructure and have superior mechanical properties shown by biological structures like bones [263], wood [264], and insect wings [265]. Hierarchical meta-materials are suitable to develop catalysts [94], hardened structures [186], and sandwich panels [266-267]. Furthermore, by performing simulations one can control, at the level of design, the magnitude of its auxeticity, degree of aperture and size of the different pores in the system making these materials promising candidates for industrial and biomedical applications, such as stents and skin grafts [186].

Auxetic polymers as expanded polytetrafluoroethylene, ultra-high molecular weight polyethylene and expanded polypropylene [167-173] may be used in the fabrication of all-weather clothing and a large series of manufactured auxetic

fibers, yarns and fabrics are been developed for its use in the textile industry [237-243]. Auxetic polyester fibers [239-240] and nylon fibers [172,240] have been developed and auxetic yarns, constructed using non-auxetic fibers, have been designed [258]. These yarns have been used to obtain woven fabric [181], which inherit the auxetic effect from the yarn. Finally, it must be emphasized that auxetic materials have also proven useful in the development of press-fit fasteners [268], cushion seats [269-270], reinforced fatigue resistant composites and foams [183,271-273], materials with tunable magnetic, acoustic and optical reflectivity properties [274-275], vibration dampers [231-233,276], acoustic isolators [234-236] and sport applications [277-278].

2.2 Negative linear compressibility

2.2.1 NLC concept

Other important anomalous elastic properties are the negative linear compressibility (NLC) and negative area compressibility (NAC) [279-284]. The compressibility [285-287], the inverse of bulk modulus, provides a measurement of the relative volume change of a material resulting from an isotropic pressure change. In general, a material contracts in all directions when the pressure increases. The systems displaying the NLC property exhibit a volume expansion when subjected to a positive pressure applied in a certain direction. One of the necessary conditions for material stability is the positivity of overall compressibility [284]. NLC is not related to unstable materials and may refer not only to the positive variation of the volume when the material is submitted to a compression directed along a given direction, but also to the increase of one or two single directions of the unit cell of a material under the application of a hydrostatic pressure [279,282]. In the first case the directional derivative of the volume with respect to pressure is negative. In the second one, the volume does not increase and the positive variation of the parameters in some directions is compensated by a larger negative variation of the parameters in the remaining directions. If two lattice parameters increase upon the action of an isotropic compressive pressure, the observed effect is denominated negative area compressibility (NAC).

Although positivity of bulk modulus is required for mechanical stability, negative values can be stabilized by an external constraint in a certain composite [288,179-180]. Negative modulus can be also stabilized in non-equilibrium situations involving the flow of fluid, heat or electric current [289-290]. Other important negative properties include the negative thermal expansion (NTE) [291-292], the negative permeability (NP) [293-294] and the negative refractive index (NRI) [295]. Negative piezoelectric coefficients [287] are also possible. Stars and star clusters exhibit negative specific heat (NSH) [296-297]. As it happens with negative bulk modulus, this last situation also violates stability constraints, in this case

thermodynamic stability conditions. However, stars are not in equilibrium and are not extensive systems, so thermodynamic stability constraints do not apply.

2.2.2 NLC materials

NLC behavior was firstly observed in tellurium by Bridgman in 1922 [285]. Bridgman also observed NLC in arsenic in 1933 [286]. Baughman and his collaborators [279-280] explained the effect and proposed a wine-rack structural mechanism to explain the NLC effect. This property is relatively uncommon phenomenon in nature and, up to 2010, it was observed in only 14 materials [81]. In a review performed by Barnes in 2017 [298], only 46 materials exhibiting NLC were collected despite of the great effort dedicated in recent years in the search of this kind of materials. A number of biological structures in nature make use of NLC [185,299]. Materials whose density increases upon stretching have been found in the muscle systems of some living organisms [300-301]. A biological structure displaying NLC is the lipid bilayer [302-304], whose thickness has been reported to increase up to 4% under the effect of hydrostatic pressures of about 2 Kbar [304].

Some natural materials displaying NLC are elemental Se [305], LaNbO_4 [306], CsH_2PO_4 [307], BaAsO_4 [308], $\text{Ag}_3[\text{Co}(\text{CN})_6]$ [309], methanol monohydrate [310-311], $\text{KMn}[\text{Ag}(\text{CN})_2]_3$ [312], $[\text{NH}_4][\text{Zn}(\text{HCOO})_3]$ [101], zinc dicyanoaurate [313-314], ammonium oxalate monohydrate (oxammitte mineral) [102], lithium L-tartrate [315], $\text{Cd}(\text{NH}_3)_2[\text{Cd}(\text{CN})_4]$ [103], platinum sulfide (cooperite mineral) [104], and $\alpha - \text{BiB}_3\text{O}_6$ [105]. Compressibility data of some crystals as cesium biphthalate [279] are consistent with the presence of NLC. Weng *et al.* in 2008 [281] checked the elastic compliance data for the natural orthorhombic and monoclinic single crystals listed by Simmons [316]. They found that for orthorhombic symmetry only barite at high temperatures (greater than 400K) and Rochelle salt in some particular crystallization may exhibit NLC. Similarly, for monoclinic crystals, they only found six kinds of materials that may possess this property: ethylene diamine tartrate, L-rhamnose monohydrate, naphthalene, sodium thiosulphate, tartaric acid and taurine. The presence of NLC in these compounds should be confirmed experimentally. Some superconducting materials exhibit NLC, probably due to the behavior of these materials when cooled, which leads to a fast contraction in one or more directions. Three examples of these compounds are cobalt-germanium [317], EuFe_2As_2 [318], and TlGaSe_2 [319]. Negative area compressibility is believed to be much more infrequent than negative linear compressibility. The number of known NAC materials is very small and all of them simultaneously also exhibit negative thermal expansion. Some examples are NaV_2O_5 [320], TlGaSe_2 [319] and $\text{Ag}(\text{TCM})$ (silver tricyanomethanide) [283].

Non-topological mechanisms alternative to the wine-rack mechanism have been proposed [298,321]. Barnes *et al.* [322] have proposed tetragonal beam structures which display NLC effect. Negative Poisson ratios are frequently found together with NLC or NAC. The connection of the auxetic and NLC/NAC effects has been studied in 2D structures analogous to certain types of open cell foams [323-324]. NLC materials with discrete and non-wine-rack structures seem to be very infrequent. For example, some carbon fibre laminate composites of this kind exhibited NLC [325]. As in the case of negative Poisson ratios, negative linear compressibility may appear under the effect of applied pressures and deformations. Examples are several natural zeolitic materials as natrolite, mesolite and scolecite [326].

2.2.3 NLC applications

NLC is a very relevant mechanical property and has a wide range of important applications, such as the development of ultrasensitive pressure-sensing devices, pressure driven actuators, optical telecommunication cables, artificial muscles, next-generation body armor and biomedical uses [185,282,299,313,327-328]. The most immediate application of the NLC effect is the development of pressure sensors based in the relation of volume and pressure. However, the deep understanding the mechanisms of NLC must lead to potential applications as the development of efficient biological structures, nanofluidic actuators or compensators for undesirable moisture-induced swelling of concrete/clay-based engineering materials [313]. Since NLC has been found in systems having a fixed topology, there has been a large amount of work aimed to design NLC materials using topology optimization techniques [211,294,329-332]. These techniques are also being used in order to design materials with prescribed bulk, shear or Young moduli, Poisson ratios and other properties [330-331,211,294,329,332] and may be employed to develop prototypes of a wide series of mechanical devices as bone implants [333].

