STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Volume 77 (2021)

Supporting information for article:

On the transfer of theoretical multipole parameters for restoring static electron density and revealing and treating atomic anharmonic motion. Features of chemical bonding in crystals of an isocyanuric acid derivative

Sergey A. Shteingolts, Julia K. Voronina, Liliya F. Saifina, Marina M. Shulaeva, Vyacheslav E. Semenov and Robert R. Fayzullin

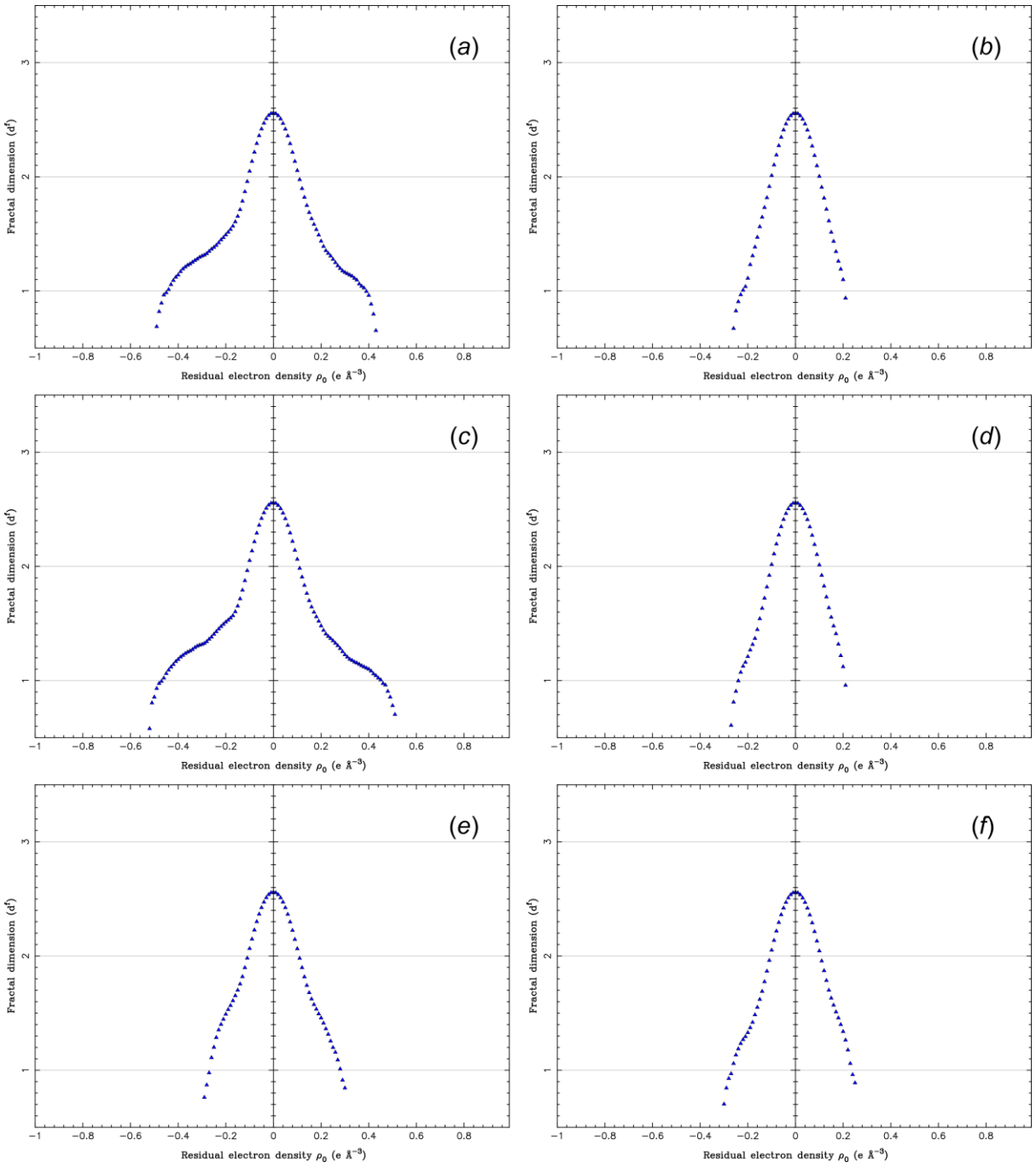

Figure S1 Fractal dimension distributions $d^f(\rho_0)$ of the residual electron density $\rho_0(\boldsymbol{r})$ in the unit cells of the studied isocyanuric acid derivative calculated for UMM (*a*), UMM-GC (*b*), KRMM (*c*), KRMM-GC (*d*), final MM after the transfer procedure before (*e*) and after the second round of anharmonic refinement (*f*).

