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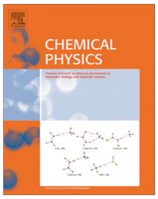

Ferroelectric behaviour in solid croconic acid using neutron scattering and first-principles density functional theory

S. Mukhopadhyay [a,d,*], M.J. Gutmann [a], M. Jura [a], D.B. Jochym [b], M. Jimenez-Ruiz [c], S. Sturniolo [b], K. Refson [b], F. Fernandez-Alonso [a,e]

[a] *ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom*
[b] *Scientific Computing Department, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom*
[c] *Institut Laue Langevin, 6 rue Jules Horowitz 38042, Grenoble Cedex 9, France*
[d] *Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, United Kingdom*
[e] *Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom*

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ABSTRACT

A combination of neutron-scattering experiments and first-principles calculations using density-functional theory have been performed to explore the structural and dynamical properties of the single-component organic ferroelectric croconic acid. Neutron diffraction and spectroscopy have been used to determine the location and underlying vibrational motions of the hydrogen ions within the crystalline lattice, respectively. On the computational front we find that dispersion corrections within the generalised-gradient approximation are essential to obtain a satisfactory crystal structure for this organic solid. Two distinct types of hydrogen ions in the crystal also have been identified, located at the 'hinge' and 'terrace' positions of a pleated, accordion-like structure. Phonon calculations and simulated neutron spectra show that the prominent doublet observed at ca. 1000 cm^{-1} arises from out-of-plane motions associated with these two types of hydrogen ions. Calculated Born-effective-charge tensors yield an anomalously high dynamic charge centered on the hydrogen ions at the hinges, a finding which serves to identify the primary motif underpinning ferroelectric behaviour in this novel material.

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1. Introduction

Croconic acid (molecular formula $C_5O_5H_2$, hereafter CA) is the first-known example of a single-component organic solid exhibiting above-room-temperature ferroelectricity in its crystalline form [1]. In spite of the relatively small size of this cyclic compound, this molecular crystal also displays the highest-known bulk polarization for a carbon-based material ($P \sim 20\ \mu\mathrm{C\ cm}^{-2}$), and its performance is comparable to the best inorganic ferroelectrics such as barium titanate ($BaTiO_3$) [2]. As such, it offers the potential for important technological applications in low cost, metal-free organic electronic and non-linear-optical devices such as non-volatile memories, capacitors, and piezoelectrics. Since previous observations of ferroelectric behaviour in organic materials had been restricted to multicomponent materials relying on charge transfer between chemically distinct donor–acceptor pairs [3,4], atomistic studies of crystalline CA become a necessary prerequisite in order to understand the physical mechanism (s) underpinning the emergence and persistence of a large bulk electric polarisation over a remarkably wide temperature range ($T = 0$–500 K).

By comparison with other well-known inorganic ferroelectrics such as the aforementioned $BaTiO_3$ or KH_2PO_4 [2], the properties of solid CA remain largely unexplored. Its room temperature structure has been studied using X-ray diffraction (XRD) following its first isolation at the beginning of this century [5], yet these as well as subsequent X-ray studies [1] were unable to locate the hydrogen ions uniquely. Kolev et al. [6] have reported vibrational assignments of matrix-isolated CA using polarization-sensitive infrared (IR) spectroscopy complemented by single-molecule ab initio calculations. In this case, hydrogen bonding between adjacent hydroxyl (OH) groups in CA is intrinsically of an intramolecular nature, with little preference for moderate-to-strong intermolecular interactions with the surrounding medium.

In a more recent study, Seliger et al. [7] have used nuclear magnetic resonance (NMR) to probe the chemical environment around the pentagonal carbon ring. Both ^{13}C and ^{17}O nuclear-quadrupole-resonance spectra of crystalline CA reveal the presence of five non-equivalent sites within a given CA molecule, and analysis of the dipolar structure of the ^{17}O data is consistent with an OH distance of 0.99 ± 0.01 Å. These authors also report significant deviations from the expected correlation between

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* Corresponding author at: ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom. Tel.: +44 012348190.
E-mail address: sanghamitra.mukhopadhyay@stfc.ac.uk (S. Mukhopadhyay).

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quadrupole coupling constants and O…O distances, an observation tentatively ascribed to strong long-range ferroelectric ordering leading to a significant redistribution of electron density in the hydrogen bonds.

From X-ray photoelectron spectroscopy experiments on CA thin films, Bisti et al. [8] have shown how the formation of a hydrogen-bonded network in solid CA translates into measurable changes to O-1s core-level line shapes. On the basis of first-principles calculations, they conclude that the main differences in the electronic density of states between the isolated molecule and the crystal occur in the range 6–12 eV. In this region, solid CA displays a characteristic doublet which is absent in the isolated molecule. This spectral feature is characterized by significant contributions from carbon, oxygen, as well as hydrogen.

To fill the above gap in our present knowledge and understanding of solid CA, we have performed a detailed characterization of this material using a combination of neutron-scattering experiments and first-principles calculations within the framework of density-functional theory (DFT). As a natural continuation of a recent study [9], the present work explores in detail the range of validity of commonly used DFT functionals in order to arrive at an atomistic description of this material consistent with neutron-diffraction (ND) and inelastic-neutron-scattering (INS) data. Using an experimentally validated computational model, we calculate Born-effective-charge tensors and response functions so as to identify which ionic motions are primarily responsible for the observed ferroelectric response in crystalline CA.