3. Computational solid-state methods

The generalized gradient approximation (GGA) together with Perdew–Burke–Ernzerhof functional [334] supplemented with Grimme empirical dispersion correction [335], was used to study the crystal structures and mechanical properties of the cyclic oxocarbon deltoid, squaric, and croconic acids. The addition of dispersion corrections improved the computed structural and mechanical properties in a significant way as a consequence of the better description of the hydrogen bonding present in their unit cell structures. This approach, referred to as DFT-D2, is implemented in the CASTEP program [336], a module of the Materials Studio package [337], which was employed to model the structures of the materials considered. The pseudopotentials employed for the hydrogen, carbon and oxygen ions in the structures of these

materials were standard norm-conserving pseudopotentials [338] provided by CASTEP.

The atomic positions and unit cell parameters were optimized by using the Broyden–Fletcher–Goldfarb–Shanno method [82] with a convergence threshold on atomic forces of 0.01 eV/Å. This method was also used in order to optimize the structures of the materials considered under the effect of different applied pressures. The structures of the materials considered in this work were optimized in calculations with augmented complexity by increasing the calculation parameters. These parameters, the kinetic energy cut-off (ϵ) and k-point mesh [339] were chosen to ensure good convergence for computed structures and energies. The structures were only accepted as satisfactory if the computed X-ray powder diffraction pattern obtained from the computed crystal structure [340] was in agreement with the experimental pattern. The precise calculation parameters used to determine the final results may be found in Table 1.

The elastic constants required to calculate the mechanical properties of the considered materials and to study the mechanical stability of their crystal structures were obtained from stress-strain relationships using the finite deformation method [341]. In this technique, the individual elastic constants are determined from the stress tensor resulting from the response of the material to finite programmed symmetry-adapted strains [287]. The energy-based methods and the use of Density Functional Perturbation Theory [342] appear to be less efficient than this stress-based method for the calculation of the elasticity matrix [341]. The derivatives of the bulk modulus with respect to pressure were determined by performing fits of the unit cell volumes and associated pressures to a fourth-order Birch-Murnahan [343] equation of state (EOS). The unit cell volumes in the vicinity of the optimized structure were calculated by optimizing the geometry of the material considered under seventeen different applied isotropic pressures within -1.0 to 11.0 GPa. The fits of the pressure-volume data to the chosen EOS were carried out using EOSFIT 5.2 computer program [344].

4. Results and discussion

4.1 Crystal structures

4.1.1 Deltic acid (2,3-dihydroxycyclopropen-1-one)

4.1.1.a Calculated crystal structure

The orthorhombic crystal structure of the deltic acid was optimized by performing increasingly complex computations using very demanding convergence criteria. Table 1 gives the final calculation parameters used. The final calculations were performed with a large kinetic cut-off of 950 eV and a k-mesh comprising 90 k-points. The calculated lattice parameters, volume, and density are given in Table 2, where they are compared with the experimental values given by Semmingsen

and Groth [13]. The experimental data were reproduced accurately. The differences in the calculated cell volume and density compared with the experimental values were about 1.3%.

The computed crystal structure of the deltic acid is shown in Fig. 1, where views of the unit cell from [100], [001], and [001] directions are provided. A larger scale view of the structure is shown in Fig. 2.A, where a $2 \times 2 \times 2$ supercell is displayed. The last figure allows to appreciate adequately the chain structure of this material. As can be seen, the structure of this material is composed of hydrogen bonded pairs of deltic acid molecules forming dimers. The deltic acid molecules have C_{2v} symmetry. In turn, these dimers are hydrogen bonded to other dimers to form chains. The different chains are held together only by weak van der Waals forces.

4.1.1.b Bond lengths and angles

The computed bond distances and bond angles are shown in Table 3 and Table 4, respectively, where they are compared with the corresponding experimental values from Semmingsen and Groth [13]. The atom numbering convention employed is shown in Fig. S1 of the Supplementary Information. Note that in the notation employed in the tables for the bond distances and angles, the super-index # is used to differentiate two distinct atoms of the same kind belonging to the same molecule in the crystal. As can be seen, the calculated values are in good agreement with their experimental counterparts. The two equivalent larger C1–C2 bonds and the C2–C2[#] bond in the 3-membered carbon ring have bond distances of 1.397 and 1.373 Å, respectively, which are comparable to the calculated distances of 1.409 and 1.386 Å. These values are intermediate between the distances commonly associated to single and double bonds. The carbonyl group in the deltic acid accepts two equivalent, strong hydrogen bonds (O2–H1 $\cdots$ O1'), which are almost linear and have $R(\text{H1}\cdots\text{O1}')=1.501$ Å. The calculated value of this distance, 1.509 Å, is in excellent agreement with the experimental one.

4.1.2 Squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione)

4.1.2.a Calculated crystal structure

Table 1 gives the final calculation parameters used to determine the properties of the monoclinic crystal structure of the squaric acid. As for deltic acid, the final calculations were performed with a large kinetic cut-off of 950 eV. The selected k-mesh was also very dense and comprised 75 k-points. The calculated lattice parameters, volume, and density are given in Table 2. The results are in very good agreement with the experimental values given by Wang *et al.* [14]. The differences in the calculated cell volume and density compared with the experimental values were about 1.6%.

Table 1. Material data and calculation parameters.

Material	Structural formula	Crystal system	Space group	ε (eV)	k-mesh
Deltic acid	$C_3O_3H_2$	Orthorhombic	<i>Pnam</i> (no. 62)	950	$6 \times 6 \times 5$ (90 k-points)
Squaric acid	$C_4O_4H_2$	Monoclinic	<i>P21/m</i> (no. 11)	950	$5 \times 5 \times 6$ (75 k-points)
Croconic acid	$C_5O_5H_2$	Orthorhombic	<i>Pca21</i> (no. 29)	950	$5 \times 8 \times 5$ (80 k-points)

Table 2. Calculated lattice parameters of cyclic oxocarbon acids.

Parameter	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)	Vol. (Å ³)	Dens. (g·cm ⁻³)
Deltic acid								
DFT	6.2379	6.5698	7.8621	90	90	90	322.2021	1.774
Exp. [13]	6.173	6.520	7.899	90	90	90	317.92	1.798
Squaric acid								
DFT	6.1039	6.0902	5.2647	90	90.12	90	195.7094	1.935
Exp. [14]	6.119	6.133	5.297	90	90.05	90	198.78	1.905
Exp. [15]	6.125	6.130	5.312	90	90	90	199.45	1.899
Exp. [16]	6.137	6.137	5.337	90	90	90	201.01	1.884
Exp. [17,18]	6.129	6.140	5.273	90	90.00	90	198.43	1.908
Croconic acid								
DFT	8.7088	5.0983	10.7921	90	90	90	479.1682	1.969
Exp. [19]	8.7110	5.169	10.962	90	90	90	493.59	1.912
Exp. [20]	8.7108	5.1683	10.9562	90	90	90	493.25	1.913

Figure 1. Calculated crystal structures of (A) deltic, (B) squaric and (C) croconic acids. For each acid, the corresponding views of the unit cell from [100], [010] and [001] directions are given. Color code: Grey-C; Red-O; White-H.

Figure 2. Views of $2 \times 2 \times 2$ supercells of (A) deltic, (B) squaric and (C) croconic acids. Color code: Grey-C; Red-O; White-H.

Table 3. Bond distances in the deltic acid (in Å).

Bond	Exp. [13]	Calc.
C-C		
C1-C2	1.397	1.409
C2-C2 [#]	1.373	1.386
C-O		
C1-O1	1.265	1.271
C2-O2	1.301	1.301
O-H		
O2-H1	1.054	1.036
Hydrogen bonds		
O2...O1'	2.555	2.541
H1...O1'	1.501	1.509

Table 4. Bond angles in the deltic acid (in degrees).