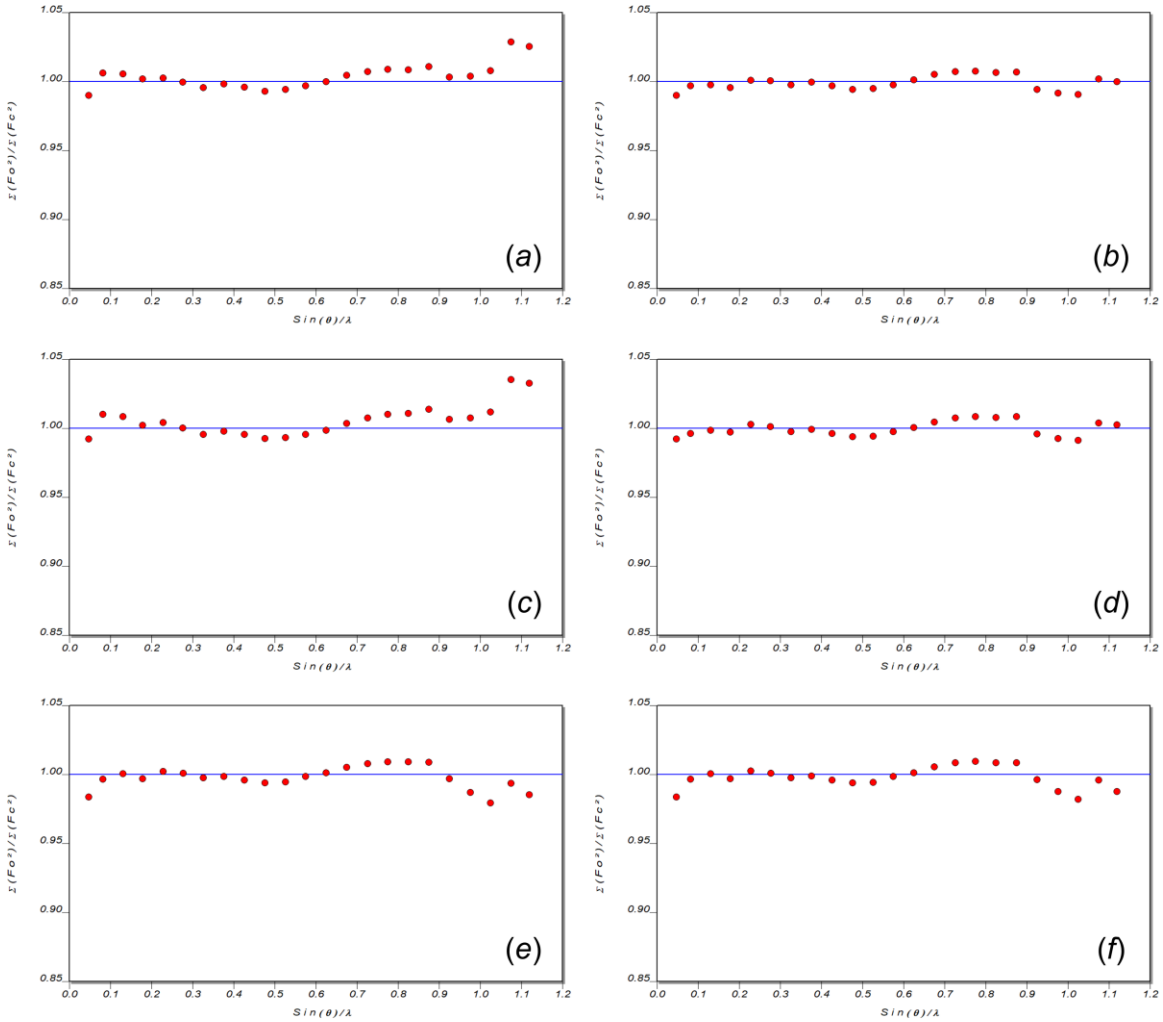

Figure S2 DRK scatterplots for UMM (a), UMM-GC (b), KRMM (*c*), KRMM-GC (*d*), final MM after the transfer procedure before (*e*) and after the second round of anharmonic refinement (*f*).

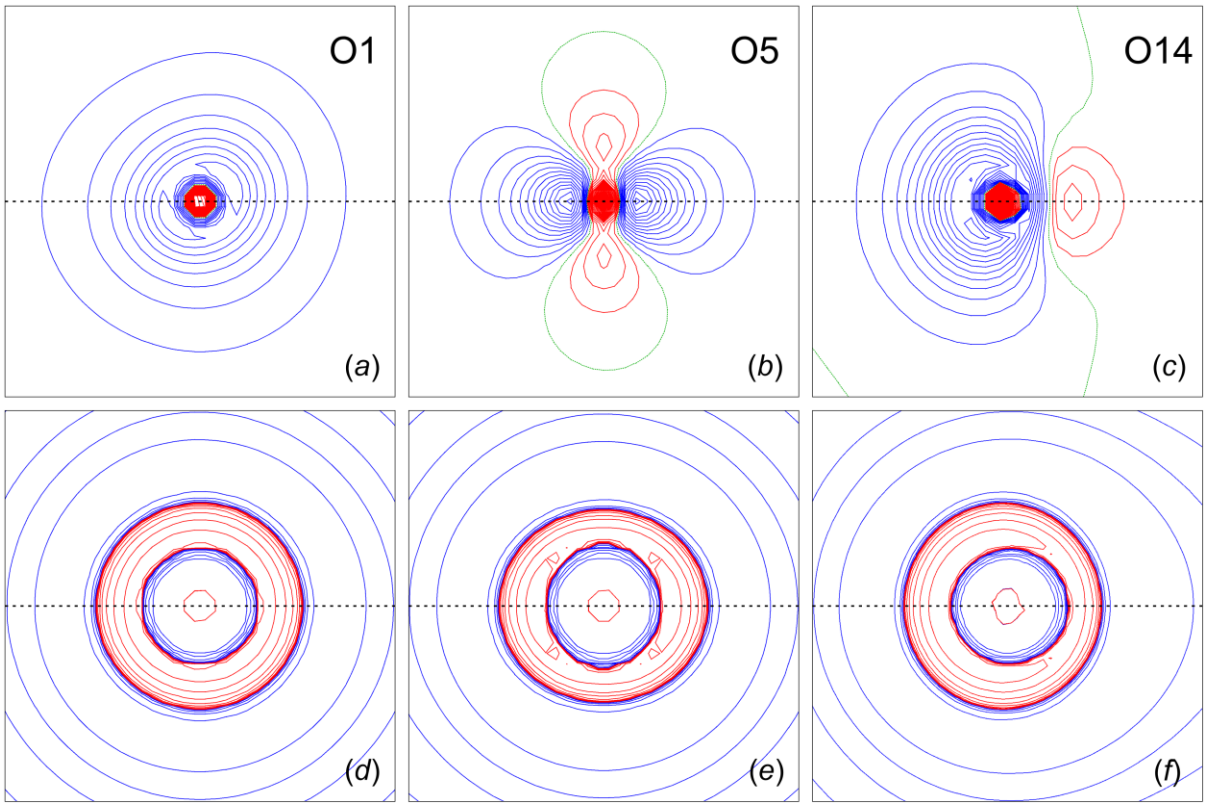

Figure S3 Contour maps of deformation electron density $\delta\rho(\boldsymbol{r})$ (*a*-*c*) and the Laplacian of electron density $\nabla^2\rho(\boldsymbol{r})$ (*d*-*f*) in the planes of the labelled oxygen atoms of the sulfonyl (*a*, *d*) and ester (*b*, *c*, *e*, *f*) functional groups calculated from the wavefunction for the optimized crystal structure of 5-substituted-1,3-dimethyl-isocyanurate. The maps (*a*, *d*) are plotted in a plane perpendicular to the S1–O1 bond line, maps (*b*, *e*) are perpendicular to the C13–O5 bond line, and maps (*c*, *f*) are perpendicular to the plane of the C13–O14–C15 fragment. The contour step for (*a*, *b*, *c*) is set to 0.1 e Å^{-3}. The width and length of each map are 1 Å. The black dotted lines on the maps correspond to the atomic planes as shown in Figure S8. Hereinafter, blue, green and red colours are reserved for positive, zero and negative function values, respectively; the contour step for the $\delta\rho(\boldsymbol{r})$-maps is equal to 0.1 e Å^{-3}; the logarithmic scale in the form of $\pm$ 2, 4, 8·10^n ($-3 \le n \le 2$) e Å^{-5} is adopted for $\nabla^2\rho(\boldsymbol{r})$-maps.

