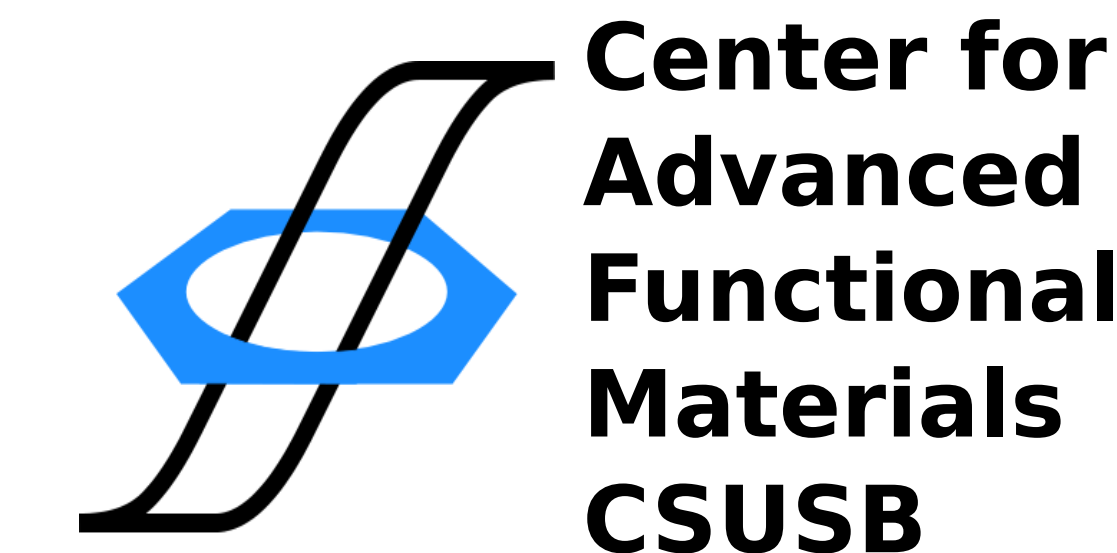




Possible mechanisms for the interconversion of polar forms for the ferroelectric diisopropylammonium halides

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Abstract

Diisopropylammonium chloride (DIPAC) and diisopropylammonium bromide (DIPAB) crystallize in the P21 phase, and have recently been shown to undergo a ferroelectric transition along the b crystallographic axis. These crystals revert to a centrosymmetric disordered phase P21/m above their Curie temperatures, 440 K and 426 K, respectively. The mechanism for the interconversion of the two polar forms during the ferroelectric transition has not yet been reported. This work explores three possible models for the polar reversal for the DIPAC system, (1) an internal double-hydrogen atom migration requiring minimal rotation of the isopropyl groups, (2) 180° rotation of one isopropyl group, or (3) halide-assisted double hydrogen atom migration. Plane wave density functional method calculations were used to model transition state structures, energies, and piezoelectric force constants for the three models. Molecular dynamics was used to look for modes of relaxation from the proposed transition state models. Overall, the 180° rotation model is predicted to have a significantly lower energy barrier than the double hydrogen transfer, while the halogen-assisted mechanism provides a valid alternative to rotation.

Introduction

The recent discoveries of ferroelectric crystalline DIPAC¹ and DIPAB² herald an underexplored area of organoferroelectrics. Ferroelectric materials are those that possess a dipole moment, which can be reversed by the application of an electric field. DIPAB in particular, is reported to have impressive experimental parameters² including a large dielectric constant, high Curie temperature, and low dielectric loss. These salts generate their polarization switching through ionic motion, so-called displacive mechanism, similar to traditional inorganic ferroelectrics such as lead zirconium titanate. The only computational model reported to date assumes the diisopropyl ammonium ion undergoes a conformational change to induce polarization reversal; this is a much smaller movement but similar in concept to the chain realignment needed for the polymeric PVDF to polarize.

