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Supporting information for article:

Exploring the rare S-H···S hydrogen bond using charge density analysis in isomers of mercaptobenzoic acid

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Supporting information

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Figure S8: Comparison of integrated QTAIM charges for all the atoms in 2 -mercaptobenzoic acid calculated using different DFT functional.

Table S1 Topological parameters for intramolecular covalent bonds obtained from experimental multipole and theoretical TOPOND model in 2-mercaptobenzoic acid (1st Line Experimental and 2nd Line theoretical in *italics*).

	R_{ij} (Å)	ρ (eÅ^{-3})	$\nabla^2\rho$ (eÅ^{-5})	λ_1	λ_2	λ_3	ε
S1–C3	1.770	1.26(2)	-5.39(4)	-7.67	-7.05	9.32	0.09
		1.26	*-2.63*	*-5.01*	*-3.45*	*5.83*	*0.46*
S1–H1S	1.307	1.54(5)	-13.6(1)	-12.15	-8.33	6.90	0.46
		1.35	*-0.67*	*-6.34*	*-4.92*	*10.58*	*0.29*
O1–C1	1.318	2.28(3)	-25.3(1)	-21.10	-16.84	12.67	0.25
		2.18	*-16.39*	*-17.38*	*-17.28*	*18.24*	*0.01*
O1–H1O	1.006	2.23(6)	-39.0(5)	-35.82	-35.23	32.00	0.02
		1.98	*-47.11*	*-34.68*	*-34.20*	*21.74*	*0.01*
O2–C1	1.232	2.86(3)	-39.0(2)	-28.18	-24.23	13.38	0.16
		2.67	*-10.43*	*-24.41*	*-22.73*	*36.73*	*0.07*
C1–C2	1.480	1.84(2)	-13.77(5)	-14.06	-11.42	11.71	0.23
		1.85	*-18.65*	*-13.88*	*-12.41*	*7.66*	*0.12*
C2–C3	1.410	1.97(2)	-15.89(6)	-15.23	-11.70	11.04	0.30
		2.02	*-20.05*	*-14.92*	*-12.58*	*7.45*	*0.19*
C2–C7	1.405	2.04(2)	-16.33(6)	-15.32	-12.39	11.39	0.24
		2.06	*-20.72*	*-15.23*	*-12.94*	*7.42*	*0.18*

Table S2 Topological parameters for intramolecular covalent bonds obtained from theoretical TOPOND model in 3-mercaptobenzoic acid

	R_{ij} (Å)	ρ (eÅ^{-3})	$\nabla^2\rho$ (eÅ^{-5})	λ_1	λ_2	λ_3	ε
O2–H2	0.995	1.950	-46.37	-34.63	-34.20	22.46	0.01
C5–H5	1.067	1.923	-24.32	-18.29	-18.15	12.15	0.01
C6–H6	1.067	1.937	-24.75	-18.80	-18.68	12.70	0.01
C3–H3	1.068	1.923	-24.34	-18.44	-18.22	12.29	0.01

C2–H2A	1.068	1.930	-24.44	-18.44	-18.27	12.27	0.01
O1–C7	1.261	2.531	-16.70	-22.00	-20.63	25.93	0.07
O2–C7	1.290	2.308	-12.94	-19.45	-19.28	25.79	0.01
S1–H1	1.325	1.336	-0.70	-6.27	-4.80	10.34	0.31
C3–C2	1.377	2.173	-23.09	-16.46	-13.98	7.37	0.18
C5–C6	1.385	2.132	-22.00	-15.93	-13.45	7.37	0.18
C1–C6	1.389	2.126	-22.19	-15.93	-13.62	7.35	0.17
C4–C3	1.392	2.099	-21.38	-15.62	-13.13	7.37	0.19
C1–C2	1.403	2.065	-20.80	-15.33	-12.89	7.45	0.19
C4–C5	1.404	2.065	-20.82	-15.35	-13.01	7.54	0.18
C1–C7	1.482	1.856	-18.89	-13.93	-12.68	7.71	0.10
S1–C4	1.777	1.255	-3.78	-5.06	-3.52	4.80	0.44

Table S3 Topological parameters for intramolecular covalent bonds obtained from theoretical TOPOND model in 4-mercaptobenzoic acid