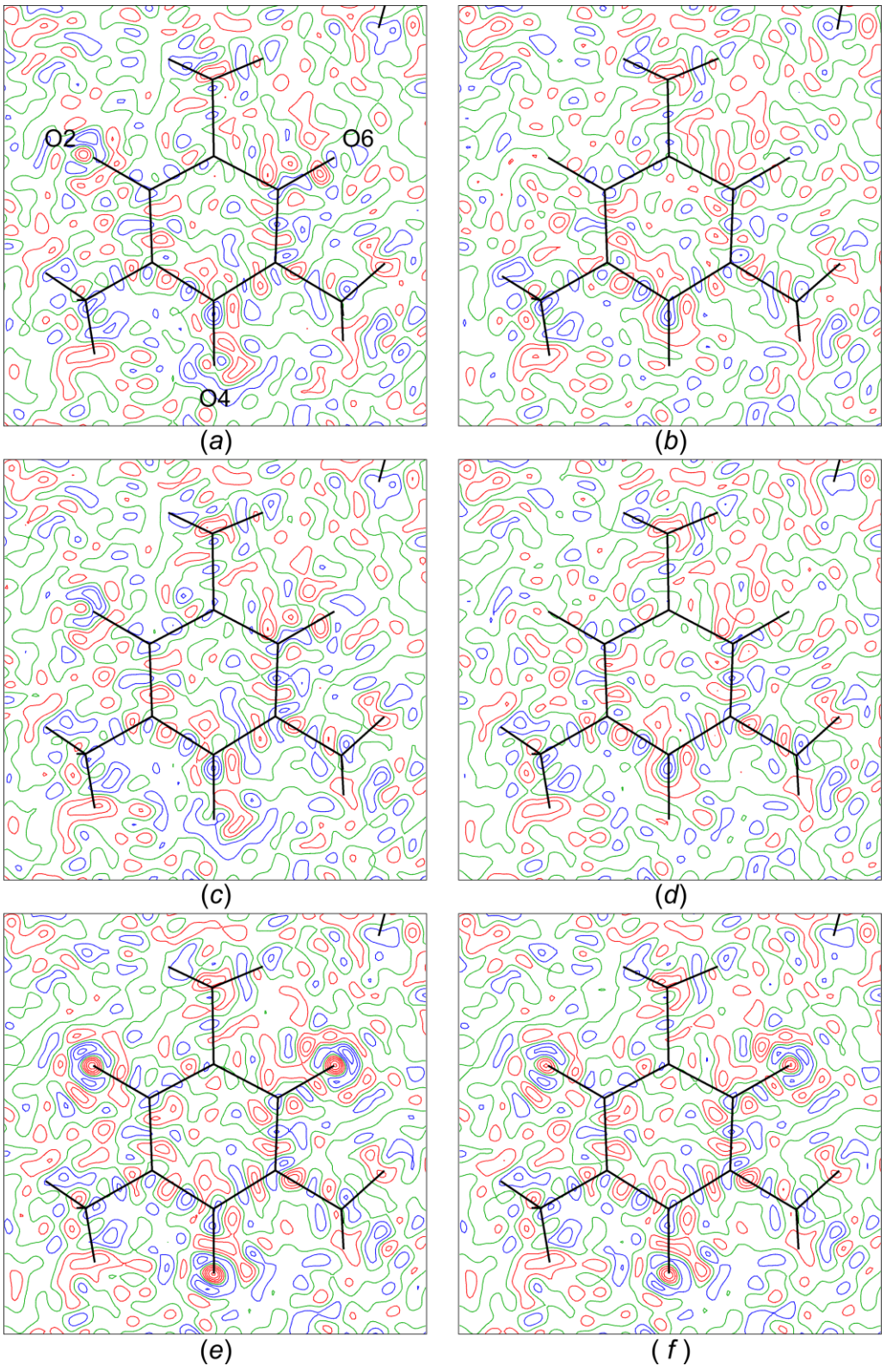

Figure S4 Contour maps of residual electron density $\rho_0(\boldsymbol{r})$ in the plane of the labelled atoms of the isocyanurate moiety calculated for UMM (*a*), UMM-GC (*b*), KRMM (*c*), KRMM-GC (*d*), final MM after the transfer procedure before (*e*) and after second round of anharmonic refinement (*f*). Blue, green and red colours correspond to positive, zero and negative function values, respectively; the contour step is set to 0.05 e Å^{-3}. Residual density is calculated for the whole resolution range.

