Supporting Information

for the paper

"Understanding the Role Structural Changes Play in the Formation of Strong and Weak Hydrogen Bonds in Diammonium Dithiocyanate Salts"

David J. Wolstenholme*[†], Jan J. Weigand[‡], Elinor Cameron[†], T. Stanley Cameron[†]

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada, B3H 4J3, and Westfälische Wilhelms-Universität Münster, Institut für Anorganische und Analytische Chemie, Corrensstrasse 30/36, D-48149 Münster, Germany

* To whom the correspondence should be addressed. D. W.: phone, +1-(902)-494-3759, e-mail, dwolsten@dal.ca.
† Dalhousie University
‡ Westfälische Wilhelms-Universität Münster

Normal Distribution plots:

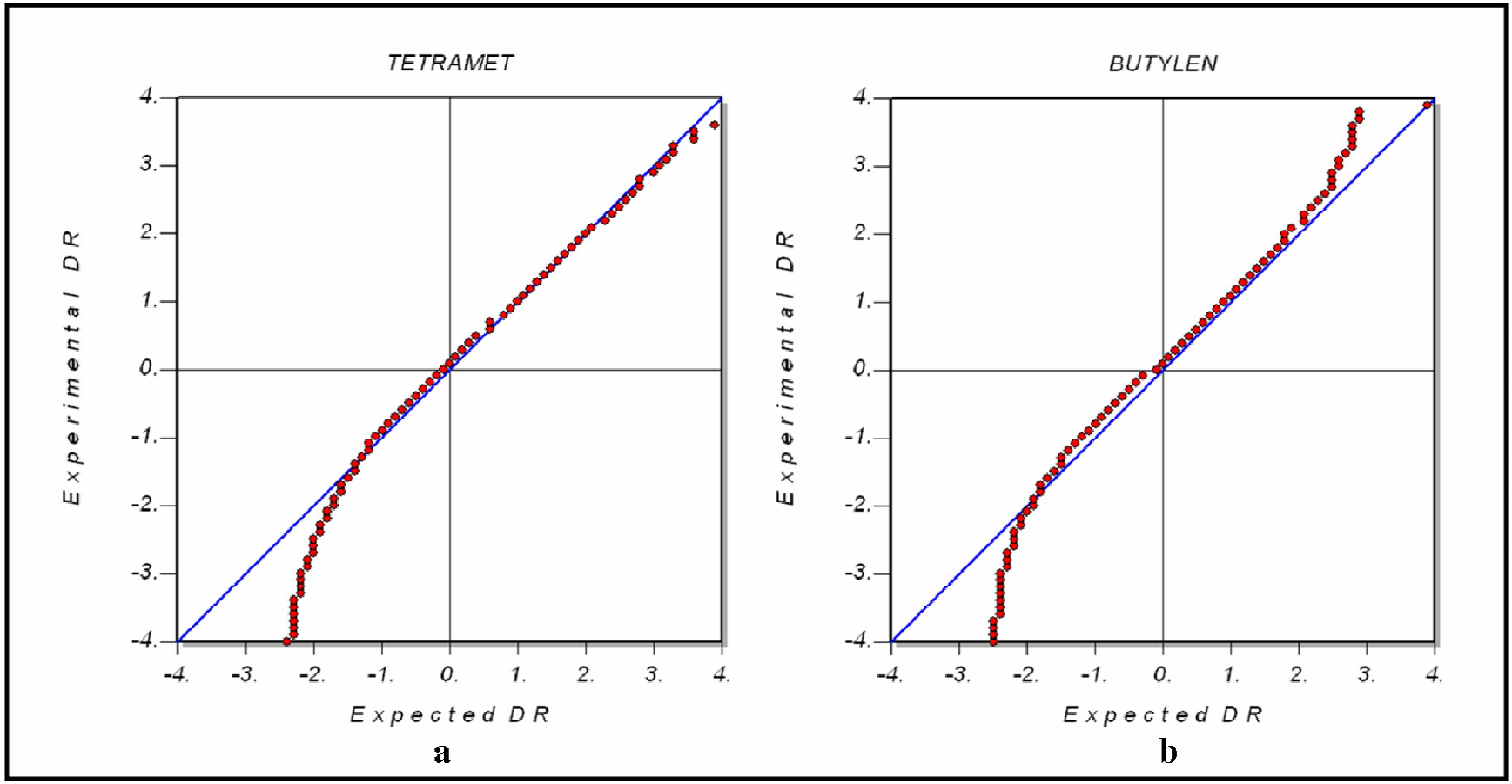

Figure S1: Normal probability plots for (a) tetramethylpropylenediammonium dithiocyanate and (b) tetramethylbutylenediammonium dithiocyanate.