	R_{ij} (Å)	ρ (eÅ^{-3})	$\nabla^2\rho$ (eÅ^{-5})	λ_1	λ_2	λ_3	ε
O2–H2	0.993	1.991	-47.09	-34.80	-34.29	22.00	0.02
C5–H5	1.067	1.937	-24.82	-18.77	-18.68	12.63	0.01
C6–H6	1.068	1.917	-24.17	-18.29	-18.05	12.17	0.01
C3–H3	1.068	1.923	-24.34	-18.41	-18.15	12.22	0.02
C2–H2A	1.068	1.923	-24.20	-18.29	-18.17	12.27	0.01
O1–C7	1.235	2.659	-11.13	-24.22	-22.75	35.83	0.07
O2–C7	1.321	2.180	-17.21	-17.45	-17.33	17.54	0.01
S1–H1	1.326	1.329	-0.36	-6.24	-4.72	10.60	0.32
C3–C2	1.379	2.153	-22.48	-16.22	-13.57	7.30	0.20
C5–C6	1.382	2.146	-22.44	-16.17	-13.59	7.35	0.19
C1–C6	1.393	2.105	-21.79	-15.76	-13.45	7.42	0.17

C4–C3	1.395	2.092	-21.35	-15.57	-13.21	7.42	0.18
C1–C2	1.398	2.092	-21.45	-15.62	-13.28	7.45	0.18
C4–C5	1.402	2.065	-20.87	-15.33	-12.97	7.42	0.18
C1–C7	1.476	1.869	-19.13	-14.07	-12.72	7.66	0.11
S1–C4	1.769	1.275	-3.54	-5.25	-3.59	5.30	0.46

Table S4 Monopole Populations, Radial Parameters and Net Atomic Charges

Atom	Pval	Kappa	P00	Kappa'	Atomic charge
S(1)	6.05	0.996	0	1.099	-0.0504
O(1)	6.149	0.996	0	1.003	-0.1487
O(2)	6.173	0.994	0	0.918	-0.1728
C(1)	4.036	1	0	0.972	-0.0357
C(2)	3.911	1.006	0	0.965	0.0893
C(3)	4.019	0.996	0	0.981	-0.019
C(4)	4.197	0.994	0	0.958	-0.1965
C(5)	4.066	1.003	0	0.973	-0.0659
C(6)	4.382	0.98	0	0.958	-0.3816
C(7)	4.232	0.995	0	0.96	-0.2317
H(1O)	0.691	1.2	0	1.2	0.3092
H(4)	0.812	1.2	0	1.2	0.1883
H(5)	0.823	1.2	0	1.2	0.177
H(6)	0.759	1.2	0	1.2	0.241
H(7)	0.788	1.2	0	1.2	0.2124
H(1S)	0.915	1.2	0	1.2	0.0847

Table S5 Dipole Population Parameters

Atom	D11+	D11-	D10
S(1)	0.013	-0.128	-0.105
O(1)	-0.037	-0.06	-0.05
O(2)	0.028	0.011	-0.081
C(1)	0.009	-0.044	0.073
C(2)	0.007	0.037	0.032
C(3)	-0.003	0.027	0.033
C(4)	-0.034	0.043	-0.038
C(5)	-0.019	0.012	-0.013
C(6)	0.019	-0.024	0.055
C(7)	-0.015	0.026	-0.008
H(1O)	0	0	0.189
H(4)	0	0	0.084
H(5)	0	0	0.145
H(6)	0	0	0.056
H(7)	0	0	0.171
H(1S)	0	0	0.207

Table S6 Quadrupole Population Parameters

Atom	Q20	Q21+	Q21-	Q22+	Q22-
S(1)	-0.155	-0.141	0.14	0.141	-0.069
O(1)	-0.015	0.045	0.015	0.037	-0.038
O(2)	-0.078	0	-0.004	-0.063	0.08
C(1)	0.183	-0.013	0.023	-0.201	-0.05
C(2)	0.041	0.016	0.008	-0.063	0.061
C(3)	0.114	-0.067	-0.059	-0.093	-0.011
C(4)	0.127	-0.075	-0.004	-0.098	-0.045
C(5)	0.077	0.061	0.012	-0.159	0.047
C(6)	0.088	-0.005	-0.029	-0.134	0.046