Angle	Exp. [13]	Calc.
C-C-C		
C1-C2-C2 [#]	60.58	60.53
C2-C1-C2 [#]	58.85	58.94
O-C-C		
O1-C1-C2 [#]	150.54	150.50
O2-C2-C1	154.26	152.54
O2-C2-C2 [#]	146.95	146.89
C-O-H		
C2-O2-H1	139.70	111.00
Hydrogen bonds		
O2-H1...O1'	178.41	173.45

The computed crystal structure of the squaric acid is shown in Fig. 1. In this Figure, views of the unit cell from [010], [001], and [100] directions are displayed. A larger scale view of the structure is shown in Fig. 2.B, where a $2 \times 2 \times 2$ supercell is shown. As may be appreciated, the structure of this material is composed of hydrogen bonded squaric acid molecules forming sheets. These sheets are electroneutral and are not bonded; they are held together by weak van der Waals forces only.

4.1.2.b Bond lengths and angles

For squaric acid, the computed bond distances and angles are shown in Table 5 and Table 6, respectively. In these tables, the computed values are compared with the experimental data from Wang *et al.* [14]. The atom numbering convention employed is shown in Fig. S2 of the Supplementary Information. As for deltic acid, the theoretical results are in

excellent agreement with their experimental counterparts. The C1-C2, C2-C3, C3-C4 and C1-C3 bonds in the 4-membered carbon ring have experimental bond distances of 1.441, 1.425, 1.470, and 1.484 Å, respectively, comparable to the calculated distances of 1.468, 1.432, 1.464, and 1.496 Å. The carbonyl groups C1-O1 and C4-O4 accept strong hydrogen bonds (O3-H1...O1' and O2-H2...O4', respectively), which are nearly linear and have $R(H1...O1')=1.434$ Å and $R(H2...O4')=1.515$ Å, in good agreement with the calculated values of 1.425 and 1.424 Å, respectively.

Table 5. Bond distances in the squaric acid (in Å).

Bond	Exp. [14]	Calc.
C-C		
C1-C2	1.441	1.468
C2-C3	1.425	1.432
C3-C4	1.470	1.464
C4-C1	1.484	1.496
C-O		
C1-O1	1.250	1.244
C2-O2	1.275	1.287
C3-O3	1.272	1.288
C4-O4	1.235	1.244
O-H		
O3-H1	1.103	1.069
O2-H2	1.027	1.069
Hydrogen bonds		
O3...O1'	2.531	2.493
H1...O1'	1.434	1.425
O2...O4'	2.541	2.492
H2...O4'	1.515	1.424

Table 6. Bond angles in the squaric acid (in degrees).

Angle	Exp. [14]	Calc.
C-C-C		
C1-C2-C3	91.71	91.16
C2-C3-C4	90.58	91.35
C3-C4-C1	88.29	88.82
C4-C1-C2	89.41	88.87
O-C-C		
O1-C1-C2	135.00	134.93
O1-C1-C4	135.59	136.40
O2-C2-C3	131.62	132.23
O2-C2-C2	136.67	136.60
O3-C3-C4	136.49	136.84
O3-C3-C2	132.92	131.82
O4-C4-C1	135.54	134.78
O4-C4-C3	136.16	136.39

4.1.3 Croconic acid (4,5-dihydroxycyclopent-4-ene-1,2,3 -trione)

4.1.3.a Calculated crystal structure

The final calculations of the croconic acid were carried out using the calculation parameters shown in Table 1. The computations were performed with a kinetic cut-off of 950 eV and a dense k-mesh including 80 k-points. The calculated lattice parameters, volume, and density are given in Table 2. The results are in good agreement with the experimental data of Horiuchi *et al.* [19]. The differences in the calculated cell volume and density with respect to the experimental values were about 2.5%. The difference between the computed and experimental results is larger in the croconic acid than in the deltic or squaric acids. This is very probably due to the fact that temperature effects are significant in the croconic acid. The experimental structure of the deltic acid was obtained from low-temperature X-ray diffraction data by structure refinement [13] and the structure of the squaric acid was determined from combined X-ray and neutron diffraction studies in which the temperature factors were taken into account [14]. However, the experimental data for croconic acid was obtained from measurements performed at room temperature [19] and the theoretical distances refer to the temperature of 0 K. Similar temperature effects were observed in the theoretical treatment of other materials [345].

The calculated structure of the croconic acid is shown in Fig. 1, where images of the unit cell from [100], [010], and [001] directions are displayed. The view of the structure given in Fig. 2.C shows a $2 \times 2 \times 2$ supercell. Clearly, the structure of the croconic acid crystal is formed of hydrogen bonded croconic acid molecules forming folded zig-zag sheets. As for squaric acid, the sheets are electroneutral and are held together by weak van der Waals forces only.

4.1.3.b Bond lengths and angles

The bond distances and angles determined from the optimized structure of the croconic acid are given in Table 7 and Table 8, respectively. In these tables, the calculated geometrical parameters are compared with the experimental ones from Horiuchi *et al.* [19]. The atom numbering convention employed is shown in Fig. S3 of the Supplementary Information. As for the previous materials, the theoretical results are in good agreement with the experimental values. The computed C-C bond distances in the 5-membered ring compare very well with the experimental bond distances. The carbonyl groups C5-O5 and C4-O4 accept almost linear hydrogen bonds ($O1-H1 \cdots O5'$ and $O2-H2 \cdots O4'$, respectively), having $R(H1 \cdots O5')=1.643$ Å and $R(H2 \cdots O4')=1.757$ Å to be compared with the calculated values of 1.488 and 1.493 Å, respectively. The larger differences in the computed hydrogen bond distances for

squaric acid in comparison with the results for deltic and squaric acids, are, as the differences in the lattice parameters, probably due to temperature effects. It must be noted that Horiuchi *et al.* [19] admitted that the hydrogen atom positions were less accurate than those of carbon and oxygen atoms. In order to evaluate the crystalline polarization of croconic acid, Horiuchi *et al.* [19] held fixed the carbon and oxygen atoms at the experimental positions but optimized the hydrogen atom positions theoretically.

Table 7. Bond distances in the croconic acid (in Å).

Bond	Exp. [19]	Calc.
C-C		
C1-C2	1.393	1.420
C2-C3	1.467	1.478
C3-C4	1.514	1.508
C4-C5	1.502	1.488
C5-C1	1.440	1.450
C-O		
C1-O1	1.301	1.297
C2-O2	1.300	1.291
C3-O3	1.213	1.223
C4-O4	1.218	1.234
C5-O5	1.233	1.245
O-H		
O1-H1	0.983	1.049
O2-H2	0.881	1.045
Hydrogen bonds		
$O1 \cdots O5'$	2.617	2.524
$H1 \cdots O5'$	1.643	1.488
$O2 \cdots O4'$	2.629	2.535
$H2 \cdots O4'$	1.757	1.493

Table 8. Bond angles in the croconic acid (in degrees).

Angle	Exp. [19]	Calc.
C-C-C		
C1-C2-C3	111.04	110.30
C2-C3-C4	105.06	104.98
C3-C4-C5	106.60	107.92
C4-C5-C1	107.03	107.06
C5-C1-C2	110.26	109.73
O-C-C		
O1-C1-C2	128.24	128.09
O1-C1-C5	121.50	122.18
O2-C2-C1	122.53	122.26
O2-C2-C3	126.43	127.44
O3-C3-C2	128.15	127.71
O3-C3-C4	126.79	127.32
O4-C4-C3	128.47	127.73
O4-C4-C5	124.93	124.35
O5-C5-C4	127.28	126.24
O5-C5-C1	125.69	126.70
C-O-H		
C1-O1-H1	116.24	114.60
C2-O2-H2	113.75	115.03
Hydrogen bonds		
$O1-H1 \cdots O5'$	170.31	167.90
$O2-H2 \cdots O4'$	169.74	175.19

4.2 X-ray powder diffraction patterns

The X-ray powder diffraction patterns for deltic, squaric and croconic acids were derived from the experimental [13,14,19] and computed structures [340] using $\text{CuK}\alpha$ radiation ($\lambda = 1.540598 \text{ \AA}$) employing the REFLEX module of Materials Studio [337]. As can be observed in Fig. 3, the calculated patterns are in excellent agreement with the experimental ones. This gives a strong support to the calculated structures and the computational treatment used for these materials. A detailed discussion of the variation of the X-ray powder diffraction patterns as a function of applied pressures will be given in Section 4.3.4.