Residual Maps:

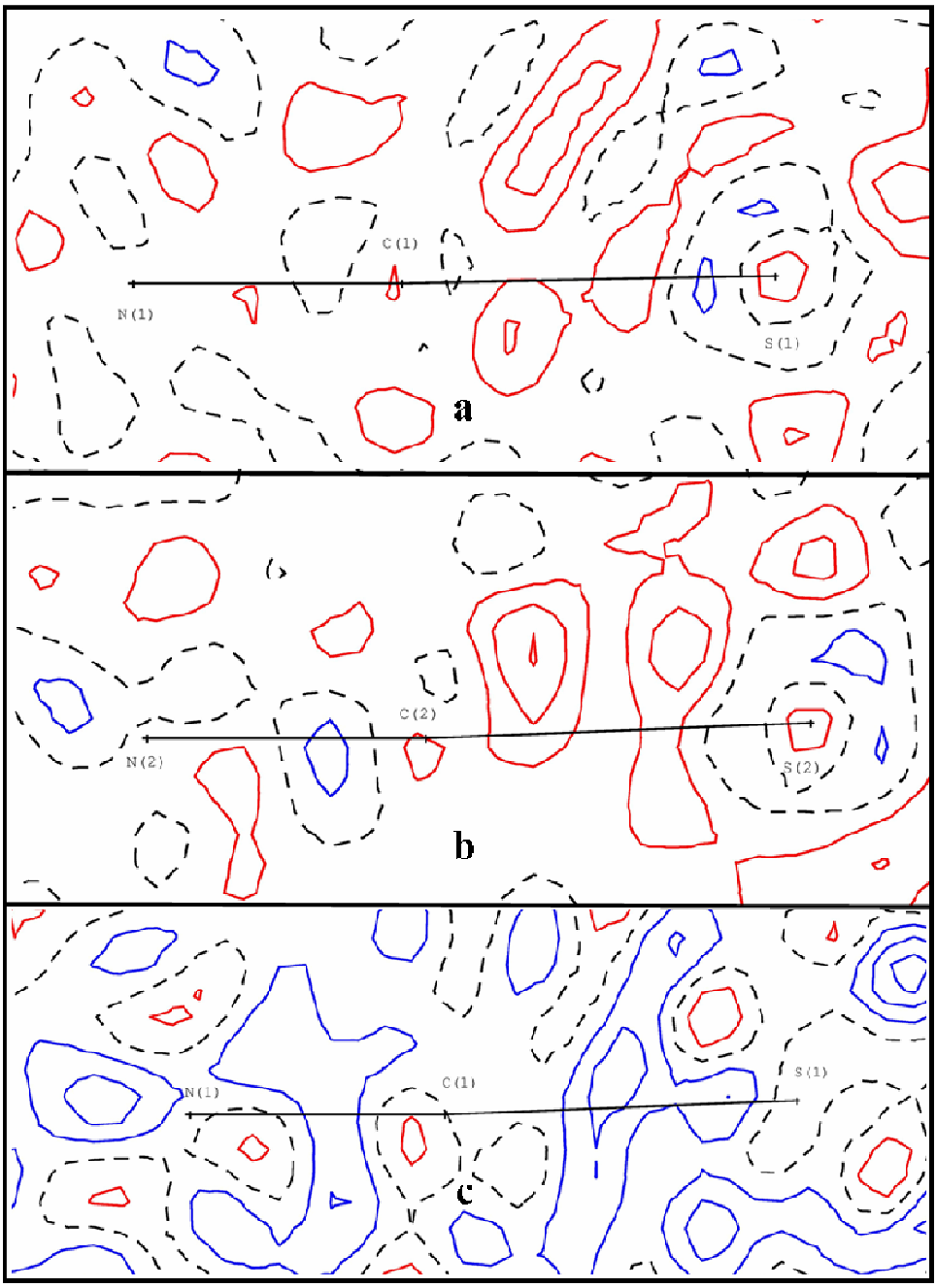

Figure S2: Residual density maps for the thiocyanate anions in (a/b) tetramethylpropylenediammonium dithiocyanate and (c) tetramethylbutylenediammonium dithiocyanate. The positive and negative contours are represented as solid blue and red lines, respectively. The zero contour line is represented by dashed lines. The contours are taken in intervals of 0.05 eÅ^{-3}. **note** the overall min and max residuals peaks in (a) -0.131, 0.091, (b) -0.154, 0.091, and (c) -0.141, 0.178 eÅ^{-3}.