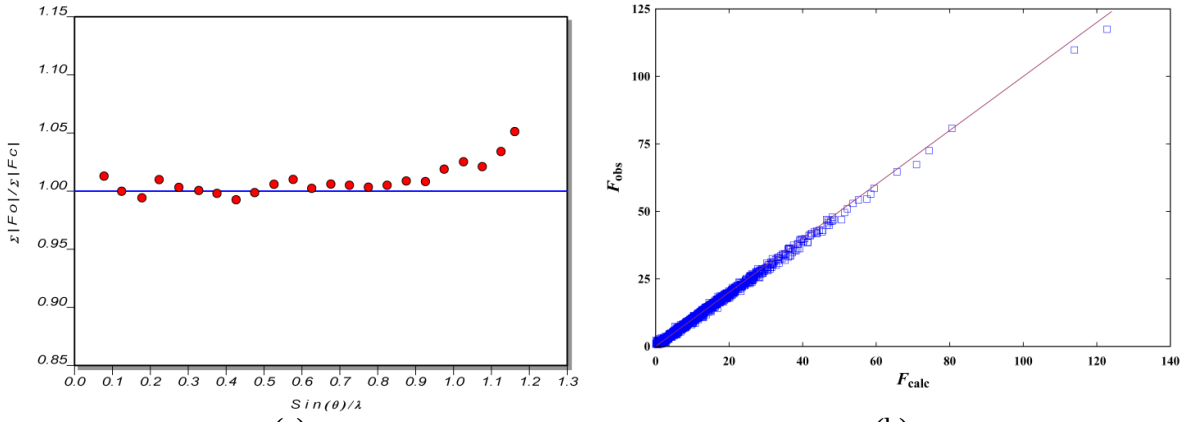
C(7)	0.087	-0.049	0.025	-0.172	0.022
H(1O)	0.139	0	0	0	0
H(4)	0.004	0	0	0	0
H(5)	0.019	0	0	0	0
H(6)	-0.057	0	0	0	0
H(7)	0.022	0	0	0	0
H(1S)	0.099	0	0	0	0

Table S7 Octupole Population Parameters.

Atom	O30	O31+	O31-	O32+	O32-	O33+	O33-
S(1)	0.142	-0.011	0.033	0.036	0.011	-0.017	0.008
O(1)	0.078	0.022	-0.019	0.032	0.013	-0.015	0.026
O(2)	0.025	0	0.037	0.029	0.003	0.037	0.02
C(1)	0.334	0.031	-0.036	0.224	-0.004	-0.029	0.01
C(2)	0.163	-0.029	0.018	0.142	-0.002	0.035	-0.003
C(3)	0.231	-0.012	-0.015	0.188	0.009	-0.008	0.034
C(4)	0.222	-0.062	0.111	0.157	0.004	-0.033	-0.002
C(5)	0.269	-0.005	-0.051	0.132	0.007	0.004	-0.009
C(6)	0.256	-0.014	-0.105	0.156	0.005	-0.014	0.019
C(7)	0.205	-0.009	0.096	0.188	0.007	-0.026	0.024

Table S8 Hexadecapole Population Parameters

Atom	H40	H41+	H41-	H42+	H42-	H43+	H43-	H44+	H44-
S(1)	0.025	0.061	-0.007	0.1	-0.008	-0.075	-0.041	0.125	0.011
O(1)	0	0	0	0	0	0	0	0	0
O(2)	0	0	0	0	0	0	0	0	0
C(1)	0	0	0	0	0	0	0	0	0
C(2)	0	0	0	0	0	0	0	0	0
C(3)	0	0	0	0	0	0	0	0	0
C(4)	0	0	0	0	0	0	0	0	0
C(5)	0	0	0	0	0	0	0	0	0
C(6)	0	0	0	0	0	0	0	0	0
C(7)	0	0	0	0	0	0	0	0	0



(a) (b)

Figure S1 (a) ΣF_{obs} /ΣF_{cal} binned with resolution shells and plotted against (sinθ)/λ. (b) Scatter plots depicting the variation of F_{obs} with F_{cal} for 2-mercaptobenzoic acid.