Computational Methods

All calculations were performed using the Vienna *ab initio* Software Package³ (VASP) using projector augmented wave⁴ (PAW) potentials supplied by VASP; these were generated using the generalized gradient approximation (GGA) as parameterized by Perdew, Burke, and Ernzerhof⁵ (PBE) for the exchange-correlation functional. We used the default energy cutoff of 400 eV for all calculations. Geometry optimizations were run at 0 K and 0 ATM. K-point meshes were generated automatically using the Monkhorst-pack method: a 9x9x9 input matrix was used for either method for the single cell geometry optimization, and 11x11x11 for energy calculations; and a 1x1x1 input mesh was used for the supercell calculations. VASP-recommended values for generating grid points were then used for each run. Geometry convergence was assumed when energy differences reached 0.1 eV. Starting geometries for DIAC and DIAB were generated using coordinates in the Cambridge Crystallographic Database⁶, and all other input geometries (ground state and proposed transition states) were built by hand with the assistance of one or more of the following programs: Avogadro, Mercury, VESTA, as well as data manipulations using Microsoft Excel and text editors.

Calculated structures of DIPAC halides:

Structures were minimized for the known systems DIPAC and DIPAB, and for the corresponding unknown diisopropylammonium salts of fluoride (DIPAF) and iodide (DIPAI). All four showed a stable minimum monoclinic structure of approximately P21 symmetry, and the parameters in Table 1.

Table 1: Parameters for calculated unit cells for DIPAF, DIPAC, DIPAB and DIPAI (calculated) compared to experimental systems

System	a	b	c	β	volume
DIPAF	7.307	7.803	7.684	115.2	396.42
DIPAC	7.616	7.932	7.750	115.21	423.56
DIPAB	7.799	8.066	7.863	116.34	443.30
DIPAI	8.268	8.528	8.310	116.29	525.30
DIPAC _{exp}	7.615	7.932	7.750	115.2	423.56
DIPAB _{exp}	7.859	8.082	7.892	116.29	449.38

a, b and c crystallographic axes in Å; β in degrees
 α and γ are 90 deg for monoclinic cells; volume in Å³