Residual Maps:

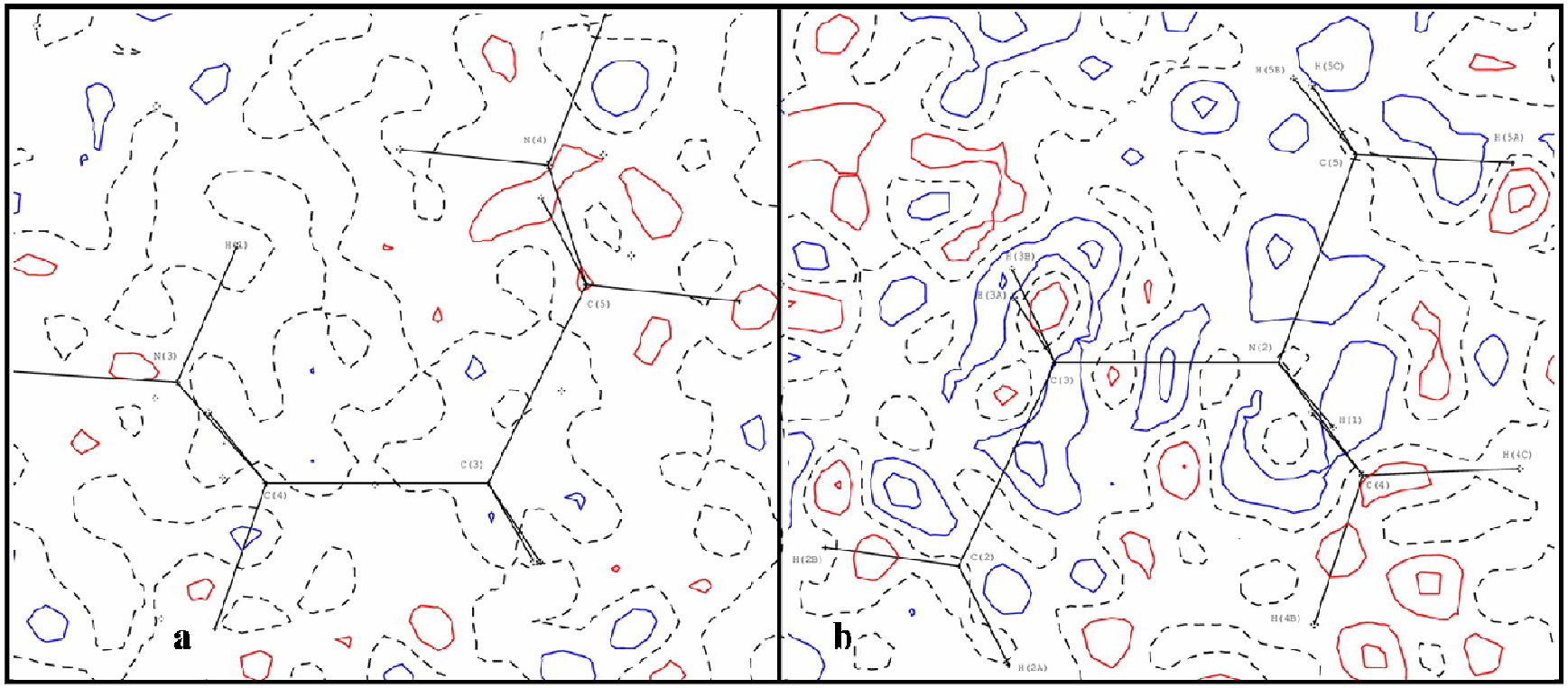

Figure S2: Residual density maps for the diammonium dications in (a) tetramethylpropylenediammonium dithiocyanate and (b) tetramethylbutylenediammonium dithiocyanate. The positive and negative contours are represented as solid blue and red lines, respectively. The zero contour line is represented by dashed lines. The contours are taken in intervals of 0.05 eÅ^{-3}. **note** the overall min and max residuals peaks in (a) -0.077, 0.119 and (b) -0.121, 0.127 eÅ^{-3}.

