STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Volume 76 (2020)

Supporting information for article:

Crystal structure, vibrational frequencies and polarizability distribution in hydrogen-bonded salts of pyromellitic acid

Leonardo H. R. Dos Santos, Anna Krawczuk, Chris H. J. Franco and Renata Diniz

Supporting information

S1. Characterization of compounds 1-4

Table S1 X-ray diffraction data collection and refinement details

Compound	**1**		**2**		**3**		**4**	
Temperature / K	120	293	120	293	120	293	120	293
Chemical formula	$C_{20}H_{26}N_4O_{12}$	$C_{20}H_{26}N_4O_{12}$	$C_{22}H_{16}N_2O_{12}$	$C_{22}H_{16}N_2O_{12}$	$C_{24}H_{24}N_2O_{14}$	$C_{24}H_{24}N_2O_{14}$	$C_{24}H_{20}N_2O_{12}$	$C_{24}H_{20}N_2O_{12}$
CCDC code	1960157	1960161	1960158	1960162	1960159	1960163	1960160	1960164
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a / Å	9.1747 (2)	9.2348 (2)	7.1378 (1)	7.0774 (2)	7.3815 (4)	7.4644 (3)	6.5293 (3)	6.6312 (2)
b / Å	17.6168 (4)	17.6801 (4)	7.3637 (2)	7.5332 (3)	7.7144 (4)	7.7371 (3)	9.5176 (5)	9.5284 (3)
c / Å	7.2527 (2)	7.3278 (2)	19.3563 (4)	19.4180 (6)	10.3085 (5)	10.3355 (4)	9.8073 (5)	9.8203 (3)
α / °	90	90	90	90	79.986 (4)	80.204 (3)	66.586 (5)	66.511 (3)
β / °	100.559 (2)	101.340 (2)	95.135 (2)	94.931 (3)	89.329 (4)	89.508 (3)	88.062 (4)	87.534 (2)
γ / °	90	90	90	90	88.548 (4)	87.937 (3)	83.612 (4)	83.336 (2)
V / Å^3	1152.40 (5)	1173.07 (5)	1013.30 (4)	1031.45 (6)	577.86 (5)	587.82 (4)	555.77 (5)	565.25 (3)
Z	2	2	2	2	1	1	1	1

D_c / Mg m^{-3}	1.483	1.456	1.640	1.611	1.622	1.594	1.579	1.552
F(000)	540	540	516	516	294	294	274	274
Crystal size / mm	0.40 × 0.37 × 0.35	0.40 × 0.37 × 0.35	0.20 × 0.15 × 0.15	0.20 × 0.15 × 0.15	0.42 × 0.40 × 40	0.99 × 0.49 × 0.34	0.40 × 0.35 × 0.33	0.40 × 0.35 × 0.33
μ / mm^{-1}	0.124	0.122	0.137	0.134	0.136	0.133	0.129	0.127
T_{min} / T_{max}	0.791/1.000	0.800/1.000	0.971/1.000	0.791/1.000	0.829/1.000	0.925/1.000	0.939/1.000	0.853/1.000
No. of measured, independent reflections	24298, 4070	23723, 6041	21726, 3567	5414, 2441	12130, 3928	14512, 3019	12081, 3772	15972, 3895
No. of observed [$I > 2\sigma(I)$] reflections	3324	3343	3050	1707	3087	2553	3071	3303
θ range / °	2.3-32.8	3.1-37.9	2.1-32.9	2.9-29.5	2.7-32.8	2.6-29.6	2.3-32.6	3.1-32.8
Range of h, k, l	-13 ≤ h ≤ 13	-15 ≤ h ≤ 13	-10 ≤ h ≤ 10	-7 ≤ h ≤ 9	-11 ≤ h ≤ 11	-9 ≤ h ≤ 10	-9 ≤ h ≤ 9	-10 ≤ h ≤ 9
	-26 ≤ k ≤ 26	-29 ≤ k ≤ 29	-11 ≤ k ≤ 11	-10 ≤ k ≤ 7	-11 ≤ k ≤ 11	-10 ≤ k ≤ 10	-13 ≤ k ≤ 14	-14 ≤ k ≤ 14
	-10 ≤ l ≤ 10	-9 ≤ l ≤ 12	-29 ≤ l ≤ 29	-26 ≤ l ≤ 23	-15 ≤ l ≤ 15	-14 ≤ l ≤ 14	-14 ≤ l ≤ 14	-14 ≤ l ≤ 14
R_{int}	0.035	0.040	0.037	0.025	0.031	0.030	0.031	0.031
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0415, 0.109, 1.04	0.0481, 0.125, 0.86	0.0403, 0.109, 1.06	0.0337, 0.0872, 0.95	0.0413, 0.120, 1.05	0.0421, 0.121, 1.03	0.0413, 0.118, 1.04	0.0443, 0.134, 1.07
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e Å^{-3}	0.45, –0.45	0.40, –0.33	0.50, –0.35	0.24, –0.16	0.36, –0.33	0.27, –0.30	0.46, –0.30	0.40, –0.42