2. Methodology

Commercially available powders (Sigma Aldrich No. 391700, 98% purity) were used to grow single-crystal CA specimens under an inert helium atmosphere following the recipe given by Braga et al. [5]. Repeated crystallization runs were carried out via slow evaporation over a period of several weeks to obtain well-defined, millimeter-sized platelets.

Single-crystal ND measurements were performed on the SXD [10] diffractometer at the ISIS Pulsed Neutron and Muon Source and INS spectra were measured at T = 5 K on the recently commissioned IN1-Lagrange neutron spectrometer at the Institute Laue Langevin (France) [11]. For the INS measurements, a single-crystal specimen of mass 100 mg was ground to a fine powder and kept under a helium atmosphere at all times in the absence of light so as to prevent unwanted oxidation and decomposition. On IN1-Lagrange, an incident-energy range of 216–3500 cm^{-1} was achieved by means of a doubly focused Cu (220) monochromator reflection, giving a high flux and a moderate instrumental resolution of $\Delta E/E \sim 3\%$, where E denotes energy transfer. In this configuration, the accessible E range was 180–3465 cm^{-1} with a fixed final energy of 36 cm^{-1}.

Electronic-structure calculations were performed with the CASTEP code [12]. All calculations used optimized norm-conserving pseudopotentials [13] generated with the Perdew–Burke–Ernzerhof (PBE) [14] functional within the generalized-gradient approximation (GGA). Dispersion corrections to the PBE functional (PBE + D) were included following the methodology of Tkatchenko and Scheffler [15,16]. A plane-wave cutoff of 800 eV and a Brillouin-zone (BZ) sampling of $6 \times 6 \times 3$ k-points (18 points when symmetry-reduced) were found to be sufficient to converge energy and atomic forces below 9.6×10^{-3} eV/ion and 1.0×10^{-3} eV/Å, respectively. Self-consistent single-point energy minimizations used a tolerance of 2.5×10^{-9} eV. Full-geometry optimizations were performed with a force tolerance of 1.0×10^{-3} eV/Å using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm.

Phonon frequencies and eigenvectors of the resulting minimum-energy structures were calculated via diagonalization of dynamical matrices computed using density-functional perturbation theory (DFPT) and linear-response methods [17], or via direct calculation of finite displacements. In CASTEP, use of DFPT methods with dispersion-corrected functionals is not currently implemented and, therefore, only the PBE functional was used in these calculations. These correction terms have been included in the finite-displacement calculations. Using DFPT, phonon dispersion calculations were performed on a total of 8-q points followed by interpolation to obtain a total of 209 q-points within the BZ. For finite-displacement calculations, we used a $2 \times 2 \times 2$ supercell matrix interpolated to 32 q-points in the BZ. INS spectra were obtained from calculated eigenvectors and eigenenergies using the ACLIMAX program [18,19]. These synthetic INS spectra included fundamentals as well as overtone and combination bands up to tenth order.

3. Results and discussion

CA is a molecular crystal where pentagonal units are arranged into planar sheets having a width of about two molecular units on the a-b plane and extending indefinitely along the crystallographic c-axis. The net result from this packing arrangement is a characteristic zig-zag structure, as shown in Fig. 1. This crystal-lattice topology represents a significant departure from the strictly layered structure of its closely related molecular cousin squaric acid ($C_4O_4H_2$, hereafter SA). SA is antiferroelectric up to 373 K, then a paraelectric. In its antiferroelectric phase, there is a complete cancellation of electric dipoles across layers, a situation which cannot be fulfilled in crystalline CA. In light of these geometrical considerations, it is quite remarkable that switching the molecular building block from a four- to a five-membered carbon ring with essentially the same chemical functionality leads to such remarkable changes to both lattice structure as well as bulk electrical response, i.e., from an antiferroelectric material to a high-performance, above-room-temperature ferroelectric.

To gain further insight into the location of the hydrogen ions in solid CA, our low-temperature ND data were refined within the non-centrosymmetric space group $Pca2_1$. A summary of the most prominent structural findings relevant to the present work is given in Table 1. These data indicate that each molecular unit contains

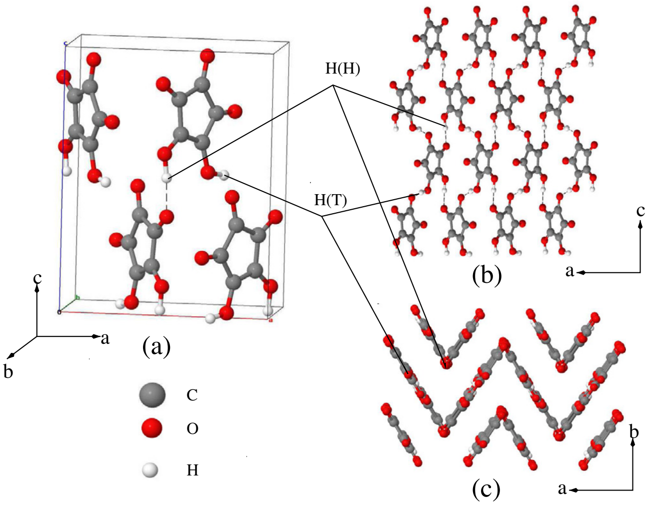

Fig. 1. Crystal structure of CA from single-crystal ND experiments: (a) unit cell; (b) along the b axis; and (c) along c. For further details, see the text.

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