Laplacian Maps:

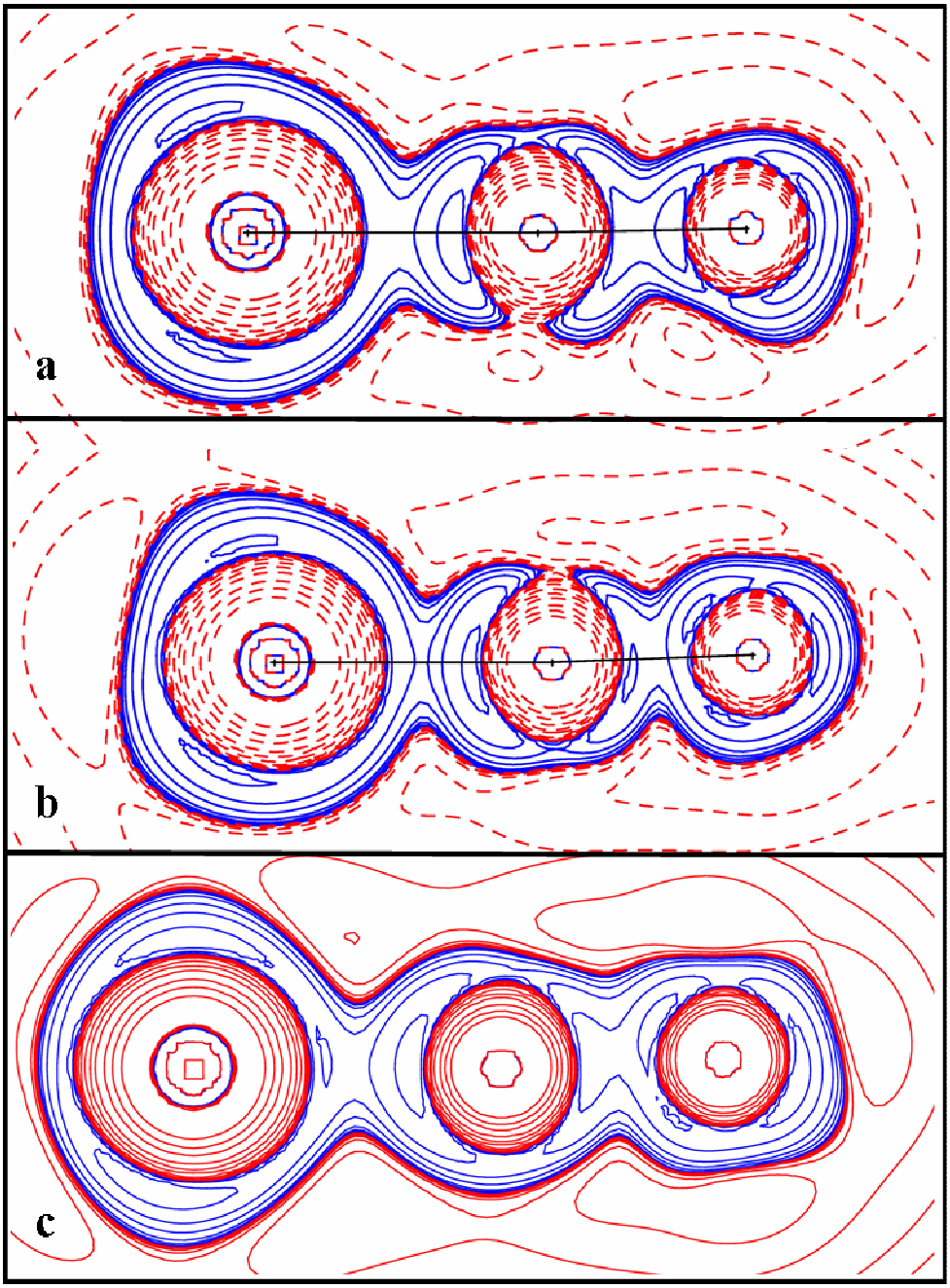

Figure S3: Laplacian [$\nabla^2\rho_b(\mathbf{r})$] distribution for the thiocyanate anions in (a/b) tetramethylpropylenediammonium dithiocyanate and (c) tetramethylbutylenediammonium dithiocyanate. The contours are drawn at logarithmic intervals in $-\nabla^2\rho_b$ eÅ^{-5} shown with blue and red solid lines representing the positive and negative contours, respectively.