Figure 3. X-Ray powder patterns of the deltic (A), squaric (B) and croconic (C) acids using $\text{CuK}\alpha$ radiation. The X-Ray powder diffraction patterns computed from the experimental [13,14,19] and calculated geometries are displayed for the three materials.

4.3 Mechanical properties and stability

4.3.1 Mechanical stability

Materials with monoclinic and orthorhombic unit cells have 13 and 9 non-degenerate elastic constants in the symmetric stiffness C matrix [287,89], respectively. The computed values of these constants for the deltic, squaric, and croconic acids are given in Table 9. In this table, the standard Voigt notation for the indices of the elements of the C matrix (C_{ij}) is used [287]. For orthorhombic systems a set of necessary and sufficient Born conditions [346] for mechanical stability are known [347,89]. These conditions can be written as a set of algebraic inequalities among products of elastic constants:

$$C_{ii} > 0 \quad (i = 1, 4, 5, 6)$$

$$C_{11}C_{22} - C_{12}C_{12} > 0$$

$$C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{11}C_{23}C_{23} - C_{22}C_{13}C_{13} - C_{33}C_{12}C_{12} > 0$$

These conditions were adequately satisfied by the computed stiffness tensors for deltic and croconic acids. In the case of monoclinic materials, the generic necessary and sufficient Born criterion of stability is that all eigenvalues of the stiffness C matrix be positive [347]. The stiffness matrix of the squaric acid was diagonalized numerically and all eigenvalues were positive. Therefore, the three materials considered are mechanically stable.

Table 9. Computed elastic constants of the oxocarbon acids.

ij	C_{ij}		
	Deltic acid	Squaric acid	Croconic acid
11	12.53	80.19	24.17
22	13.06	73.75	18.87
33	97.27	17.64	100.51
44	9.90	6.91	8.87
55	8.03	6.70	15.14
66	11.15	22.85	16.79
12	7.19	-8.10	14.52
13	6.13	9.46	6.57
15	0.00	-0.96	0.00
23	9.17	0.91	4.15
25	0.00	-0.37	0.00
35	0.00	-0.07	0.00
46	0.00	4.12	0.00

4.3.2 Mechanical properties

The mechanical properties of polycrystalline deltic, squaric, and croconic acids were determined according to the Voigt [349], Reuss [349], and Hill [350] schemes. These schemes provide very different results for systems characterized by a large anisotropy [83,89]. As may be observed in Table 9 the three materials considered are very anisotropic mechanically because the corresponding elastic constants are very different in the three directions ($i = 1, 2, 3$, for the x, y , and z directions). The Reuss approach was chosen as the best one in the three cases because it provided the best approximation to the bulk modulus computed from the equation of state (see Section 4.3.3). The same situation was encountered for the highly anisotropic uranyl carbonate

mineral rutherfordine [83]. The results obtained for the bulk, shear, and Young moduli, and the Poisson ratio (B , G , E , and ν , respectively) are given in Table 10. Also, the ductility [351] and hardness [352] indices were determined. The deltic and squaric acids are brittle because the ductility index, D , is smaller than 1.75 [353,351]. However, the croconic acid is ductile. The computed values of the Vickers hardness, H , for these compounds were 0.9, 2.6, and 0.5, respectively. These values correspond to materials of very low hardness [88,352].

Table 10. Computed mechanical properties of the deltic, squaric and croconic acids. The values of the bulk, shear and Young moduli (B , G and E , respectively) are given in GPa.

Property	Deltic acid	Squaric acid	Croconic acid
B	9.92	13.63	16.04
G	6.79	10.25	8.78
E	16.59	24.59	22.28
ν	0.22	0.20	0.27
D	1.46	1.33	1.82
H	0.93	2.59	0.52

In order to assess the elastic anisotropy of these materials, shear anisotropic factors were obtained. These factors give a measure of the degree of anisotropy in the bonding between atoms in different planes and are important parameters to study the material durability [353-354]. Shear anisotropic factors for the {100} (A_1), {010} (A_2), and {001} (A_3) crystallographic planes were computed. These factors may be written as [353-354]:

$$A_1 = 4 C_{44} / (C_{11} + C_{33})$$

$$A_2 = 4 C_{55} / (C_{22} + C_{33} - C_{23})$$

$$A_3 = 4 C_{66} / (C_{11} + C_{22} - 2 C_{12})$$

For an isotropic crystal, the factors A_1 , A_2 , and A_3 must be one, while any value smaller or greater than unity is a measure of the degree of elastic anisotropy possessed by a crystal. As seen in Table 11, the {001}, {010}, and {001} planes are the most anisotropic for the deltic, squaric, and croconic acid, respectively (A_3 , A_2 , and A_3 , respectively), are the factors more different from unity for the three acids).

Finally, we obtained the universal anisotropy index [79],

$$A^U = 5 \left(\frac{G_V}{G_R} \right) + \left(\frac{B_V}{B_R} \right) - 6$$

where G_V and G_R are the values of the shear modulus in the Voigt and Reuss schemes and G_V and G_R are the values of the bulk modulus in the same approximations. The departure of A^U from zero defines the extent of single-crystal anisotropy and accounts for both the shear and the bulk contributions unlike all other existing anisotropy measures. A^U is independent of the scheme used to determine the polycrystalline elastic properties because it is defined in terms of the bulk and shear moduli in both Voigt and Reuss approximations [79]. For the three materials considered, the computed universal anisotropy was quite large. The precise values were 5.1, 4.5, and 4.5 for the deltic, squaric, and croconic acids, respectively. This large anisotropy is in agreement with the large difference between the values of the

elastic constants along the different directions and derives directly from the differences in bonding strength between the atoms belonging to the unit cells of these materials along the different directions. In the case of the squaric and croconic acids, the bonding in the direction perpendicular to the layers characterizing their structures is very weak. The same occurs for deltic acid in the two directions orthogonal to the direction of propagation of the chains.

Table 11. Computed anisotropy factors for deltic, squaric and croconic acids.

Factor	Deltic acid	Squaric acid	Croconic acid
A_1	0.41	0.35	0.32
A_2	0.35	0.30	0.55
A_3	3.98	0.54	4.79
A^U	5.09	4.49	4.48

4.3.3 Bulk modulus derivatives

Lattice volumes around the optimized structures of these acids were calculated by optimizing the structures at 17 different applied isotropic pressures in the range -1.0 to 11.0 GPa. Then, the calculated pressure-volume data were fitted to a fourth-order Birch–Murnaghan equation of state [343] using the EOSFIT 5.2 program [344]. The fit produces the best possible values of the parameters in the EOS. These parameters include the bulk modulus and their first and second derivatives with respect to pressure at the temperature of 0 K. The results are shown in Table 12, where they are compared with the results obtained for the bulk modulus obtained from the elastic constants in the Reuss approximation. The bulk moduli obtained in both approaches agree satisfactorily.

Table 12. Computed bulk modulus and pressure derivatives derived from the EOS for deltic, squaric and croconic acids. The values of the bulk modulus computed from the elastic constants are given in the last row of the table for comparison.