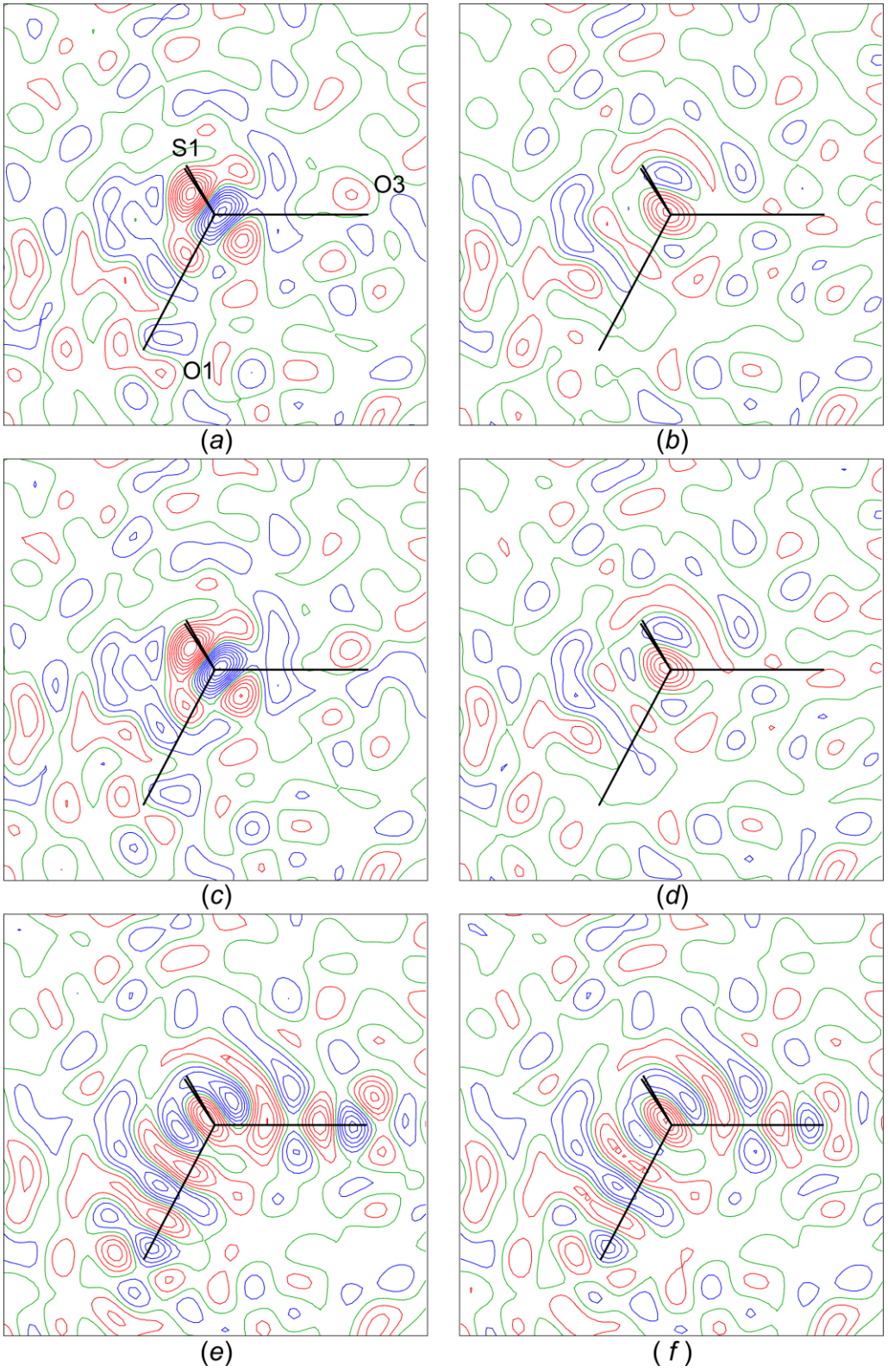

Figure S5 Contour maps of residual electron density $\rho_0(\boldsymbol{r})$ in the plane labelled atoms of the sulfonyl group calculated for UMM (*a*), UMM-GC (*b*), KRMM (*c*), KRMM-GC (*d*), final MM after the transfer procedure before (*e*) and after second round of anharmonic refinement (*f*). Blue, green and red colours correspond to positive, zero and negative function values, respectively; the contour step is set to 0.05 e Å^{-3}. Residual density is calculated for the whole resolution range.

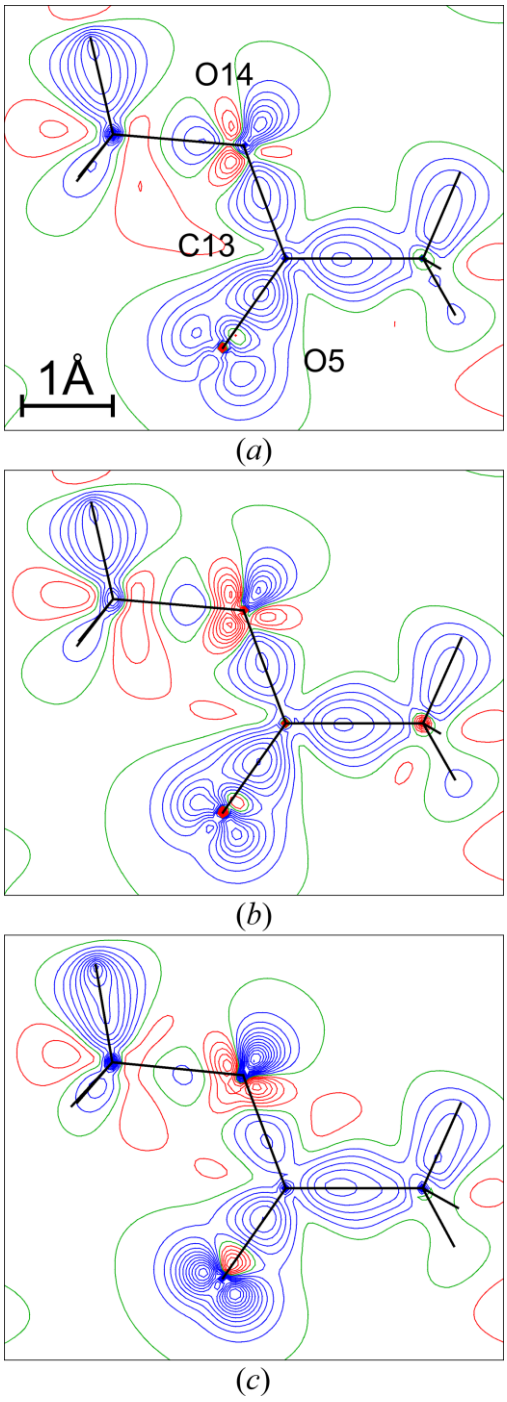

Figure S6 Contour maps of deformation electron density $\delta\rho(\boldsymbol{r})$ in the plane of the ester group calculated for UMM (*a*), final MM after the transfer procedure (*b*) and theoretical MM (*c*). The atoms shown in the maps are not concerned by anharmonic modelling. Blue, green and red colours correspond to positive, zero and negative function values, respectively; the contour step is set to 0.1 e Å^{-3}.