Laplacian Maps:

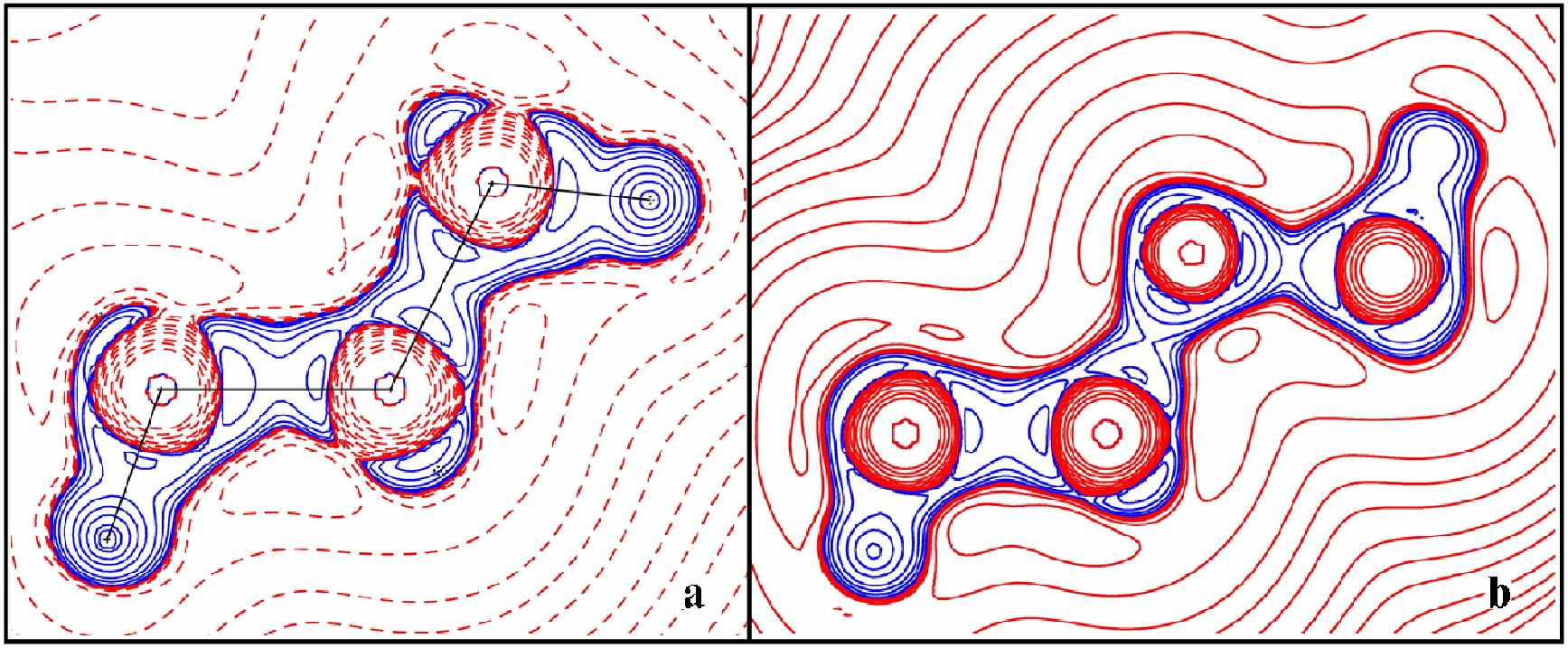

Figure S3: Laplacian [$\nabla^2\rho_b(\mathbf{r})$] distribution for the diammonium dications in (a) tetramethylpropylenediammonium dithiocyanate and (b) tetramethylbutylenediammonium dithiocyanate. The contours are drawn at logarithmic intervals in $-\nabla^2\rho_b$ eÅ^{-5} shown with blue and red solid lines representing the positive and negative contours, respectively.