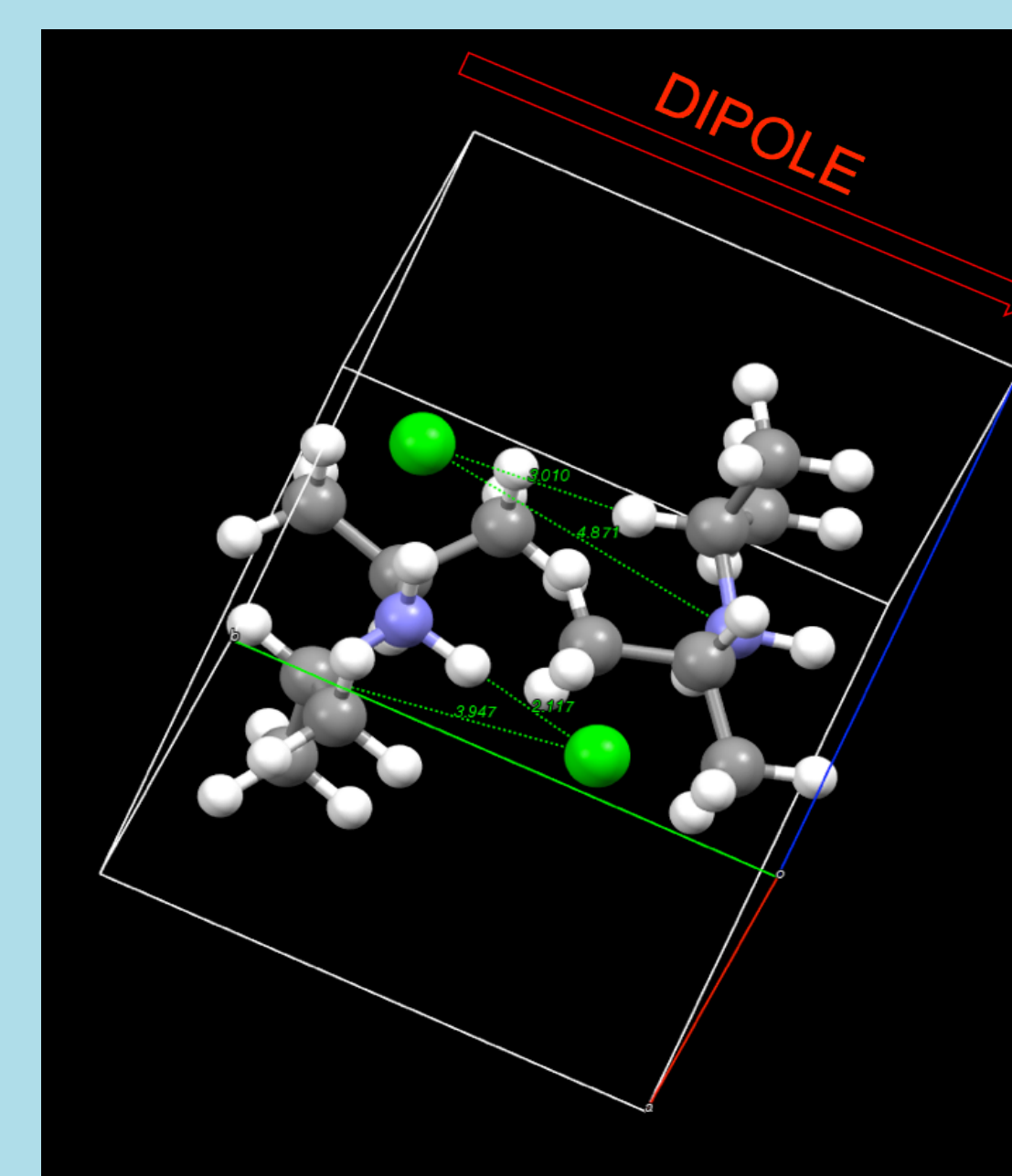
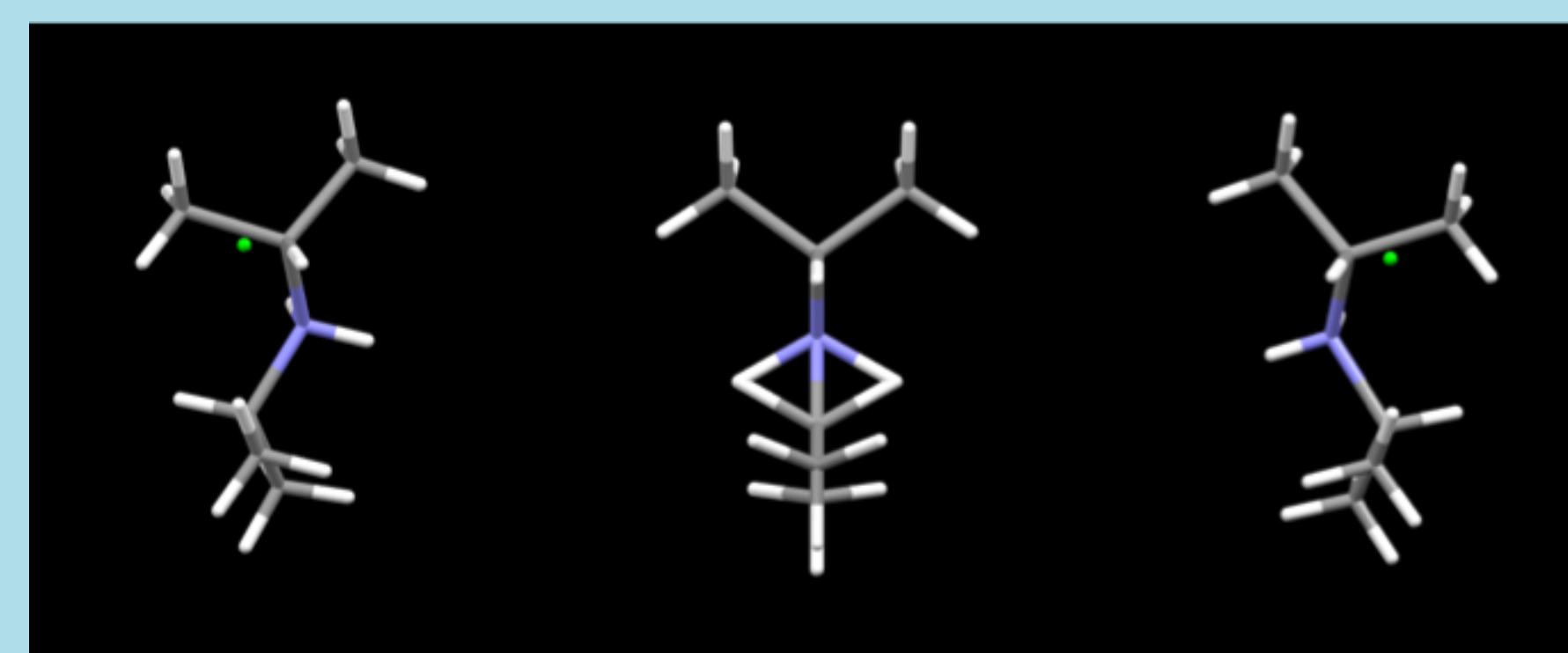