$R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$, $wR = \Sigma[w(F_o^2-F_c^2)^2]^{1/2}/\Sigma[w(F_o^2)^2]^{1/2}$, $S = \Sigma[w(F_o^2-F_c^2)^2]^{1/2}/(n-p)^{1/2}$, $R_{int} = \Sigma[n/(n-1)]^{1/2}\Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma(F_o^2)$

Table S2 Elemental analysis

	1		**2**		**3**		**4**	
	$C_{20}H_{26}N_4O_{12}$		$C_{22}H_{16}N_2O_{12}$		$C_{24}H_{24}N_2O_{14}$		$C_{24}H_{20}N_2O_{12}$	
	Anal. Calc.	Found	Anal. Calc.	Found	Anal. Calc.	Found	Anal. Calc.	Found
%C	46.69	48.56	52.80	55.18	51.06	53.61	54.55	51.82
%H	5.10	4.85	3.23	3.36	4.29	4.46	3.82	4.05
%N	10.89	10.78	5.60	5.49	4.96	5.01	5.30	5.46

Besides the well-known ability of carboxylic acids to crystallize as hydrogen-bonded dimers, samples of **1**-**4** are morphologically homogeneous, thus attesting purity. Powder X-ray diffraction could not be performed because just a few single crystals of each compound were obtained.