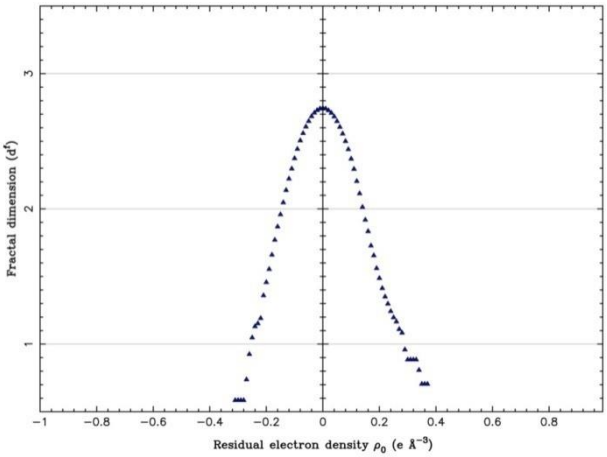


Figure S2 Fractal dimension plot for experimental multipole refinement on 2-mercaptobenzoic acid.

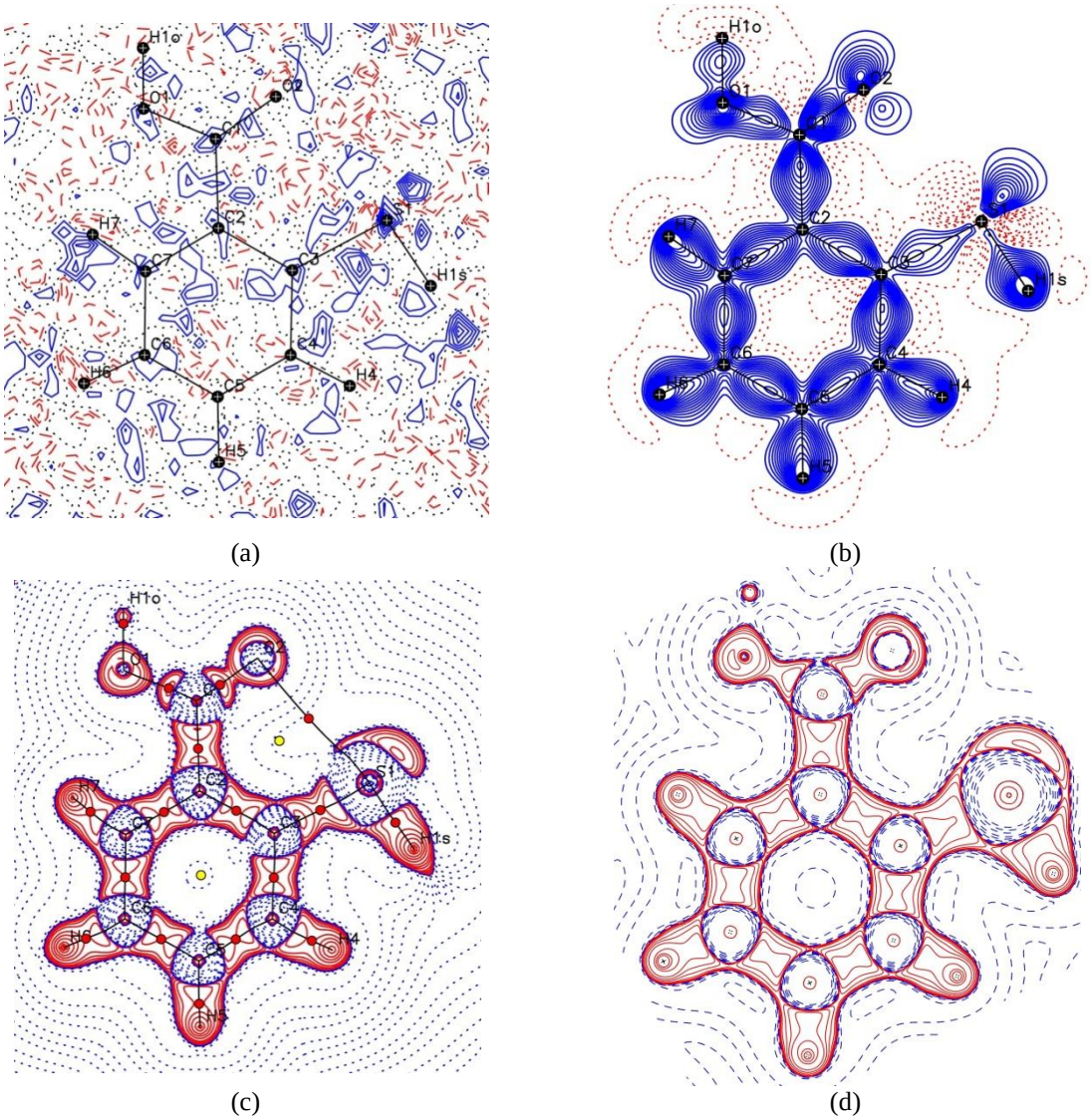
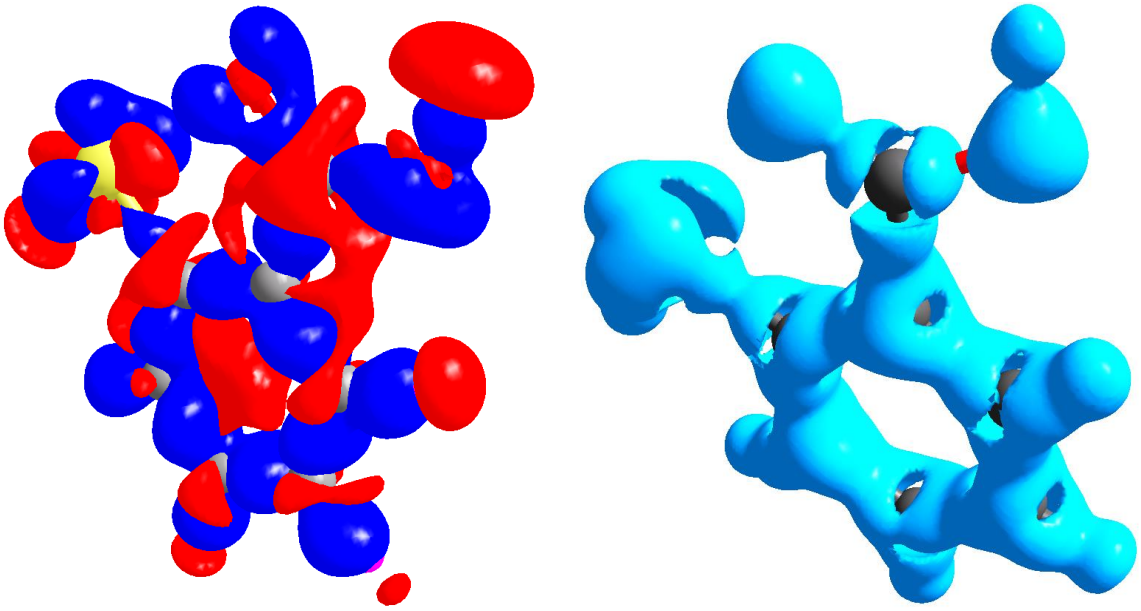