Experimental Deformation Maps:

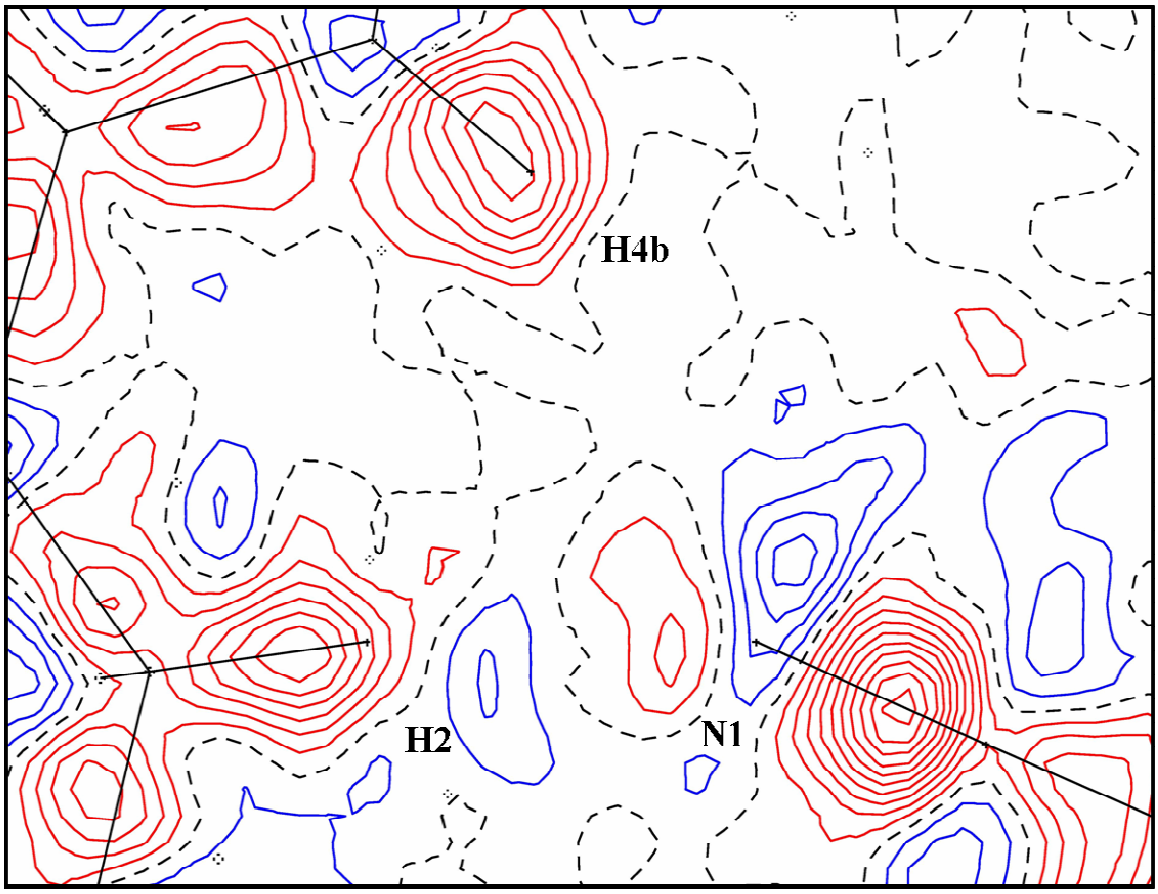

Figure S4: An experimental deformation density map for the N4-H2···N1 and C4-H4b···N1 bifurcated hydrogen bonds plotted in the H2···N1···H4b plane of salt II. The positive and negative accumulations of electron density are represented by red and blue contours, respectively. All contours increase in increments of 0.05 eÅ^{-3}. The dashed line represents the zero contour line, separating the positive and negative electron densities.