Property	Deltic acid	Squaric acid	Croconic acid
EOS			
B (GPa)	11.17±0.18	16.64±0.18	16.57±0.21
B'	9.77±0.36	9.43±0.28	9.25±0.31
B'' (GPa ⁻¹)	-3.62±0.62	-2.74±0.35	-2.56±0.38
χ^2	0.084	0.043	0.096
Elastic constants			
B (GPa)	9.92±0.58	13.63±0.25	16.04±0.26

4.3.4 Anomalous mechanical properties

4.3.4.a Deltic acid

4.3.4.a.i Negative Poisson ratio

Visualizing the variation of the elastic properties with the strain orientation is, except for the case of isotropic materials, quite complicated. Marmier *et al.* [81] developed the EIAM software with the purpose of reducing this difficulty to a large extent. Tridimensional representations of the most important elastic properties for the deltic acid were obtained using this software and are displayed in Fig. 4.

Table 13. Minimum and maximum Poisson ratios in the deltic, squaric and croconic acids. The directions for the associated longitudinal and transverse directions are also given.

ν_{min}	U_{min}^L	U_{min}^T	ν_{max}	U_{max}^L	U_{max}^T
Deltic acid					
-0.09	(-0.70, -0.71, 0.00)	(0.71, -0.70, 0.00)	0.63	(0.00, 0.00, 1.00)	(0.00, 1.00, 0.00)
Squaric acid					
-0.12	(0.00, -1.00, 0.00)	(0.99, 0.02, 0.16)	0.58	(-0.90, -0.43, -0.02)	(0.26, -0.51, -0.82)
Croconic acid					
-0.13	(0.61, 0.00, 0.80)	(0.80, 0.00, -0.61)	0.81	(0.78, 0.00, -0.63)	(0.00, 1.00, 0.00)

For the case of the shear modulus and Poisson ratios, depending on two directions (the longitudinal and transverse directions, see Section 2.1.1), Fig. 4.C and Fig. 4.D provide a representation of surface of maximum G and ν , respectively, that is, the surface formed with the maximum values of these properties for the given direction of the longitudinal strain and all possible transverse directions. The visualization of these maximum surfaces is very useful since they are commonly very similar for structurally related compounds [86-87]. They may be used in order to recognize shearing effects in the phase transformations occurring between several related materials [90,86]. However, whereas the surfaces of minimum Poisson ratio are quite variable even for related compounds, their observation is also very useful, since it reveals possible negative values of the Poisson ratio. For the deltic acid, the surface of minimum Poisson ratio, displayed in Fig. 5.A, shows that this acid is an NPR material, although the value of the lowest Poisson ratio is only about -0.1 (see Table 13).

4.3.4.a.ii Lattice parameters and X-ray powder diffraction pattern as a function of the applied pressure

In order to understand the structural variations produced by the application of pressure in the deltic acid, the structure of this material was optimized under the effect of different pressures applied along the direction of the minimum Poisson ratio (given in Table 13). The lattice parameters and volumes obtained for twelve applied pressures along this direction are reported in Table 14. The corresponding X-ray powder diffraction patterns were determined from the optimized structures and six of these patterns are displayed in Fig. 6. The displacements of the main reflections in the X-Ray pattern due to the effect of the applied pressures are collected in Table 15.

The material is compressed along U_{min}^L for positive pressures and the volume decreases properly (as it does the length along U_{min}^L which in this case is nearly coincident with the [110] crystallographic direction). Similarly, the material expands for negative pressures. The parameter d of the main [120] reflection and most other reflections decrease (or, equivalently, the corresponding 2θ values increase, see Fig. 6), as expected from the increase of the applied external pressure (see Table 15). Notably, [110], which is the reflection with larger negative variation, maps the simultaneous decrease of both a and b lattice parameters and gives nearly the variation of the distance along the U_{min}^L direction. The decrease of d parameter associated to the reflection [200] maps directly the decrease of the single a lattice parameter. There are also many reflections which displace towards larger

d (or, equivalently, the corresponding values of 2θ decrease). For example, the displacement of the [004] reflection is due to the increase of the c lattice parameter

Figure 4. Elastic properties of the deltic acid as a function of the orientation of the applied strain: (A) Compressibility; (B) Young modulus; (C) Maximum shear modulus; (D) Maximum Poisson ratio.

Figure 5. Computed surfaces of minimum, average, and maximum Poisson ratio of the deltic (A), squaric (B) and croconic (C) acids.

Table 14. Computed lattice parameters and volumes in the deltic acid at different applied pressures directed along U_{min}^L direction.

P (GPa)	a (Å)	b (Å)	c (Å)	Vol. (Å ³)
-0.4771	6.5640	7.0750	7.8030	362.3797
-0.2412	6.3267	6.7168	7.8396	333.1429
0.0	6.6279	6.5698	7.8621	322.2020
0.2383	6.1985	6.4330	7.8846	314.4015
0.4783	6.1520	6.3233	7.9039	307.4694
0.6989	6.0824	6.2471	7.9340	301.4727
0.9326	6.0358	6.1850	7.9550	296.9684
1.1781	5.9919	6.1385	7.9681	293.0768
1.4404	5.96667	6.0872	7.9774	289.7422
1.8817	5.8379	6.0554	8.0016	282.8635
2.3529	5.7751	5.9948	8.0287	277.9556
2.8120	5.7054	5.9542	8.0483	273.4107

Figure 6. X-ray powder diffraction pattern for the deltic acid as a function of the applied pressure.

Table 15. Displacement of some of the most intense reflections in the X-ray powder diffraction pattern for the deltic acid. The 2θ and d values associated to the X-ray powder diffraction pattern for the deltic acid at zero pressure are also given. The values of 2θ and d associated with each reflection [hkl] are given in degrees and Å, respectively.

[hkl]	$2\theta(0)$	$d(0)$	$\Delta(0.0-0.478)$	$\Delta(0.478-0.933)$	$\Delta(0.933-1.440)$	$\Delta(1.440-1.882)$	$\Delta(1.882-2.353)$	$\Delta(2.353-2.812)$
[230]	50.909	1.792	-0.054	-0.036	-0.025	-0.018	-0.017	-0.017
[332]	66.342	1.408	-0.030	-0.024	-0.016	-0.016	-0.012	-0.012
[220]	39.823	2.262	-0.057	-0.045	-0.029	-0.029	-0.022	-0.022
[013]	36.897	2.434	-0.002	0.005	0.000	0.004	0.003	0.003
[004]	46.146	1.966	0.011	0.013	0.006	0.006	0.007	0.007
[211]	33.766	2.652	-0.042	-0.044	-0.028	-0.041	-0.023	-0.023
[202]	36.754	2.443	-0.016	-0.023	-0.015	-0.031	-0.014	-0.014
[011]	17.578	5.041	-0.104	-0.055	-0.043	-0.011	-0.025	-0.025
[111]	22.660	3.921	-0.070	-0.055	-0.038	-0.038	-0.028	-0.028
[200]	28.597	3.119	-0.043	-0.058	-0.035	-0.064	-0.031	-0.031
[212]	39.311	2.290	-0.024	-0.025	-0.017	-0.027	-0.014	-0.014
[022]	35.588	2.521	-0.052	-0.027	-0.022	-0.005	-0.012	-0.012
[110]	19.609	4.524	-0.114	-0.090	-0.059	-0.058	-0.044	-0.044
[112]	30.093	2.967	-0.024	-0.017	-0.014	-0.014	-0.009	-0.009
[120]	30.737	2.907	-0.095	-0.060	-0.041	-0.023	-0.027	-0.027

Table 16. Selected interatomic distances (in Å) in the deltic acid at different applied pressures directed along the direction of minimum Poisson ratio. The last row in the table (Δ) gives the variation of the interatomic distances at $P=2.812$ GPa with respect to those at $P=0.0$ GPa.