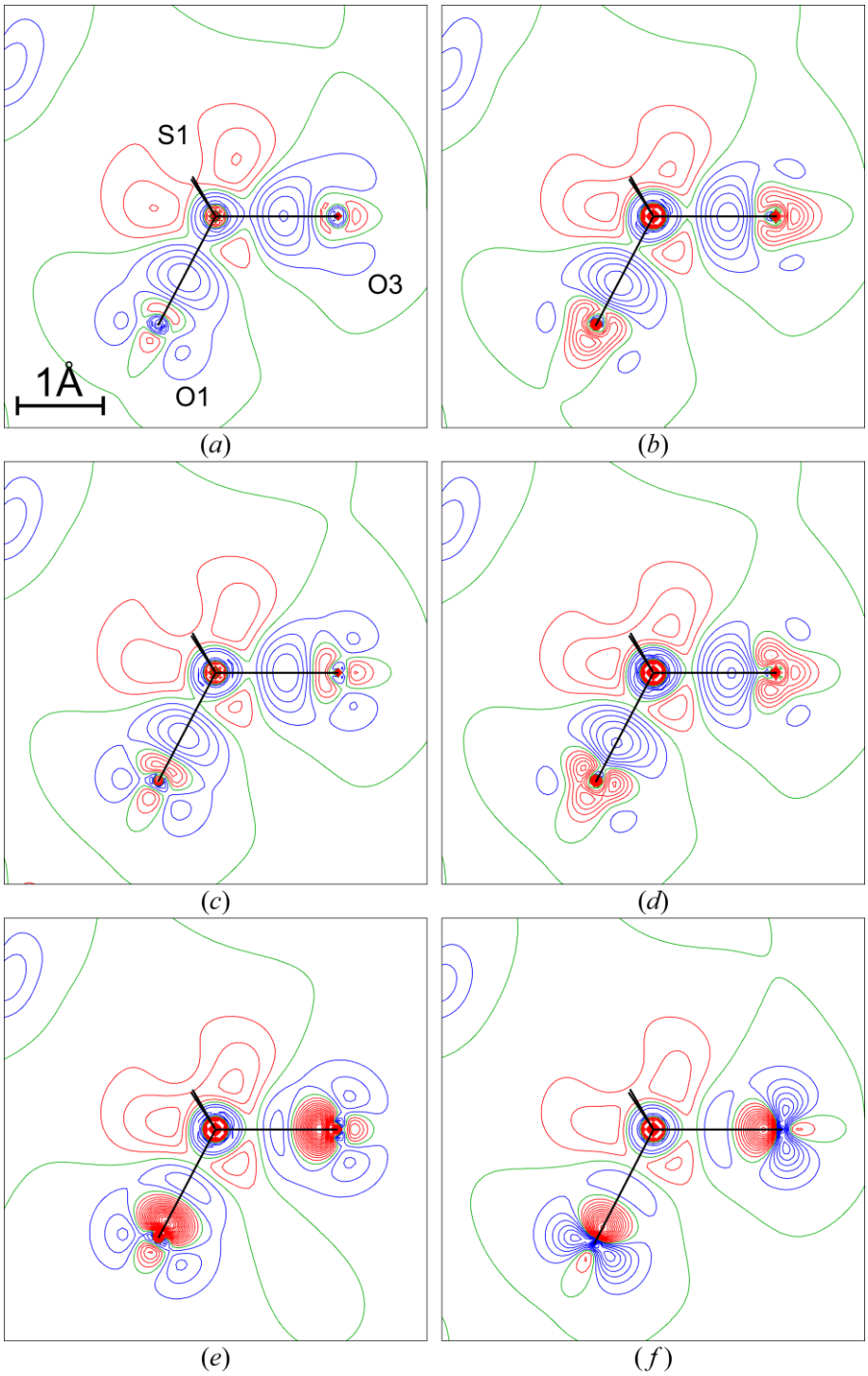

Figure S7 Contour maps of deformation electron density $\delta\rho(\boldsymbol{r})$ in the plane of the labelled atoms of the sulfonyl group calculated for UMM (*a*), UMM-GC (*b*), KRMM (*c*), KRMM-GC (*d*), final MM after the transfer procedure (*e*) and theoretical MM (*f*). Blue, green and red colours correspond to positive, zero and negative function values, respectively; the contour step is set to 0.1 e Å^{-3}.

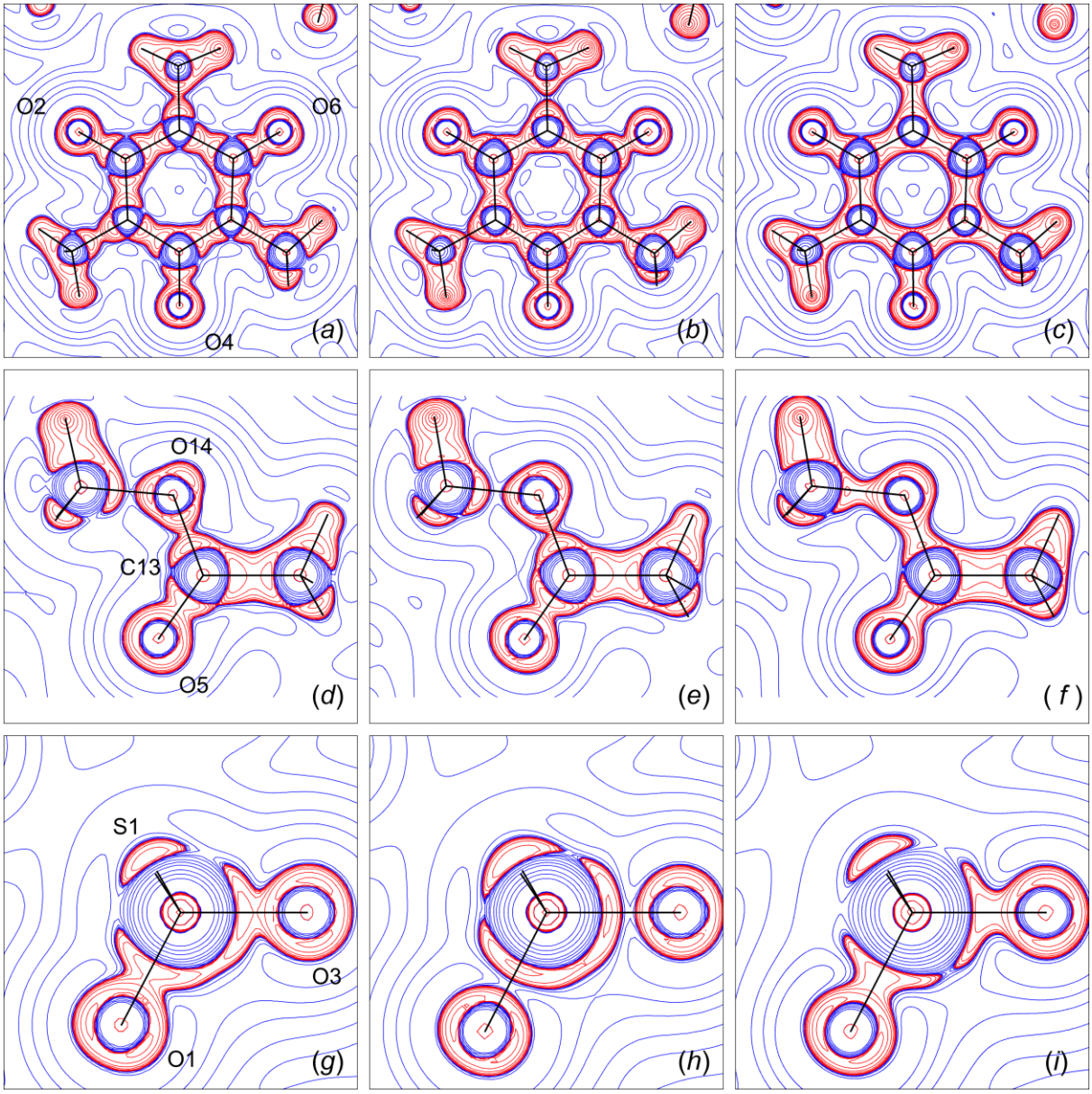

Figure S8 Contour maps of the Laplacian of electron density $\nabla^2\rho(\boldsymbol{r})$ in the planes of labelled atoms for the isocyanurate moiety, ester fragment and sulfonyl group calculated from final MM after the transfer procedure (*a*, *d*, *g*), theoretical MM (*b*, *e*, *h*) and wavefunction-derived electron density (*c*, *f*, *i*). The logarithmic scale in the form of ± 2, 4, $8\cdot10^n$ ($-3 \le n \le 2$) e Å^{-5} is adopted; blue, green and red colours are reserved for positive, zero and negative function values, respectively.

