Supporting Information

for the paper

"Understanding the Electronic Structure, Reactivity, and Hydrogen Bonding for a 1,2-Diphosphonium Dication"

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Spherical and Multipole Refinement Details

A sweep of the data was performed using ω scans from 20.0° to 200.0° in steps of 5.0° at $\chi = 0$ and $\Phi = 0$. A second sweep was then performed using ω scans from 20.0° to 95.0° in steps of 5.0° at $\chi = 54.0°$ and $\Phi = 180.0°$. The exposure rate in both sweeps was 20.0 [min/5.0°]. The crystal-to-detector distance was fixed throughout the data collection to 127.4 mm.

Residual Maps

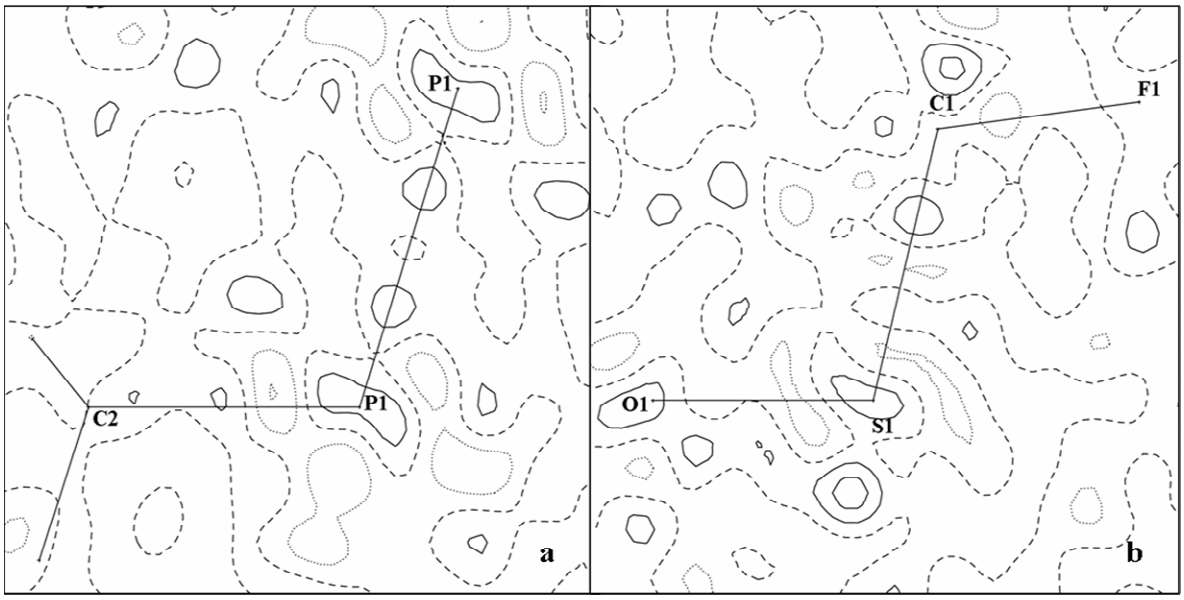

Figure S1: Residual density map with positive contours as solid lines, negative contours as dotted lines, and the zero contour line as dashes. All contours are in intervals of 0.1 eÅ^{-3}. (a) C2-P1-P1 plane of the dication with $\Delta\rho_{min/max}$ = -0.209/0.157 eÅ^{-3} (b) O1-S1-C1 plane of the triflate anion with $\Delta\rho_{min/max}$ = -0.195/0.259 eÅ^{-3}