P (GPa)	H1-H1 (R1)	H1-O1	O1-C2*	H1-H1' (R2)	R1+R2
-0.477	5.226	3.679	3.219	2.577	7.803
-0.241	5.235	3.688	3.265	2.605	7.84
0.0	5.242	3.692	3.326	2.620	7.862
0.238	5.249	3.696	3.265	2.636	7.885
0.478	5.254	3.699	3.219	2.650	7.904
0.699	5.256	3.703	3.220	2.678	7.934
0.933	5.259	3.705	3.203	2.696	7.955
1.178	5.263	3.709	3.192	2.705	7.968
1.440	5.268	3.708	3.164	2.710	7.978
1.882	5.270	3.711	3.143	2.732	8.002
2.353	5.273	3.710	3.116	2.756	8.029
2.812	5.276	3.710	3.094	2.773	8.049
Δ	+0.034	+0.018	-0.232	+0.153	+0.187

4.3.4.a.iii Crystal structure deformation

Table 16 reports the values of selected interatomic distances between the atoms in the structure of the deltic acid. The distances between the atoms within the deltic acid molecules in the crystal, change only very slightly under the applied pressures. As shown in the first two columns of Table 16, the variation of the H1-H1 and H1-O1 distances (Fig. S1 of the Supplementary Information), providing an approximate measure of the size of a deltic acid molecule, are small. The main changes arising from the application of pressure are the increase of the distance between the deltic acid molecule units along a chain and the decrease of the distance between two chains. The first of these two effects may be easily appreciated by observing the variation of the H1-H1' distance in Table 16. The hydrogen atoms H1 and H1' are placed in two contiguous molecules of a given chain (Fig. S1 of the Supplementary Information). The decrease of the distance between two chains may also be easily seen by observing the O1-C2* distances in Table 16, where the O and C atoms are placed in different chains. The convention employed in this work (see Fig. S1 of the Supplementary Information) is that the prime indicates atoms placed in contiguous molecules located in the same chain and the star denotes atoms placed in molecules located in different chains.

The sum of the observed changes in H1-H1 and H1-H1' distances accounts exactly for the change in c lattice parameter (0.19 Å; see the R1+R2 column in Table 16). This parameter increases due to the increase of the distance between the deltic acid molecules within the chains. The decrease in the interchain distance is the responsible of the change in both a and b lattice parameters. Accompanying the decrease of the interchain distance (nearly along [110] direction), originated by the application of pressure along U_{min}^L , there is also a decrease of the distances between the chains placed perpendicularly to the first ones, and a large increase of the distances between the molecules within the chains leading to the increase of c lattice parameter. The normal behavior could be the simultaneous increase of the distance between the chains along U_{min}^T , and the increase of the distance between

molecules along c direction. However, the first distances decrease leading to the NPRs.

4.3.4.b Squaric acid

4.3.4.b.i Negative Poisson ratio

The 3D representations of the most important elastic properties of the squaric acid are shown in Fig. 7. Similarly, the representation of the surfaces of minimum, average and maximum Poisson ratios for squaric acid are displayed in Fig. 5.B, where it is shown that solid squaric acid is, as deltic acid, an NPR material. The value of the lowest Poisson ratio is also small (-0.12 , see Table 13).

4.3.4.b.ii Lattice parameters and X-ray powder diffraction pattern as a function of the applied pressure

The lattice parameters and volumes obtained for twelve different applied pressures along the direction of the minimum Poisson ratio are reported in Table 17. The corresponding X-ray powder diffraction patterns of the squaric acid at six different pressures are displayed in Fig. 8. The displacements of the main reflections in the X-Ray pattern due to the effect of the applied pressures are shown in Table 18.

Figure 7. Elastic properties of the squaric acid as a function of the orientation of the applied strain: (A) Compressibility; (B) Young modulus; (C) Maximum shear modulus; (D) Maximum Poisson ratio.

Table 17. Computed lattice parameters and volumes in the squaric acid at different applied pressures directed along the direction of minimum Poisson ratio.

P (GPa)	a (Å)	b (Å)	c (Å)	γ (Å)	Vol. (Å ³)
-0.3378	6.1122	6.1686	5.2393	89.81	197.5427
-0.1754	6.1074	6.1322	5.2511	89.95	196.6633
0.0	6.1039	6.0902	5.2647	90.12	195.7094
0.1647	6.1006	6.0587	5.2660	90.19	194.6367
0.3407	6.0964	6.0250	5.2763	90.28	193.7983
0.4964	6.0926	5.9938	5.2912	90.37	193.2206
0.6700	6.0892	5.9627	5.3007	90.45	192.4549
0.8362	6.0847	5.9326	5.3118	90.56	191.7359
1.0011	6.0819	5.9029	5.3209	90.68	191.0114
1.3343	6.0767	5.8504	5.3376	90.86	189.7386
1.6665	6.0737	5.8001	5.3562	91.02	188.6605
2.0097	6.0680	5.7533	5.3738	91.19	187.5652

Figure 8. X-ray powder diffraction pattern for the squaric acid as a function of the applied pressure.

Table 18. Displacement of some of the most intense reflections in the X-ray powder diffraction pattern for the squaric acid. The 2θ and d values associated to the X-ray powder diffraction pattern for the squaric acid at zero pressure are also given. The values of 2θ and d associated with each reflection [hkl] are given in degrees and Å, respectively.

[hkl]	$2\theta(0)$	$d(0)$	$\Delta(0.0-0.341)$	$\Delta(0.341-0.670)$	$\Delta(0.670-1.001)$	$\Delta(1.001-1.334)$	$\Delta(1.334-1.667)$	$\Delta(1.667-2.010)$
[213]	62.936	1.4756	0.000	0.003	0.002	0.001	0.002	0.002
[1-2-3]	62.929	1.4758	-0.001	0.001	0.001	0.000	0.001	0.001
[004]	71.642	1.3162	0.003	0.006	0.005	0.004	0.005	0.004
[2-11]	37.055	2.4241	-0.003	-0.001	-0.001	-0.001	0.000	-0.001
[121]	37.148	2.4183	-0.018	-0.016	-0.017	-0.015	-0.014	-0.014
[211]	37.107	2.4209	-0.007	-0.006	-0.007	-0.006	-0.005	-0.006
[1-2-1]	37.096	2.4216	-0.014	-0.012	-0.011	-0.010	-0.010	-0.009
[011]	22.303	3.9828	-0.014	-0.008	-0.009	-0.009	-0.008	-0.008
[101]	22.281	3.9867	0.003	0.008	0.006	0.006	0.007	0.006
[002]	34.031	2.6323	0.006	0.012	0.010	0.008	0.009	0.009

Table 19. Selected bond distances (in Å) in the squaric acid at different applied pressures directed along the direction of minimum Poisson ratio. The last row in the table (Δ) gives the variation of the bond distances at P=2.010 GPa with respect to those at P=0 GPa.

P (GPa)	O1-C2 (R1)	O2-C3 (R3)	C1*-C1**	C2-O1' (R2)	C3-O2' (R4)	R1+R2	R3+R4
-0.338	2.509	2.484	5.239	3.664	3.630	6.173	6.114
-0.175	2.508	2.486	5.251	3.629	3.623	6.137	6.109
0.0	2.506	2.487	5.265	3.588	3.619	6.094	6.106
0.165	2.504	2.489	5.266	3.577	3.613	6.081	6.102
0.341	2.502	2.490	5.276	3.525	3.608	6.027	6.098
0.496	2.500	2.492	5.291	3.495	3.602	5.995	6.094
0.670	2.499	2.494	5.301	3.465	3.597	5.964	6.091
0.836	2.498	2.496	5.312	3.436	3.590	5.934	6.086
1.001	2.497	2.497	5.321	3.407	3.586	5.904	6.083
1.334	2.494	2.500	5.338	3.536	3.578	6.03	6.078
1.667	2.492	2.503	5.356	3.309	3.572	5.801	6.075
2.010	2.489	2.506	5.374	3.264	3.563	5.753	6.069
Δ	-0.017	+0.019	+0.109	-0.324	-0.056	-0.341	-0.037