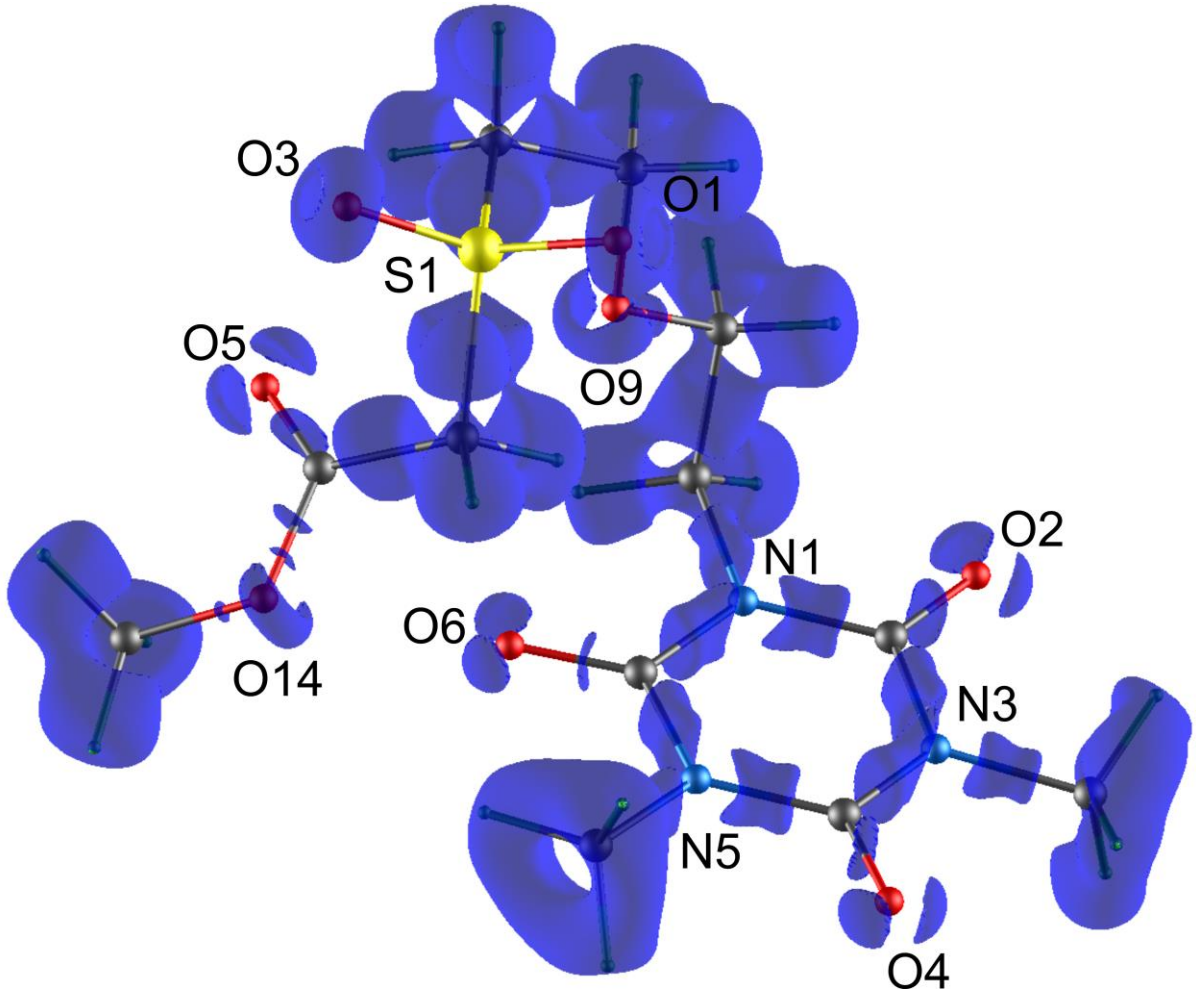

Figure S9 Isosurfaces (blue solid) of approximated local electronic temperature at $t(\boldsymbol{r})$ = 0.38 a.u. for the experimental model.

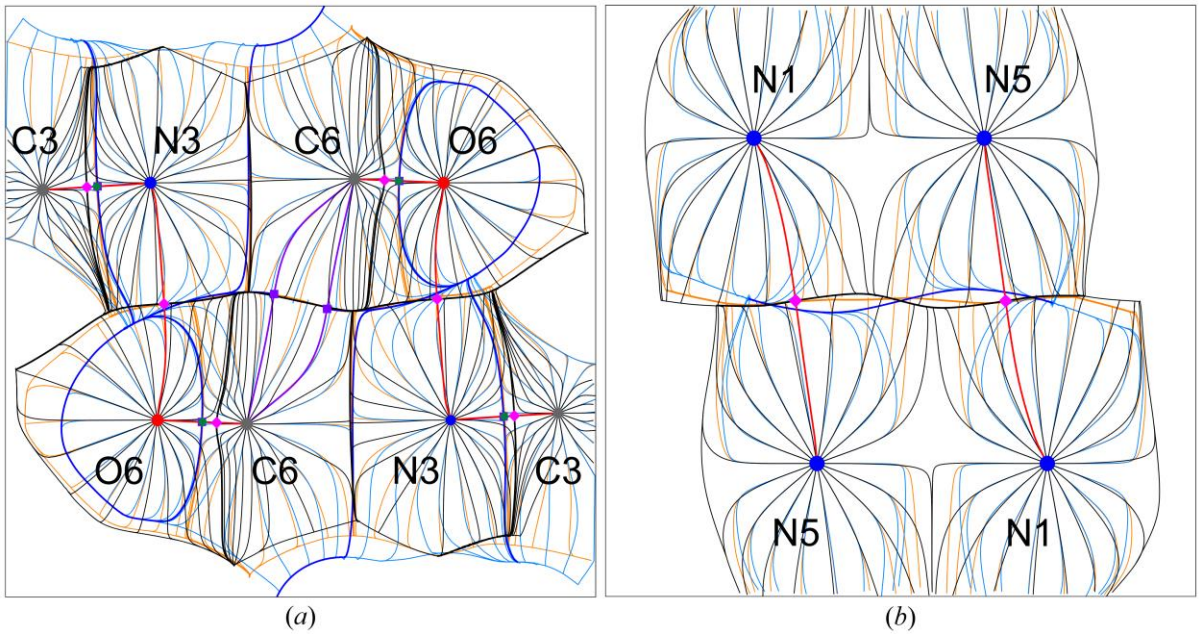

Figure S10 Superposition of theoretical multipole-derived gradient fields of electron density $\nabla\rho(\boldsymbol{r})$, kinetic $\nabla\varphi_k(\boldsymbol{r})$ and electrostatic $\nabla\varphi_{es}(\boldsymbol{r})$ potentials coloured in black, orange and blue, respectively, in the plane of homoatomic N1···N5 contacts constituting the centrosymmetric π···π interaction. Critical points (3, –1) in $\rho(\boldsymbol{r})$ are shown by magenta rhombuses. Gradient paths in $\rho(\boldsymbol{r})$ connecting the field attractors are shown by red lines.