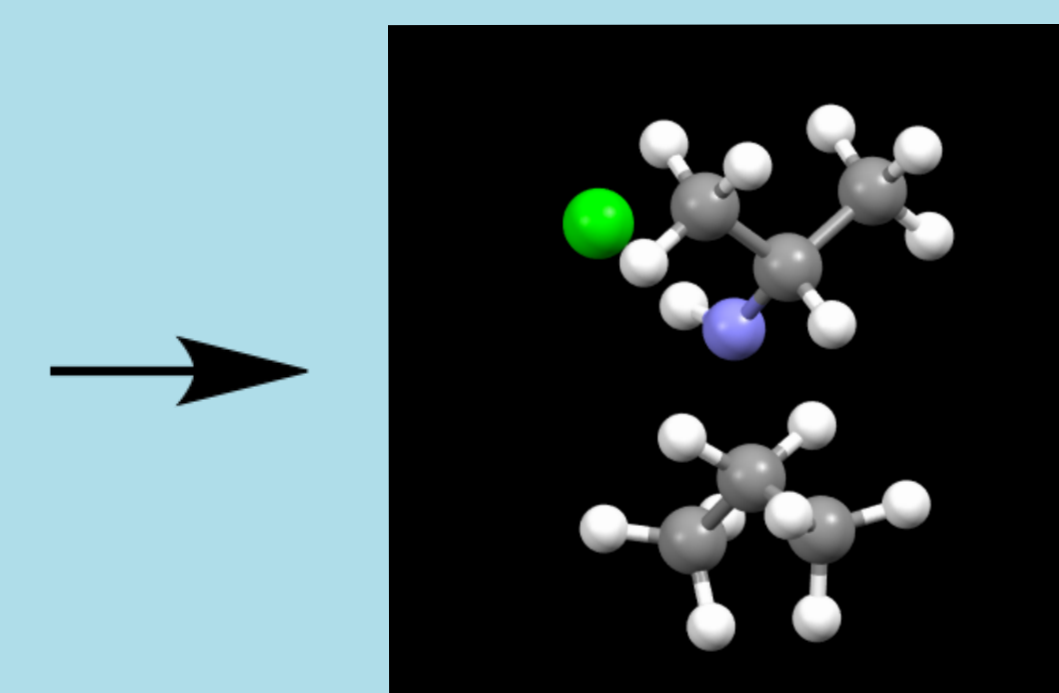