Figure S3 (a) Residual density (b) deformation density ($\Delta\rho(r)= \rho_{multipole}-\rho_{spherical}$) (c) Laplacian maps obtained after multipolar refinement of the experimental charge density data of 2-

mercaptobenzoic acid. (d) Laplacian map obtained from theory. Blue (solid lines), red (broken lines) colors represent positive, negative contours respectively (reversed in case of Laplacian). Contours are drawn at the intervals of ±0.05 eÅ^{-3}. Laplacian is plotted on logarithmic contours.



(a) (b)

Figure S4 3D deformation density and 3D Laplacian plot of the interaction region from (a) & (b) intramolecular S···O chalcogen bonding. Blue represents charge concentration (CC) and red represents charge depletion (CD) in deformation maps drawn at the intervals of ±0.08 eÅ^{-3}. 3D Laplacian isosurfaces is plotted at 2 eÅ^{-5}.

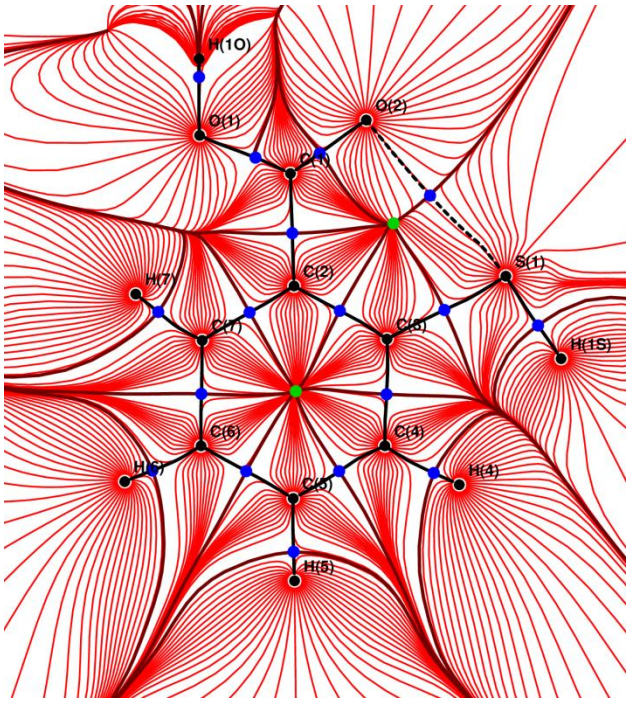
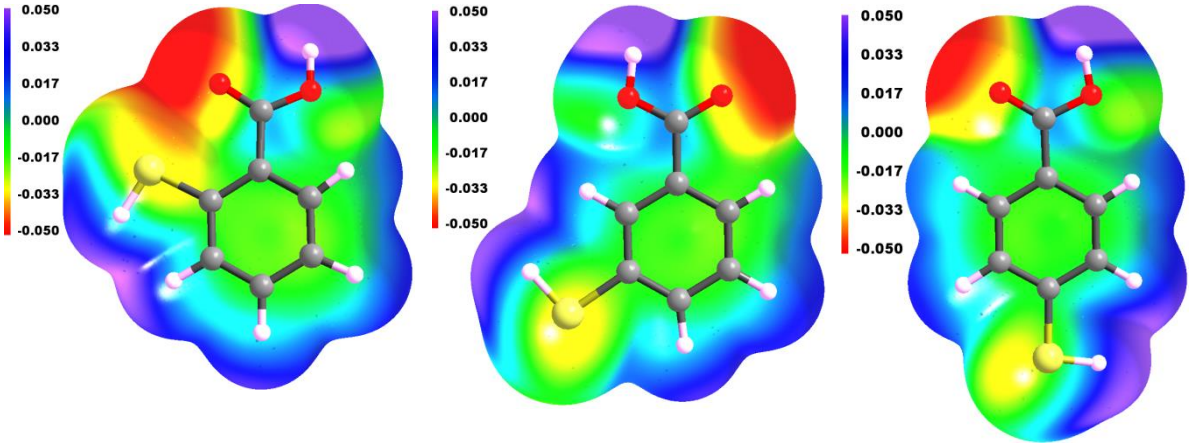


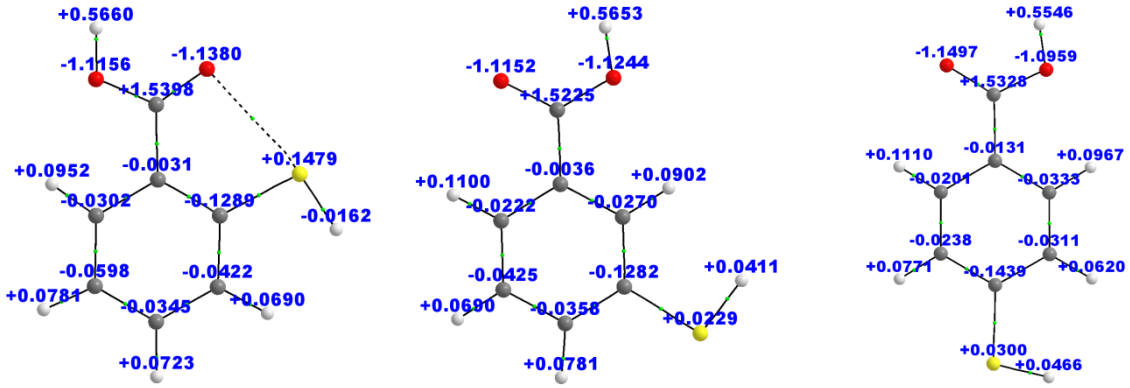
Figure S5 Gradient density trajectory map for 2-mercaptobenzoic acid. The gradient vector field, shown in terms of trajectories of ∇ρ, is indicated with red lines. The zero flux surfaces are displayed

by brown lines. Intramolecular bond paths are indicated by heavy and dashed black lines, respectively. The (3, –3) and (3, –1) critical points are shown, respectively, by the black and blue colored dots.