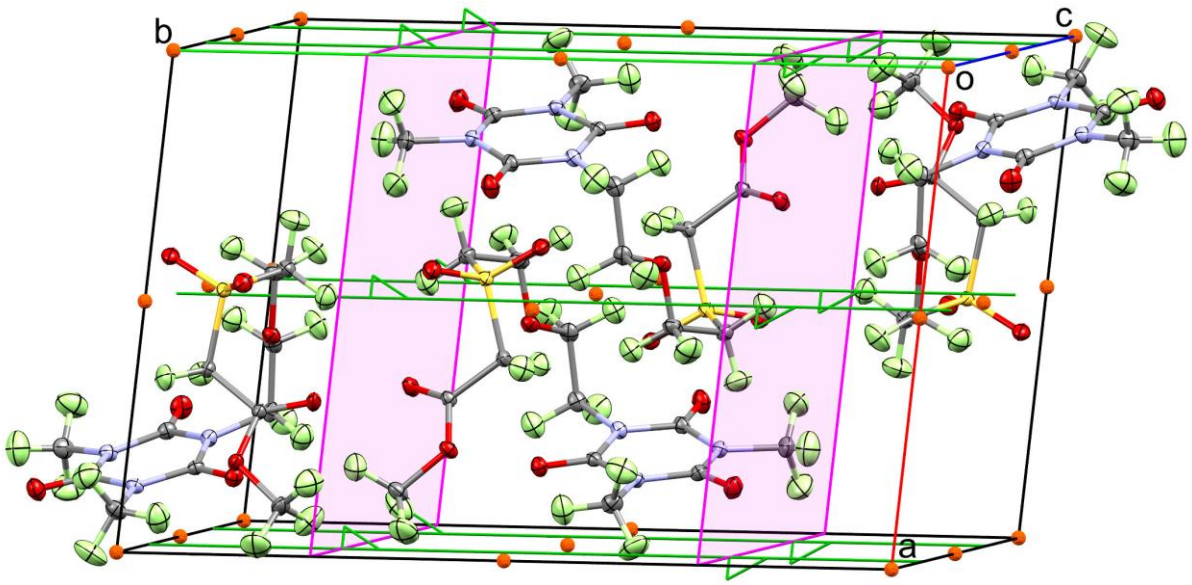

Figure S11 Packing of 5-substituted-1,3-dimethylisocyanurate in the unit cell ($P2_1/c$).

Table S1 Laplacian critical points (3, +3) calculated from solid-state theoretical calculations in regions of valence shell charge concentrations of oxygen atoms with their selected geometrical and topological characteristics.

Atom	CP (3, +3)	Angle, °	*d*, Å	ρ_{CP}, e Å^{-3}	$\nabla^2\rho_{CP}$, e Å^{-5}	l_1, e Å^{-7}	l_2, e Å^{-7}	l_3, e Å^{-7}
O2	CP1	145.94	0.334	6.562	135.53	–16545.50	–433.63	–351.55
	CP2		0.334	6.544	134.57	–16430.07	–431.10	–345.75
O4	CP1	146.50	0.334	6.562	135.73	–16550.08	–436.50	–356.13
	CP2		0.334	6.549	134.90	–16467.91	–432.14	–351.38
O6	CP1	145.87	0.334	6.547	134.98	–16477.31	–427.83	–355.60
	CP2		0.334	6.571	136.26	–16619.97	–433.37	–360.69
O1	CP1	152.05	0.338	6.201	116.72	–14890.16	–423.87	–30.38
	CP2		0.337	6.165	114.79	–14646.76	–416.98	–21.98
O3	CP1	151.05	0.338	6.193	116.44	–14840.27	–425.54	–28.17
	CP2		0.337	6.186	116.17	–14796.17	–421.95	–30.46
O5	CP1	143.24	0.333	6.594	137.87	–16731.55	–421.85	–400.11
	CP2		0.333	6.588	137.40	–16739.26	–418.45	–397.80
O9	CP1	137.67	0.332	6.825	149.76	–17654.29	–722.14	–336.44
	CP2		0.332	6.887	153.12	–18020.83	–740.89	–354.49
O14	CP1	n/a	0.334	6.655	137.90	–16855.66	–561.72	–41.70

Angle is the valence angle between the two CPs (3, +3) and the atomic nucleus; d is the distance between CP (3, +3) and the nuclei; ρ_{CP} is the value of electron density at CP (3, +3) in $\nabla^2\rho(\boldsymbol{r})$; $\nabla^2\rho_{CP}$ is the Laplacian of electron density at CP (3, +3) in $\nabla^2\rho(\boldsymbol{r})$; l_1, l_2 and l_3 are the eigenvalues of Hessian matrix of Laplacian of electron density.

Table S2 Selected properties integrated over the volumes of the atomic basins of the studied isocyanuric acid derivative in the crystal.

For each atomic basin, the first, second and third rows of the table contain data obtained from the exact theoretical periodic wavefunction and derived electron density (optimized geometry), the theoretical multipole model (optimized geometry) and the final, experimental model after the transfer procedure.

Atom	$\rho(\Omega)$	$V(\Omega)$	$L(\Omega)$	$G(\Omega)$
S1	13.696	7.787	0.0168	397.165
	13.892	8.411	0.0115	399.060
	13.439	6.459	0.0192	398.844
O2	9.170	20.018	0.0007	75.614
	9.001	19.125	0.0038	75.723
	9.140	16.195	0.0012	75.843
O4	9.176	18.730	0.0005	75.609
	9.011	17.775	–0.0009	75.727
	9.184	18.331	0.0013	75.816
O6	9.169	16.973	0.0000	75.623
	9.022	16.064	0.0013	75.755
	9.204	19.206	0.0028	75.689
O9	9.061	13.347	0.0000	75.511
	8.826	12.604	0.0012	75.616
	8.970	12.898	0.0011	75.322
O1	9.316	18.077	–0.0003	75.607
	9.217	17.413	–0.0017	75.668
	9.427	17.676	–0.0002	75.290
O3	9.315	19.524	0.0002	75.606
	9.211	18.744	0.0008	75.660
	9.425	19.236	0.0005	75.323
O5	9.159	18.124	0.0000	75.647
	9.032	17.619	0.0005	75.740
	9.246	18.129	0.0010	75.484
O14	9.084	14.280	0.0015	75.599
	8.873	13.821	–0.0003	75.682
	9.053	14.389	–0.0028	75.405
N1	8.128	10.448	–0.0003	55.234
	7.842	9.994	0.0012	55.534
	8.057	10.553	0.0003	55.491
N3	8.123	10.534	0.0006	55.233
	7.834	10.123	0.0014	55.524
	8.114	10.877	0.0033	55.539
N5	8.126	10.627	0.0029	55.226
	7.841	10.240	0.0020	55.524
	8.079	10.860	0.0014	55.480
C2	4.224	4.336	0.0017	36.895
	4.533	4.978	0.0002	37.356
	4.148	4.113	0.0099	36.942
C4	4.222	4.236	0.0017	36.895
	4.533	4.718	0.0047	37.362