Figure 1: Unit cell of DIPAC showing the conformation and symmetry common to the four systems in Table 1. The dipole runs parallel to the b axis in the direction shown.

Transition state model 1: Double H migration

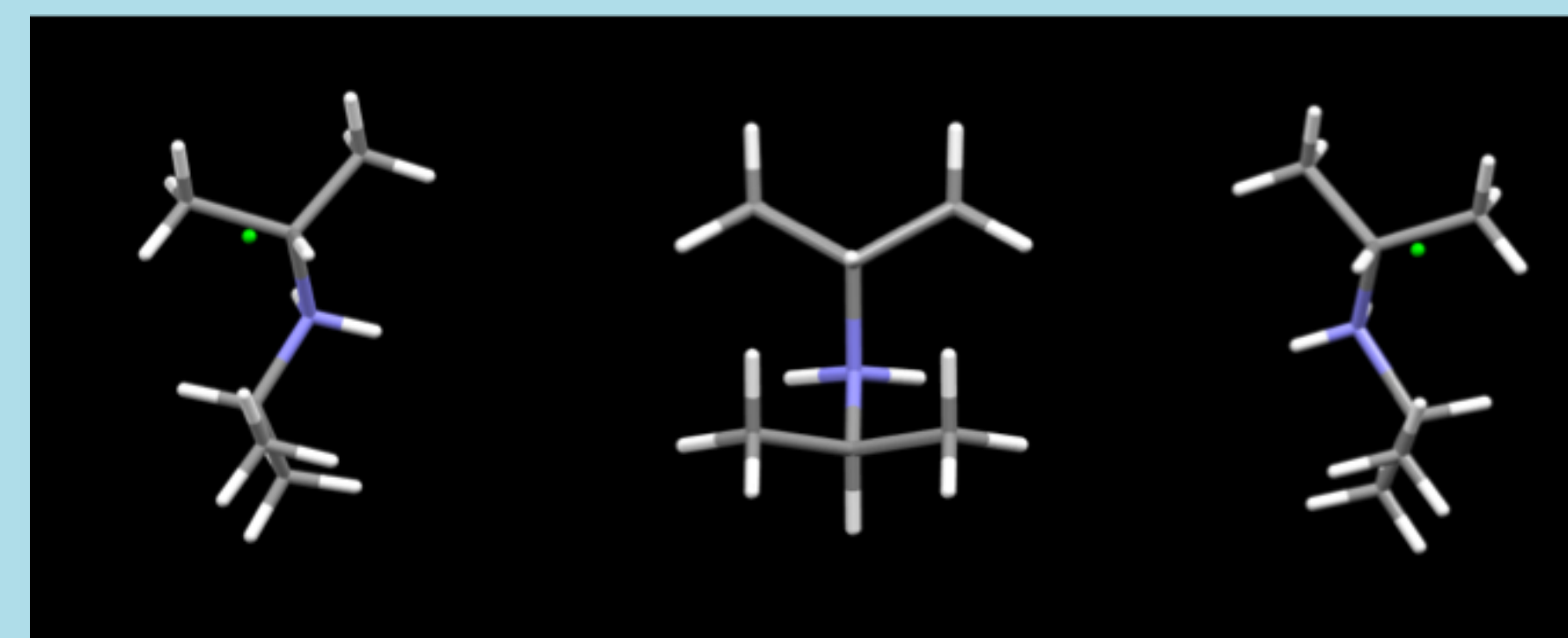


If all cells were to undergo double H migration simultaneously, the cell would expand by 0.5 Å along the c axis, and the transition would require > 750 kJ/mol activation energy