Crystal Packing Diagrams

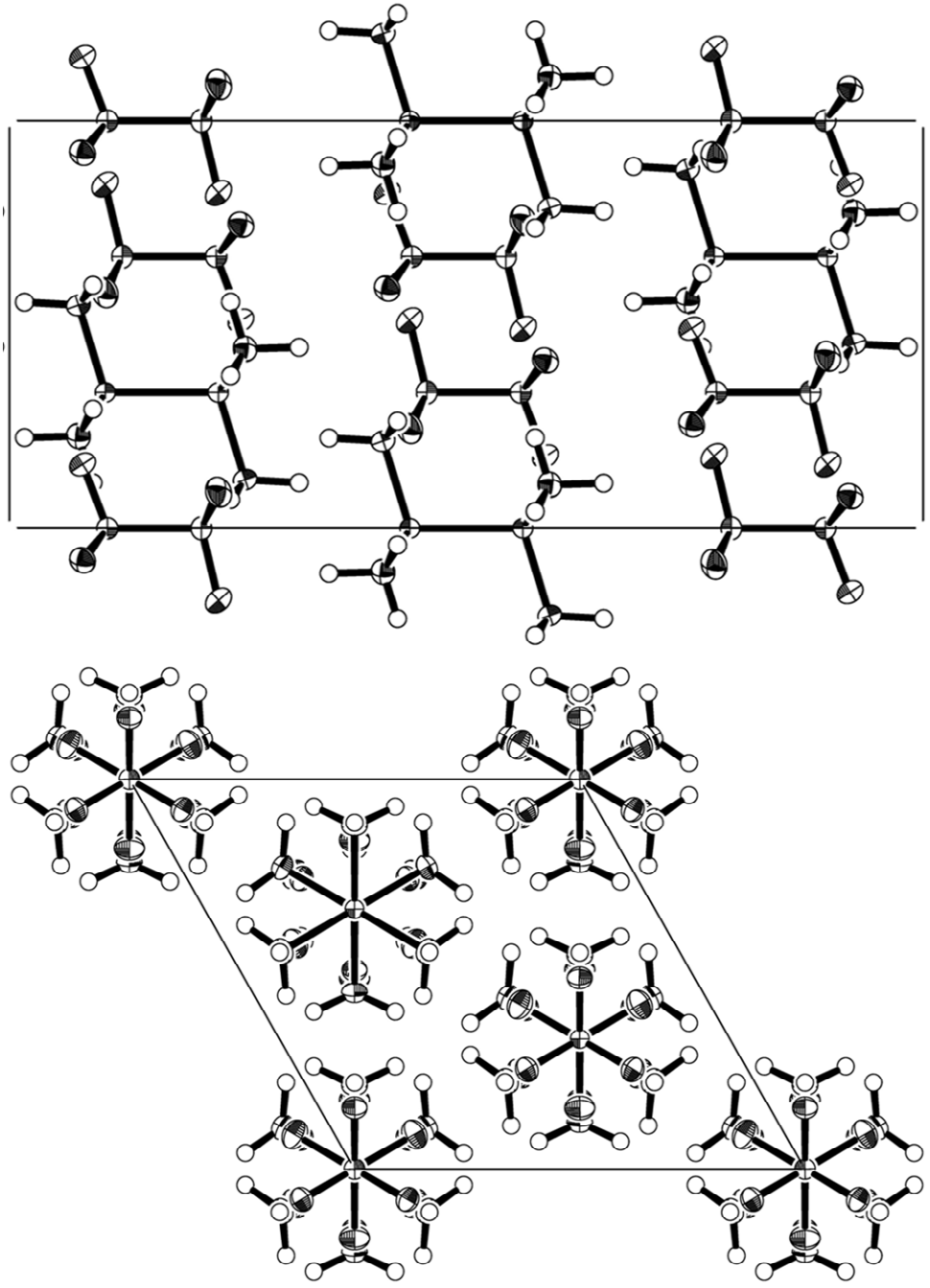

Figure S2: Packing diagram for hexamethyldiphosphonium triflate viewed down a axis and c axis

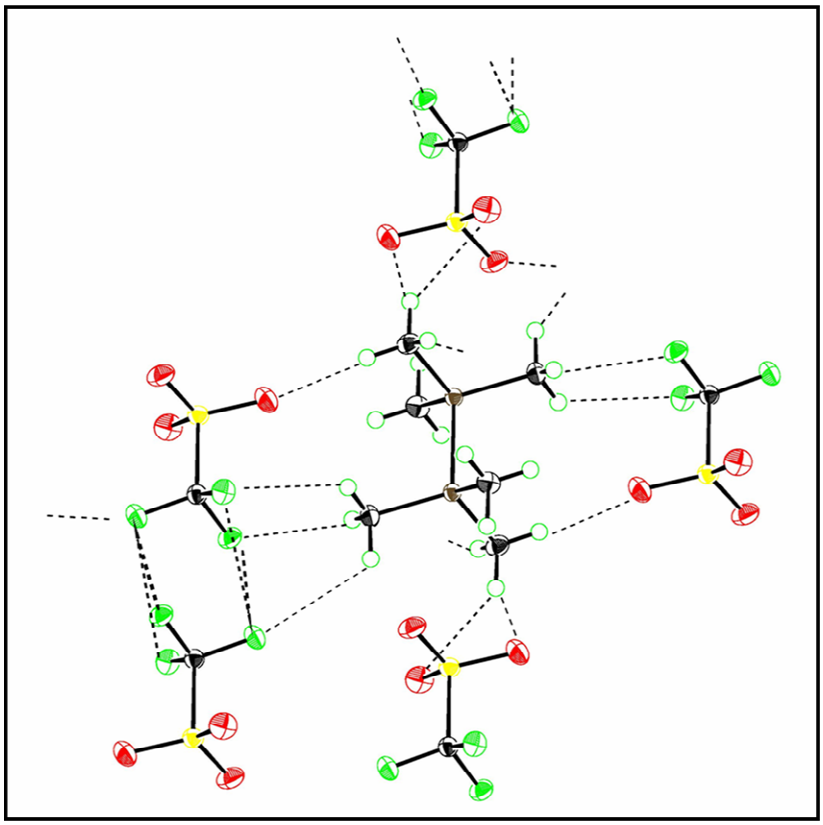

Figure S3: Packing diagram showing several of the close contacts used to stabilize the crystalline structure of hexamethyldiphosphonium triflate