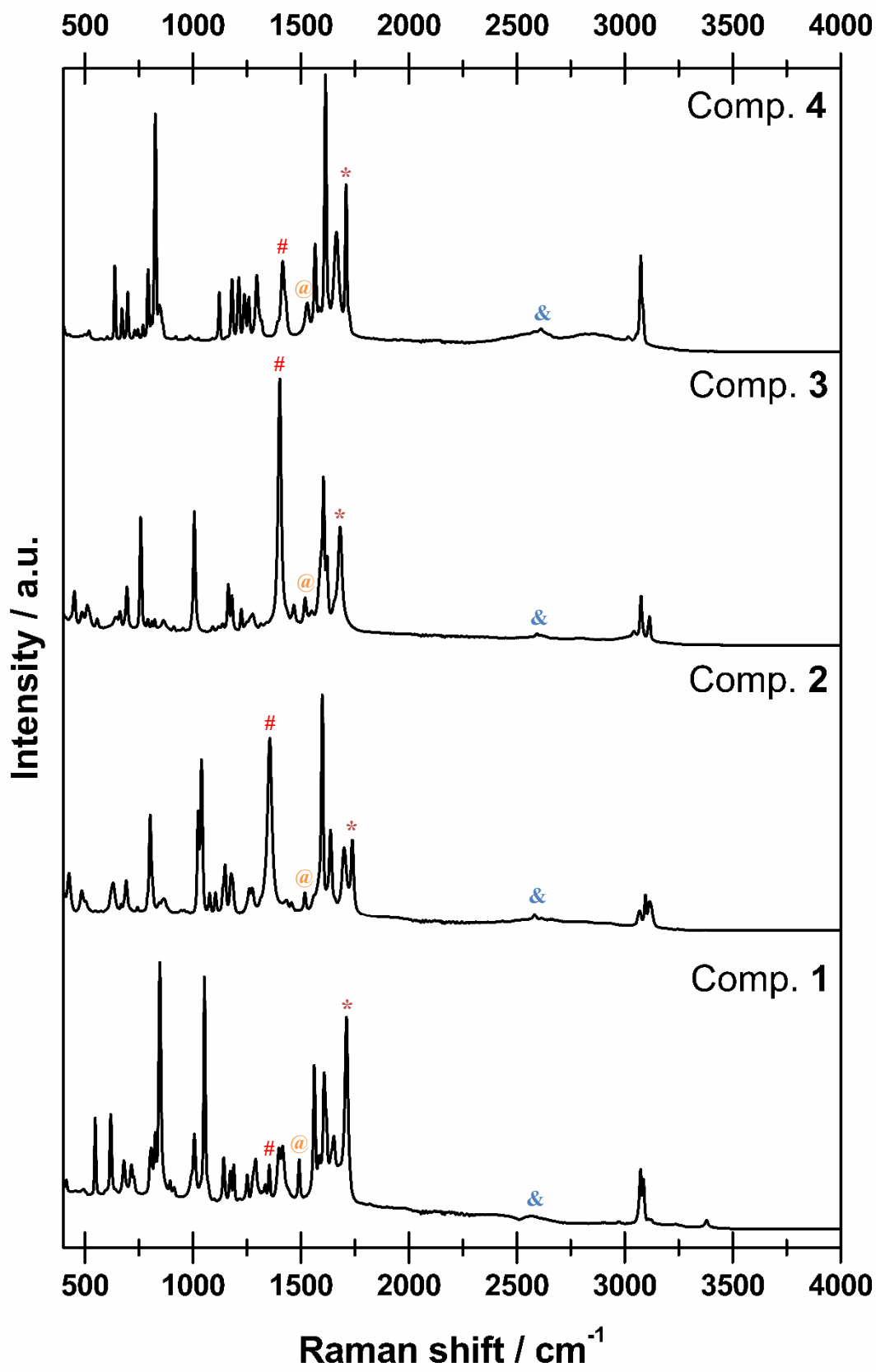
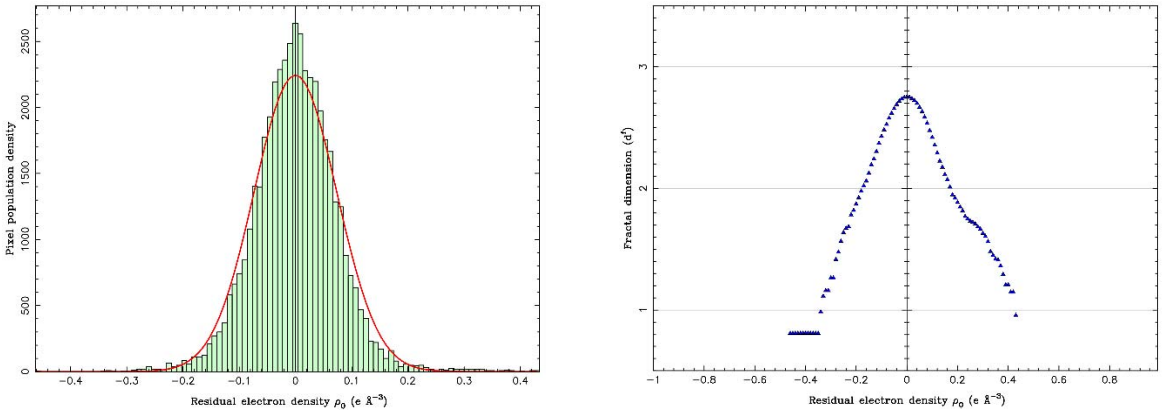


Figure S1 Experimental Raman spectra of compounds **1**-**4**. (#): ν_{sym}(COO) + δ(OH); (@): ν_{asym}(COO); (*): ν(C=O); (&): ν(OH)$_{SHB}$.