As expected, the volume decreases as the applied pressure increases as it does the length along U_{min}^L (the [010] crystallographic direction). However, the length along the transverse direction (a axis) decreases instead of increasing, that is, the material shrinks laterally when compressed. For negative pressures the material laterally expands when stretched. The parameter d of the main, [002], and [004] reflections increases because the value of the c lattice parameter increases. The d value associated to [101] also increases. However, the d values of most reflections decrease as a consequence of the applied pressures and the associated lowering of the a and b lattice parameters

4.3.4.b.iii Crystal structure deformation

The values of a series of selected interatomic distances in the structure of the squaric acid are reported in Table 19. The bond distances between the atoms within a squaric acid molecule in the crystal, change only very slightly under the applied pressures. This may be appreciated, for example, from the fact that the variations of the O1-C2 and O2-C3 distances, shown in the first two columns of Table 19, are small. The main changes arising from the application of pressure are the increase of the distance between the squaric acid molecule units in a sheet along b direction and, to a much smaller extent, along a direction (see the C2-O1' and C3-O2' distances in Table 19 and Fig. S2 of the Supplementary Information; the atoms marked with a prime belong to contiguous squaric acid molecules placed in the b and a directions, respectively), and the increase of the distance between sheets (see C1*-C1** distance in Table 19 and Fig. S2 of the Supplementary Information; the C1* and C1** atoms are located in two different sheets, equidistant to the intermediate sheet). The C1*-C1** distance in Table 19 coincides with the c lattice parameter. The interlayer distance between two continuous layers or sheets in the structure of the squaric acid is just $R(C1*-C1**)/2$.

The observed changes in O1-C2 and C2-O1' distances account for the change in b lattice parameter (-0.34 Å; see the R1+R2 column in Table 19). Similarly, the observed changes in O2-C3 and C3-O2' distances account for the change in a lattice parameter (-0.04 Å; see the R3+R4 column in Table

19). The increase in the distance between the sheets is the responsible of the change in c lattice parameter ($+0.11$ Å). The change in the distance between the layers (c direction), held together only by weak van der Waals forces, serves to adjust the structure when structural variations appear in the perpendicular {110} plane due to the effect of the applied pressures. Accompanied with the decrease of the distance between the molecules along b direction, there is also a decrease in the distances between molecules placed perpendicularly to the first ones within the sheets leading to the negative Poisson ratios.

4.3.4.c Croconic acid

4.3.4.c.i Negative Poisson ratio

The representations of the mechanical properties of the croconic acid as a function of the strain orientation are shown in Fig. 9, and the surfaces of minimum, average and maximum Poisson ratios are displayed in Fig. 5.C. As shown in the last Figure, croconic acid is also a negative Poisson ratio material.

Figure 9. Elastic properties of the croconic acid as a function of the orientation of the applied strain: (A) Compressibility; (B) Young modulus; (C) Maximum shear modulus; (D) Maximum Poisson ratio.

4.3.4.c.ii Lattice parameters and X-ray powder diffraction pattern as a function of the applied pressure. Negative linear compressibility

The lattice parameters and volumes obtained for twelve different applied pressures along the direction of the minimum Poisson ratio are reported in Table 20. The corresponding X-ray powder diffraction patterns at six different pressures are displayed in Fig. 10. The displacements of the main reflections in the X-Ray powder pattern due to the effect of the applied pressures are collected in Table 21.

Table 20. Computed lattice parameters and volumes in the croconic acid at different applied pressures directed along the direction of minimum Poisson ratio.

P (GPa)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Vol. (Å ³)
-0.4614	9.2071	4.8989	10.8892	491.1530
-0.2298	8.8744	5.0522	10.8519	486.5442
0.0	8.7088	5.0983	10.7922	479.1681
0.1160	8.6861	5.1002	10.7824	477.6604
0.2507	8.5970	5.1220	10.7584	473.7339
0.3716	8.5027	5.1660	10.7426	471.8628
0.4716	8.3908	5.2514	10.7243	472.5482
0.7053	8.1660	5.4137	10.6918	472.6632
0.7759	8.0054	5.5467	10.6798	474.2211
0.9484	7.7024	5.8565	10.6631	480.9998
1.0598	5.9567	7.9981	10.5093	500.6842
1.1801	5.8806	8.0814	10.4862	498.3407

The system is compressed along U_{min}^L (0.61, 0.00, 0.80) for positive pressures from P=0.0 GPa to P=0.395 GPa. For larger pressures the volume increases, that is croconic acid exhibits the negative linear compressibility phenomenon. As the pressure increases from 0.0 GPa, the length along U_{min}^L decreases (as it can be observed in Table 20, the *a* and *c* lattice parameters decrease). However, the length along the transverse direction also decreases instead of increasing, that is, the material shrinks laterally when compressed. For negative pressures the material laterally expands when stretched. Therefore, croconic acid is an NPR material, which under the effect of pressure exhibits NLC. A phase transition occurs at pressures of about 1.0 GPa, where the new most stable phase has also *Pca21* space symmetry. The *a* and *b* lattice parameters of the new phase (Table 20) are very different from those of the most stable phase at 0.0 GPa. The bond distances in the new phase at 1.060 GPa are very similar to those from the structure at 0.948 GPa, although the C2-C3 and C4-C5 bond lengths are reduced by about 0.01 Å (stronger single bonds). The C2-O2 length becomes 0.01 Å larger and the O2-H2 one 0.02 Å shorter. The most significant change is for the O2-H2···O4' hydrogen bond, for which the H2···O4' distance increases about 0.10 Å.

The parameter *d* of the main reflection, [210], and other additional reflections decrease as expected from the increase of the applied external pressure. The [201] reflection has the

larger negative variation of parameter *d*, because it maps the simultaneous decrease of both *a* and *c* lattice parameters. The decrease of [002] weak reflection maps directly the decrease of *c* lattice parameter. There are also many reflections displacing towards larger *d* (for example, [110], [120], [022], and [010]). The weak reflection [010] shows the largest displacement towards smaller 2θ because it maps directly the increase of the *b* lattice parameter.

As shown in Fig. 10, the X-ray diffraction patterns of the croconic acid become completely different at pressures larger than about 1.0 GPa applied along U_{min}^L direction to those from lower pressures due to the occurrence of the phase transition.

4.3.4.c.iii Crystal structure deformation

The interatomic distances within the croconic acid molecules in the crystal, change only very slightly under the applied pressures because, for example, the variations of the O5-H1, C1-C2 and C2-C3 distances are small (Table 22). The main changes arising from the application of pressure are: (i) the decrease of the distance between the croconic acid molecule units in a folded sheet along *a* direction, and to a much smaller extent, along *c* direction (see the C3-O3' and H1-O5' distances in Table 22, respectively, where the atoms marked with a prime belong to contiguous croconic acid molecules placed in the *a* and *c* directions, respectively), and (ii) the increase of the distance between sheets (O5-O5* distance in Table 22, where the O5 and O5* atoms are located in two different sheets, see Fig. S3 in the Supplementary Information).

The change in O5-O5* distance accounts exactly for the change in *b* lattice parameter (+0.07 Å). Similarly, the observed changes in O5-H1 and H1-O5' distances account exactly for the half of change in a lattice parameter (−0.049 Å). Finally, the changes in C3-O3' reflect the variation of a lattice parameter. Accompanied with the decrease of the distance between the molecules along U_{min}^L direction originated by the application of pressure along U_{min}^L , there is also a decrease in the distances between molecules placed perpendicularly to the first ones within the sheets which leads to an NPR.

For applied pressures larger than 0.372 GPa, the distance between the sheets increases enormously (0.69 Å, between 0.0948 and 0.372 GPa, see Δ' in Table 22). The decrease of the distance between croconic acid molecules along a direction is also very large (−0.44 Å). However, the extreme increase of the inter-sheet distance (or *b* lattice parameter) is not counter balanced by the decrease of the inter-molecule distances in {101} plane (or *a* and *c* lattice parameters). This is the fundamental reason for the increase in volume of the unit cell and, consequently, for the negative linear compressibility of the croconic acid at pressures larger than about 0.4 GPa.