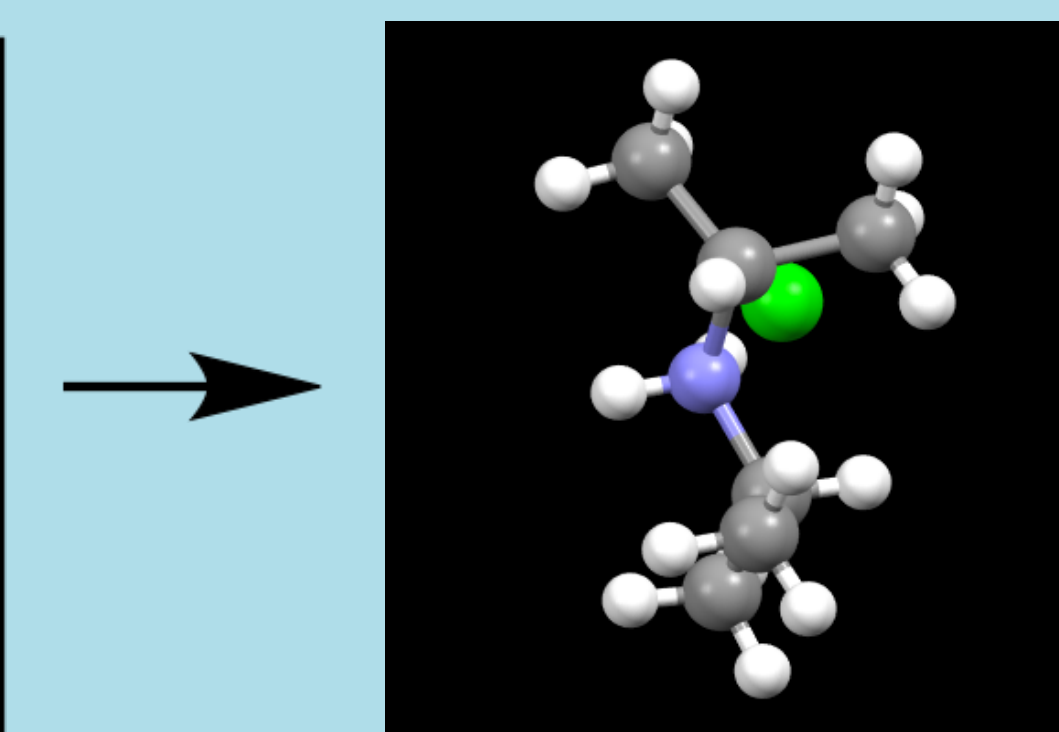


Model 1 transition state relaxes to the cleavage product shown, and does not revert to ground state geometry during molecular dynamics simulation

Transition state model 2: Rotation in a crystal



If cells were to undergo rotation simultaneously there would be no appreciable cell expansion, and the transition would require 385 kJ/mol



Model 2 transition state reverts to ground state P21 geometry during molecular dynamics simulation

Acknowledgements

National Science Foundation, CREST, NSF - HRD #1435163
Extreme Science and Engineering Discovery Environment (XSEDE), NSF-ACI-1053575.
Department of Defense, ARO # W911NF1210080
CREST TEAM, especially Douglas C. Smith, Timothy Usher, Shashi Poddar, Stephen Ducharme, Eva Zurek, Carlos Mora

Model 3: Halogen-assisted hydrogen transfer:

Strong vibrational interactions are seen between chlorine and N-H and C-H bonds highlighted in Figure 1 during molecular dynamics simulation. The corresponding distances between these positions for the DIPAC halide salts are summarized in Table 2. In all cases the X...H-N bonds are within the sum of the van der Waals radii for X+H (positive values in second to last column), and the X...H-C distances are no more than 0.56 Å away from the sum of the van der Waals radii for X + H (last column). Molecular dynamics results to date have failed to demonstrate this mechanism, but efforts are ongoing.

Table 2. Comparison of distances (in Å) between halogen (X) and H's which would undergo migration during halogen-assisted hydrogen transfer

System	X-H (N)	X-H (C)	X VDW radius*	X+H vdw	Δ X-H (N)	Δ X-H (C)
DIPAF	1.551	3.119	1.46	2.56	1.009	-0.559
DIPAC	2.086	2.881	1.76	2.86	0.774	-0.021
DIPAB	2.200	2.744	1.87	2.97	0.77	0.226
DIPAI	2.481	3.063	2.03	3.13	0.649	0.067
Hydrogen			1.1			

*Rowland, R.S. and Taylor, R., Intermolecular Non- bonded Contact Distances in Organic Crystal Structures: Comparison With Distances Expected from van der Waals Radii, *J. Phys. Chem.* **1996**, vol. 100, no. 18, pp. 7384-7391.

Conclusions and continuing work

Stable minima energy geometries have been calculated for the yet unreported DIPAI (P21) and DIPAF (P21) phases; for practical reasons, the DIPAI is likely to be more accessible experimentally. Of the transition states (TS) modeled, the 180 degree rotation of the isopropyl group in the solid state (TS model 2) is predicted to have a significantly lower energy barrier than the internal double hydrogen atom migration (TS model 1). TS model 2 structures revert to the P21 geometry during molecular dynamics; TS model 1 does not, and leads to an entirely new species upon minimization. Neither calculated energy barrier is realistic, as ferroelectric transitions are believed to occur via slower nucleation of a few polar inverted sites, following by fast reorientation of the surrounding cells until the entire crystal is reordered. These effects are currently being investigated using 2 x 2 x 2 supercells, in which one cell is either inverted, or is in the maximum energy rotational conformation. Finally, although TS model 2 is the best defined model to date, the proximity and vibrational interaction of the halide ion to the two hydrogen atoms that are exchanged suggests that a mechanism involving halogen assisted hydrogen atom transfer must be considered. Gas phase calculations of this alternative mechanism are underway.

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