Static Maps

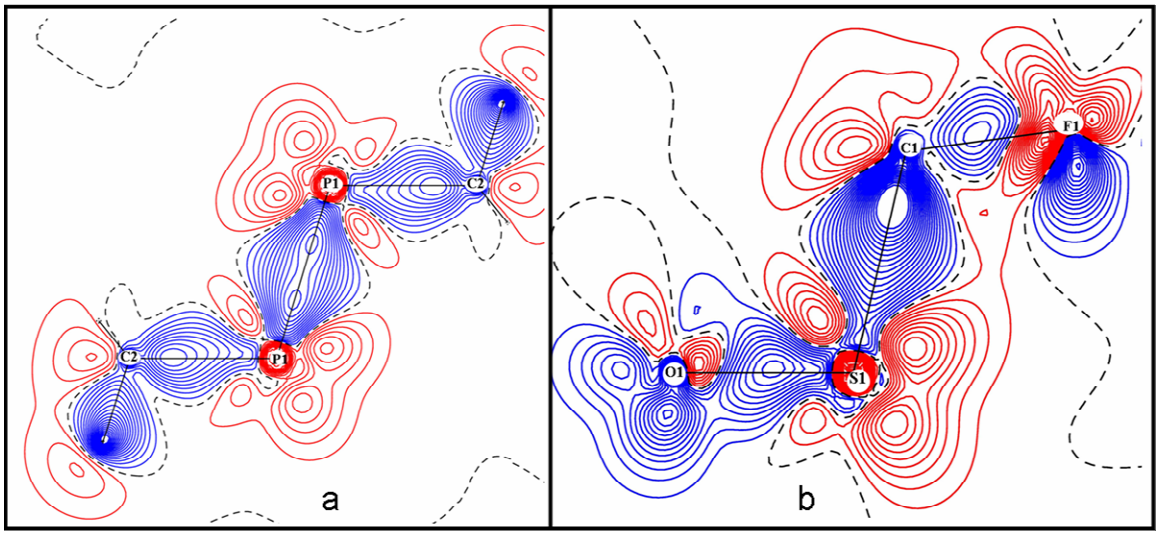

Figure S4: Static deformation maps of (a) the C-P-P plane of the dication and (b) the O-S-C plane of the triflate. The blue contours represent the positive electron distribution and the red contours represent the negative electron distribution. The dashed lines represent the zero contour line. All contours are taken in 0.05 $eÅ^{-3}$ intervals.

Laplacian Map

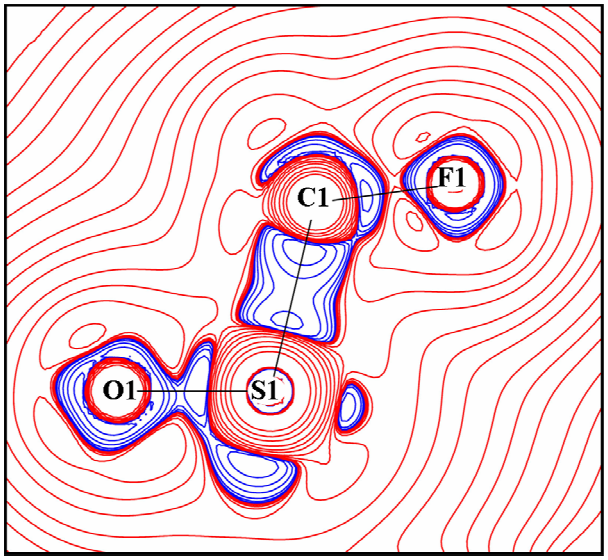

Figure S5: Laplacian distribution in the plane of the triflate anion of hexamethyldiphosphonium triflate. The contours are drawn at logarithmic intervals in $-\nabla^2\rho_b(\mathbf{r})$, shown in positive (blue) and negative (red) contours.

Theoretical Properties of the Bond Critical Points for Hexamethyldiphosphonium Triflate

bond	$\rho_b(\mathbf{r})$ (eÅ^{-3})	$\nabla^2\rho_b(\mathbf{r})$ (eÅ^{-5})	λ_1 (eÅ^{-5})	λ_2 (eÅ^{-5})	λ_3 (eÅ^{-5})	R_{ij} (Å)
P1-P1	0.82	-4.45	-3.50	-3.50	2.56	2.240
P1-C2	1.16	-5.74	-5.46	-5.25	4.98	1.815
	1.16	-5.75	-5.46	-5.25	4.96	1.816
	1.16	-5.75	-5.46	-5.25	4.96	1.816
O1-S1	1.86	19.65	-11.08	-10.40	41.14	1.488
	1.86	19.67	-11.08	-10.41	41.16	1.488
	1.86	19.65	-11.08	-10.40	41.13	1.488
S1-C1	1.28	-8.98	-7.82	-7.82	6.66	1.877
C1-F1	1.88	-6.63	-15.66	-13.32	22.35	1.343
	1.88	-6.63	-15.66	-13.32	22.36	1.343
	1.88	-6.62	-15.66	-13.32	22.35	1.343