

Prediction of properties of organic ferroelectrics and piezoelectrics by first-principles calculation

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Among hydrogen-bonded systems consisting of small organic molecules, some shows ferroelectricity or antiferroelectricity [1]. They contain neither toxic nor rare elements and are expected as environmentally friendly materials. Spontaneous polarization, which is one of the most important properties for the ferroelectrics, can be predicted by electronic-structure calculations together with the Berry phase theory. We calculated polarization values for seven representative hydrogen-bonded ferroelectrics (croconic acid (CRCA), 2-phenylmalondialdehyde (PhMDA), 3-hydroxyphenalenone (HPLN), cyclobutene-1,2-dicarboxylic acid (CBDC), 2-methylbenzimidazole (MBI), 5,6-dichloro-2-methylbenzimidazole (DC-MBI), and 3-anilinoacrolein anil (ALAA)) and the obtained results are in excellent agreement with the experimental results [2]. These calculations were performed using experimentally obtained crystal structures with only hydrogen positions computationally optimized. It is well known that hydrogen positions are difficult to accurately determine by x-ray diffraction analysis. Accurate experimental structure data are not always available. In such cases, computational optimizations for all of the crystal structure parameters are necessary. Nonetheless, the van der Waals interaction, which is often crucial in organic solids, cannot be accurately described by the local density approximation (LDA) or the generalized gradient approxima-

tion (GGA). In the present study, we apply van der Waals density-functional theory (vdW-DFT) calculations to reproduce crystal structure parameters of the seven compounds mentioned above. For the vdW-DFT method, we used two forms: the van der Waals density-functional consistent-exchange (cx) method [3] and the revised Vydrov–van Voorhis (rVV10) method [4]. Calculations were performed using the QMAS code.

Figure 1 shows the deviations of the calculated structure parameters (lattice parameters a , b , and c , and hydrogen-bond length d , namely, the $O\cdots O$ or $N\cdots N$ distance) (a) from room-temperature experimental results and (b) from 0-K extrapolated values, as well as (c) their averages and bounds [5]. The calculated results obtained by the LDA and the PBE version of the GGA are also shown. The experimental structures are at room temperature, whereas the calculation results correspond to 0 K. Unfortunately, only a limited number of low-temperature structures have been reported and the 0-K values were extrapolated using them to prepare Fig. 1 (b). The vdW-DFT results show good agreement with experimental results, implying that an important step for the computational materials design of organic ferroelectrics has been achieved. Spontaneous polarization values obtained by the vdW-DFT calculations are again in good agreement with the experimental results. The success in reproducing the structure parame-

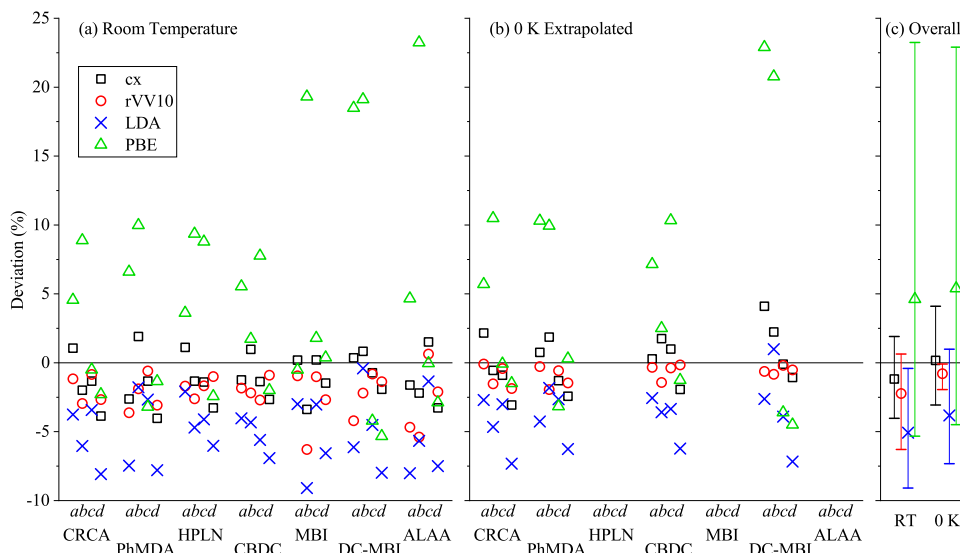


Figure 1: Deviations of calculated structure parameters (a) from room-temperature experimental results and (b) from 0-K extrapolated values, as well as (c) their averages and bounds (S. Ishibashi, S. Horiuchi, and R. Kumai, “Hydrogen-bonded single-component organic ferroelectrics revisited by van der Waals density-functional theory calculations”, *Phys. Rev. Mater.* **5**, 094409 (2021), DOI: 10.1103/PhysRevMaterials.5.094409).

ters also enables the simulation of electromechanical responses. Direct and converse piezoelectric coefficients are evaluated for CRCA, PhMDA and DC-MBI and the resultant values show acceptable agreement with the experimental values if possible objective factors are considered [5].

Organic antiferroelectrics also are promising. For example, their applications as high-power electrical energy storage materials are expected utilizing electric-field-induced phase changes. Usually, they consist of two or more polar subunits. For squaric acid (SQA), we have demonstrated that the polarization of the electric-field-induced phase can be estimated by proper summation of the subunit polarization vectors [6]. By applying this procedure, we have successfully predicted polarization values for the electric-field-induced phases of several organic antiferroelectrics and the obtained results are in excellent agreement with experimental results [7].

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