Atom	$\rho(\Omega)$	$V(\Omega)$	$L(\Omega)$	$G(\Omega)$
C13	4.407	4.904	0.0086	36.958
	4.605	5.342	0.0070	37.342
	4.316	4.547	0.0124	37.009
C15	5.351	8.682	0.0388	37.505
	5.749	9.798	0.0031	38.275
	5.952	11.445	0.0070	38.286
H3A	1.024	8.129	–0.0089	0.635
	0.938	8.061	0.0016	0.585
	0.719	5.623	0.0052	0.440
H3B	1.017	7.299	–0.0117	0.637
	0.925	7.358	0.0006	0.581
	0.718	6.006	0.0048	0.431
H3C	1.013	7.904	–0.0170	0.636
	0.922	7.607	0.0007	0.580
	0.725	5.891	0.0049	0.435
H5A	0.999	6.648	–0.0090	0.630
	0.908	6.554	0.0015	0.571
	0.794	5.475	0.0011	0.478
H5B	1.026	6.579	–0.0099	0.638
	0.940	6.430	0.0008	0.589
	0.784	7.437	0.0007	0.471
H5C	1.015	8.936	–0.0108	0.630
	0.925	8.811	0.0005	0.576
	0.760	5.495	0.0012	0.458
H7A	1.010	5.474	–0.0122	0.643
	0.922	5.531	0.0004	0.583
	0.908	5.413	0.0010	0.559
H7B	0.992	5.687	–0.0101	0.632
	0.909	5.781	0.0010	0.571
	0.893	5.688	0.0000	0.545
H8A	1.052	8.331	–0.0075	0.646
	0.967	7.997	0.0009	0.604
	0.938	7.759	0.0010	0.567
H8B	1.030	7.005	–0.0101	0.641
	0.950	6.992	0.0007	0.594
	0.942	6.679	0.0008	0.578
H10A	1.035	7.249	–0.0096	0.642
	0.952	7.257	0.0008	0.595
	0.931	7.004	0.0011	0.567
H10B	1.036	7.955	–0.0080	0.642
	0.952	8.035	0.0006	0.594

	4.167	3.926	0.0063	36.954		0.923	7.890	0.0007	0.562
C6	4.224	4.135	0.0119	36.893	H11A	0.959	5.773	–0.0179	0.611
	4.536	4.730	0.0022	37.364		0.887	5.994	0.0011	0.551
	4.155	4.003	0.0058	36.939		0.899	6.130	0.0012	0.541
C3	5.425	8.303	0.0364	37.565	H11B	0.990	7.190	–0.0102	0.616
	5.827	9.134	0.0038	38.378		0.925	7.398	0.0005	0.574
	6.284	14.091	–0.0003	38.475		0.903	7.600	–0.0002	0.536
C5	5.446	8.475	0.0348	37.573	H12A	0.930	4.718	–0.0178	0.599
	5.847	9.226	0.0044	38.389		0.868	4.791	0.0014	0.535
	6.190	12.457	0.0057	38.499		0.886	4.717	0.0019	0.546
C7	5.492	7.061	0.0333	37.635	H12B	0.983	7.415	–0.0125	0.613
	5.809	7.598	0.0043	38.373		0.920	7.615	0.0006	0.570
	5.840	7.981	0.0084	38.286		0.907	7.230	0.0008	0.553
C8	5.359	6.945	0.0195	37.534	H15A	1.014	7.029	–0.0079	0.635
	5.619	7.110	0.0056	38.184		0.924	7.189	0.0003	0.577
	5.609	7.457	0.0116	38.051		0.829	5.885	0.0005	0.498
C10	5.325	6.893	0.0223	37.507	H15B	1.001	6.341	–0.0092	0.629
	5.619	7.332	0.0081	38.167		0.916	6.379	0.0008	0.572
	5.599	7.628	0.0092	38.026		0.834	6.326	0.0011	0.505
C11	5.904	8.210	0.0302	37.861	H15C	1.024	6.957	–0.0056	0.635
	6.040	8.371	0.0064	38.438		0.934	7.047	0.0007	0.584
	6.159	8.876	0.0071	38.436		0.826	6.709	0.0006	0.497
C12	5.930	8.487	0.0316	37.880	Total	191.980	391.754	n/a	1628.364
	6.072	8.781	0.0054	38.449		191.977	391.878	n/a	1638.275
	6.086	8.971	0.0075	38.312		191.962	391.261	n/a	1633.509

For properties integrated over the volumes of the atomic basins Ω, the units of measurements are as follows: electron density $\rho(\Omega)$ [e], atomic basin volume $V(\Omega)$ [Å^3], atomic Lagrangian $L(\Omega)$ [e Å^{-2}], kinetic energy $G(\Omega)$ [a.u.]. Potential $\mathcal{V}(\Omega)$ and total $H(\Omega)$ electronic energies can be calculated according to the general virial theorem: $\mathcal{V}(\Omega) = -2G(\Omega)$ and $H(\Omega) = -G(\Omega) = \frac{1}{2}\mathcal{V}(\Omega)$. For the multipole-derived models, $g(\boldsymbol{r})$ was approximated according to Kirzhnits.

Table S3 Selected topological characteristics of the bond critical points for intermolecular contacts between the two heterocyclic moieties of the studied isocyanuric acid derivative in the crystal.

For each interaction, the first, second and third rows of the table contain data obtained from the exact theoretical periodic wavefunction and derived electron density (optimized geometry), the theoretical multipole model (optimized geometry) and the final, experimental model after the transfer procedure.

Contact *i*–*j*	R_{ij}	d_i	d_j	ρ_b	$\nabla^2\rho_b$	λ_{1_b}	λ_{2_b}	λ_{3_b}	g_b	v_b	h_b
	3.34505	1.690	1.664	0.0389	0.5477	–0.1020	–0.0683	0.7180	$4.42\cdot10^{-3}$	$-3.15\cdot10^{-3}$	$1.27\cdot10^{-3}$
N1···N5	3.34505	1.662	1.689	0.0357	0.4877	–0.0819	–0.0482	0.6193	$3.83\cdot10^{-3}$	$-2.61\cdot10^{-3}$	$1.23\cdot10^{-3}$
	3.3632(3)	1.705	1.668	0.0383	0.4837	–0.0771	–0.0386	0.6000	$3.86\cdot10^{-3}$	$-2.71\cdot10^{-3}$	$1.16\cdot10^{-3}$
	3.20282	1.675	1.639	0.0419	0.6047	–0.1029	–0.0849	0.7926	$4.97\cdot10^{-3}$	$-3.67\cdot10^{-3}$	$1.30\cdot10^{-3}$
O6···N3	3.20282	1.577	1.643	0.0393	0.5562	–0.0916	–0.0699	0.7181	$4.39\cdot10^{-3}$	$-3.01\cdot10^{-3}$	$1.38\cdot10^{-3}$
	3.2135(3)	1.578	1.651	0.0415	0.5609	–0.0916	–0.0675	0.7206	$4.47\cdot10^{-3}$	$-3.13\cdot10^{-3}$	$1.35\cdot10^{-3}$

Subscript *b* denotes the values given at a corresponding saddle critical points (3, –1) in $\rho(\boldsymbol{r})$ or this point itself. R_{ij} is the covalent bond distance [Å]; d_i and d_j are the distances from atom *i* or *j* to a corresponding bond critical point; ρ_b is the value of electron density at a BCP [e Å^{-3}]; $\nabla^2\rho_b$ is the Laplacian of electron density [e Å^{-5}]; λ_{1_b}, λ_{2_b} and λ_{3_b} are the eigenvalues of Hessian matrix of electron density [e Å^{-5}]; g_b, v_b and h_b are the kinetic, potential, and total electronic energy densities [a.u.], respectively. For the multipole-derived models, $g(\boldsymbol{r})$ was approximated according to Kirzhnits.