2-mercaptobenzoic acid 3-mercaptobenzoic acid 4-mercaptobenzoic acid

Figure S6 ESP map is drawn at isoelectron density surface at 0.001 a.u. for gas phase geometry of 2,3,4-mercaptobenzoic acids respectively. The calculations are done at wB97XD/6-311+g(d,p) level.



2-mercaptobenzoic acid 3-mercaptobenzoic acid 4-mercaptobenzoic acid

Figure S7 Integrated QTAIM charges for all the atoms in 2,3,4-mercaptobenzoic acid respectively. The wavefunction calculations are done at wB97XD/6-311+g(d,p) level.

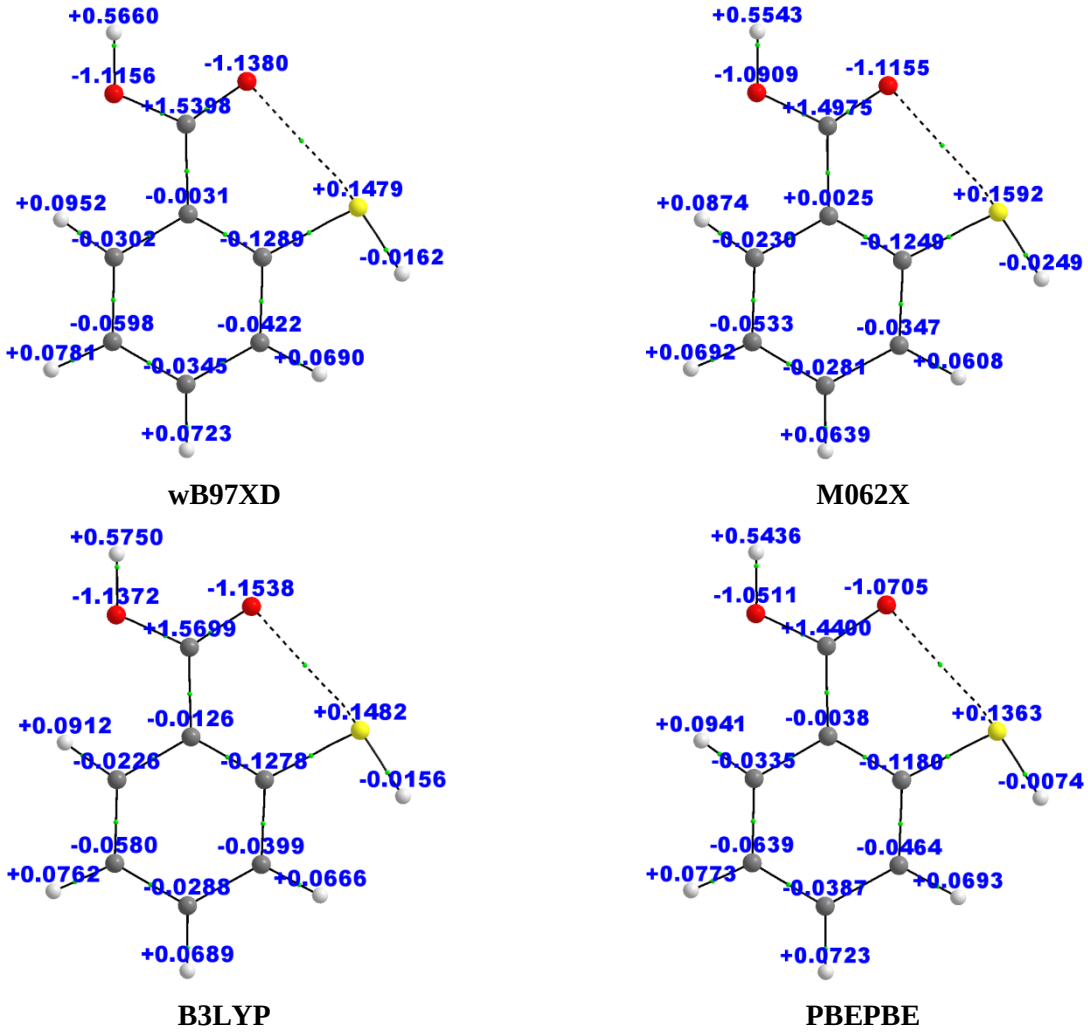


Figure S8 Comparison of integrated QTAIM charges for all the atoms in 2 -mercaptobenzoic acid calculated using different DFT functional.