Figure. 10. X-ray powder diffraction pattern for the croconic acid as a function of the applied pressure.

Table 21. Displacement of some of the most intense reflections in the X-ray powder diffraction pattern for the croconic acid. The 2θ and d values of associated to the X-ray powder diffraction pattern for the croconic acid at zero pressure are also given. The values and increments of 2θ and d associated with each reflection [hkl] are given in degrees and Å, respectively.

[hkl]	$2\theta(0)$	$d(0)$	$\Delta(0.0-0.251)$	$\Delta(0.251-0.472)$	$\Delta(0.472-0.705)$	$\Delta(0.705-0.948)$
[010]	17.380	5.0983	0.024	0.129	0.162	0.443
[110]	20.166	4.3998	0.000	0.051	0.061	0.150
[002]	16.414	5.3960	-0.017	-0.017	-0.016	-0.014
[211]	28.168	3.1655	-0.017	-0.014	-0.017	-0.038
[514]	66.413	1.4065	-0.013	-0.021	-0.023	-0.049
[312]	39.397	2.2853	-0.018	-0.025	-0.029	-0.062
[324]	59.101	1.5619	-0.005	0.001	0.001	0.005
[114]	39.134	2.3000	-0.005	0.002	0.003	0.015
[212]	31.679	2.8222	-0.014	-0.012	-0.014	-0.028
[022]	39.048	2.3049	0.007	0.046	0.057	0.152
[120]	36.704	2.4465	0.008	0.051	0.063	0.168
[113]	32.114	2.7850	-0.005	0.007	0.010	0.030
[014]	37.691	2.3847	-0.003	0.007	0.009	0.030
[111]	21.797	4.0742	-0.002	0.039	0.046	0.114
[204]	39.251	2.2935	-0.013	-0.021	-0.023	-0.045
[201]	21.994	4.0381	-0.046	-0.085	-0.093	-0.192
[310]	35.559	2.5227	-0.022	-0.032	-0.037	-0.081
[210]	26.905	3.3111	-0.019	-0.015	-0.018	-0.042

Table 22. Selected bond distances (in Å) in the croconic acid at different applied pressures directed along the direction of minimum Poisson ratio. In the table, Δ is the variation of the bond distances at $P=0.372$ GPa with respect to those at $P=0$ GPa and Δ' is the variation of the bond distances at $P=0.948$ GPa with respect to those at $P=0.372$ GPa.

P (GPa)	O5-H1 (R1)	C1-C2	C2-C3	O5-O5*	H1-O5' (R2)	C3-O3'	R1+R2
-0.461	3.929	1.420	1.477	4.899	1.527	5.301	5.456
-0.230	3.925	1.419	1.477	5.052	1.510	5.116	5.435
0.0	3.916	1.420	1.478	5.098	1.488	5.024	5.404
0.116	3.917	1.420	1.477	5.100	1.483	5.011	5.400
0.251	3.920	1.420	1.477	5.122	1.468	4.961	5.388
0.372	3.910	1.421	1.478	5.166	1.470	4.909	5.380
0.472	3.912	1.420	1.477	5.251	1.458	4.845	5.370
0.705	3.901	1.421	1.478	5.414	1.453	4.717	5.354
0.776	3.898	1.421	1.478	5.547	1.450	4.632	5.348
0.948	3.888	1.420	1.476	5.857	1.454	4.470	5.342
1.060	3.843	1.418	1.466	7.998	1.447	3.294	5.290
1.180	3.839	1.418	1.466	8.081	1.446	3.228	5.285
Δ	-0.006	+0.001	+0.000	+0.068	-0.018	-0.120	-0.024
Δ'	-0.022	+0.000	-0.001	+0.691	-0.016	-0.439	-0.038

Table 23. Lattice parameters of the pressure induced phase.

Parameter	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (deg)	β (deg)	γ (deg)	Vol. (Å ³)	Dens. (g·cm ⁻³)
DFT (P=1.060 GPa) ^a	5.9567	7.9981	10.5093	90	90	90	500.6842	1.885
DFT (P=1.180 GPa) ^b	5.8806	8.0814	10.4862	90	90	90	498.3407	1.893

^a **P**=(1.363, 0.004, 1.812) GPa; ^b **P**=(1.530, 0.008, 2.002)

4.3.4.c.iv Pressure induced phase

As shown in the previous section 4.3.4.c.ii, the croconic acid undergoes a pressure induced phase transition under the effect of an applied pressure directed along the (0.61, 0.00, 0.80) direction. The crystal space symmetry of this phase is orthorhombic, space group *Pca21*. The computed lattice parameters, cell volume and density associated to this phase for two different applied pressures is shown in Table 23. Furthermore, images of the corresponding unit cell from [100] and [010] directions are displayed in Fig. 11.

Figure. 11. Views of the unit cell of the pressure induced phase of the croconic acid from [100] (A) and [010] (B) directions.

5. Concluding remarks

- The structural and mechanical properties of three cyclic oxocarbon acids were determined by using theoretical solid-state methods based in Density Functional Theory using planewaves and pseudopotentials. A very large kinetic cut-off of 950 eV and dense k-point meshes comprising 75-90 k-points were used in order to obtain realistic descriptions of these acids. The calculated lattice parameters, bond distances and angles, and X-ray powder diffraction patterns of these materials were in excellent agreement with the corresponding experimental information. The differences between the calculated and experimental cell volumes and densities were 1.3%, 1.6% and 2.5% for the deltic, squaric and croconic acids, respectively.
- The analysis of the computed stiffness tensors of these materials showed that their crystal structures are mechanically stable since they satisfy the Born mechanical

stability conditions. Besides, a large number of relevant mechanical properties of these materials were reported including the bulk modulus and their pressure derivatives, the shear and Young moduli, the Poisson ratio, ductility and hardness indices and mechanical anisotropy measures. Since the mechanical properties of these materials have not been measured experimentally, their values were predicted. The deltic, squaric and croconic acids are highly anisotropic materials characterized by low hardness and relatively low bulk moduli. Their mechanical anisotropy is a direct consequence of their crystal structures since the chemical bonding between the atoms comprising the corresponding unit cells is very distinct for the different directions.

- These three materials display small negative Poisson ratios as shown from the analysis of the surfaces of minimum Poisson ratio. The computed values of the minimum Poisson ratio were -0.09, -0.12 and -0.13, respectively. Furthermore, their optimized structures under the effect of pressures applied in the direction of minimum Poisson ratio were determined. The study of these structures revealed that croconic acid displays the phenomenon of negative linear compressibility for applied pressures larger than ~0.4 GPa, and undergoes a pressure induced phase transition for applied pressures larger than ~1.0 GPa. Therefore, the croconic acid, which has been discovered to be a ferroelectric material [19] at room temperature, is shown to have also a very attractive mechanical behavior.
- The three materials considered in this work are molecular crystals whose structures are characterized by structural elements as chains and sheets which are not directly bonded but held together by weak van der Waals forces. The weak bonding between these elements is able to accommodate the structural variations originated by the application of pressure, but the resulting structural deformations appear to be counterintuitive and lead to the anomalous mechanical behavior of these materials.
- It may be concluded that many other simple organic materials are likely to display an anomalous mechanical behavior. Due to the wide range of structures present in natural organic minerals and the great versatility of organic synthesis, this feature points to the need of performing systematic studies of the mechanical properties of organic materials. Such studies could reveal the existence of a large number of NPR and NLC organic materials with structures closely related to those of the oxocarbon acids. This conclusion is important because the materials displaying these anomalous mechanical properties have

found a very wide range of useful applications and these properties have rarely been studied for organic materials.

Supplementary Information

Supplementary Information associated with this article contain three Figures showing the atom labelling convention employed in this paper.

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