Static Deformation Maps:

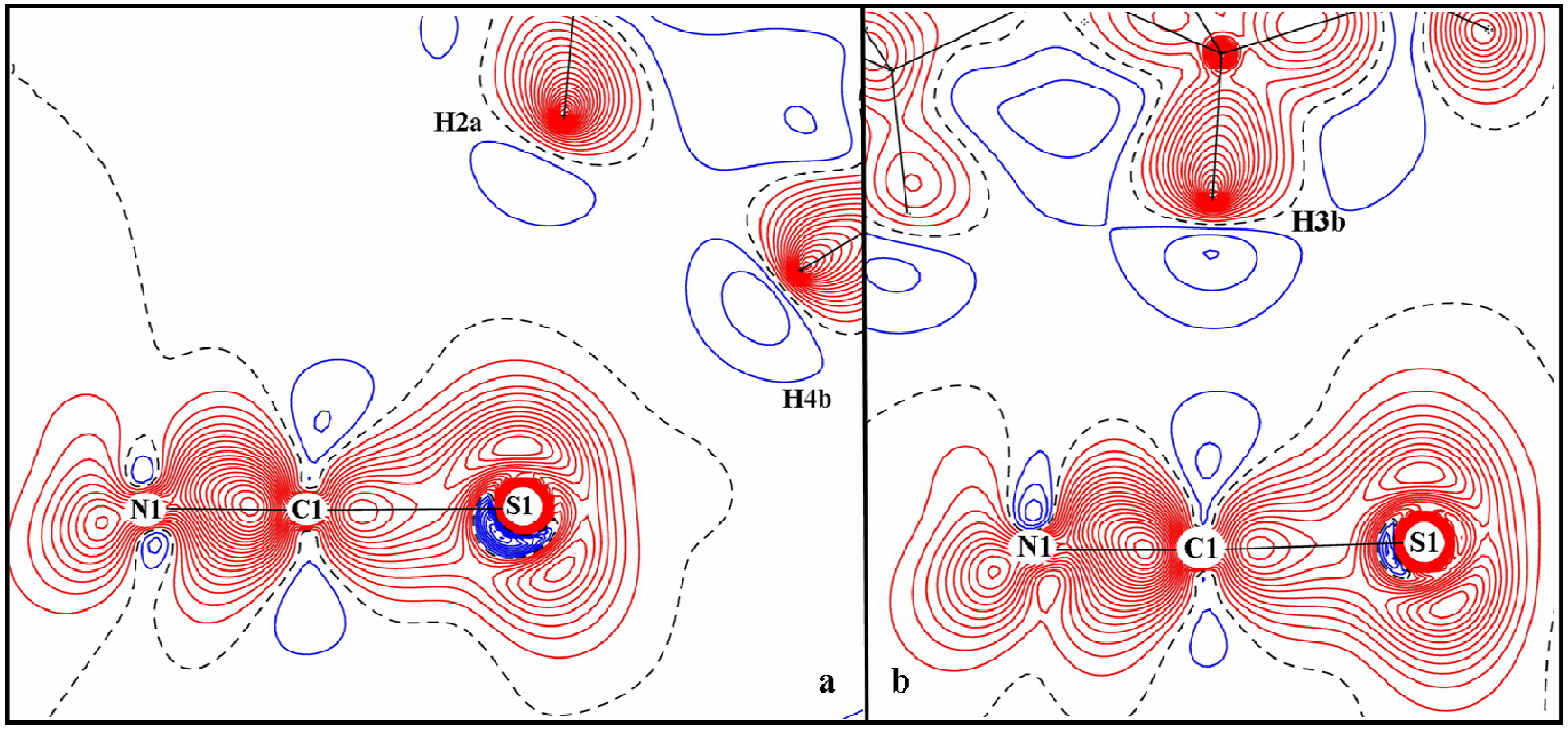

Figure S5: Static deformation maps for the (a) C2-H2a···S1 and (b) C3-H3b···C1 interactions plotted in the C2-H2a···S1 and C3-H3b···C1 planes of salt III. The positive and negative accumulations of electron density are represented by red and blue contours, respectively. All contours increase in increments of 0.05 eÅ^{-3}. The dashed line represents the zero contour line, separating the positive and negative electron densities.