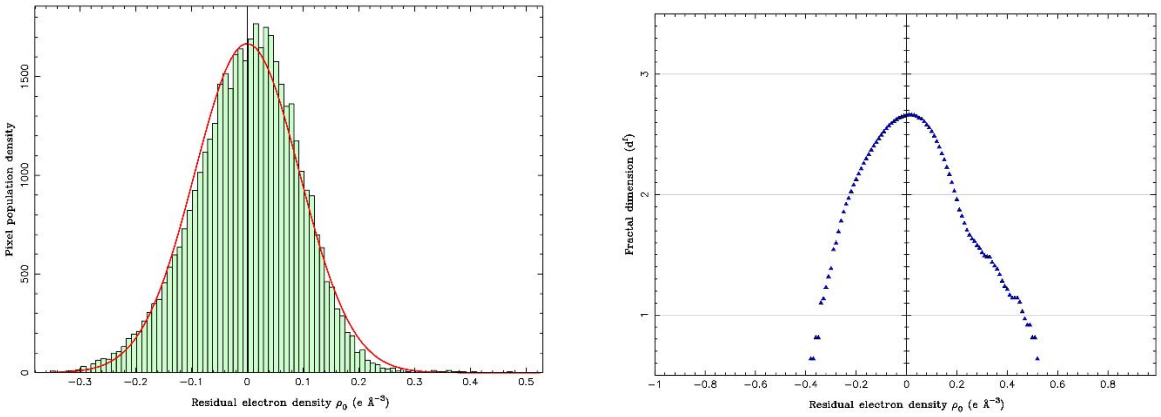
S2. Residual density analysis

The residual density analysis, as described by Meindl & Henn [Meindl, K. & Henn, J. (2008). *Acta Cryst.* A**64**, 404-418], was performed on the single-crystal X-ray diffraction data collected at 120 K using the PIXELstats module of WinGX.

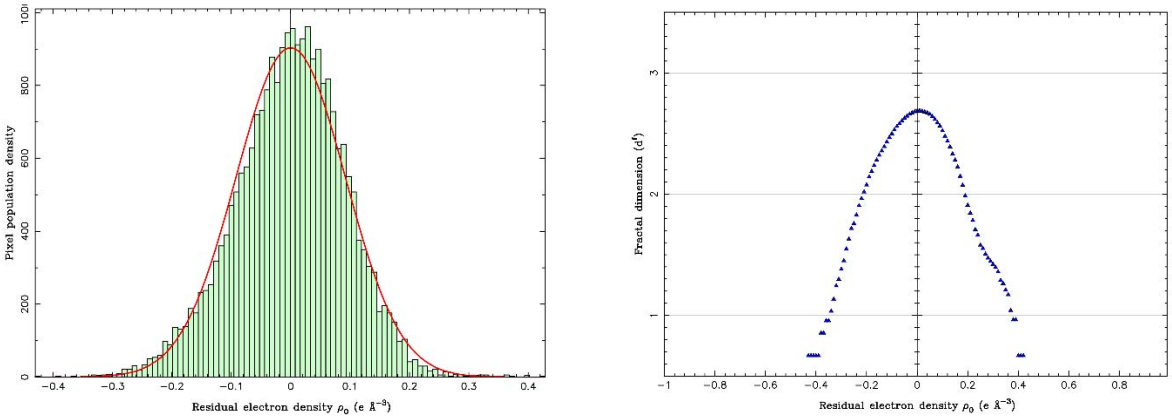
S2.1. Residual density analysis of compound 1



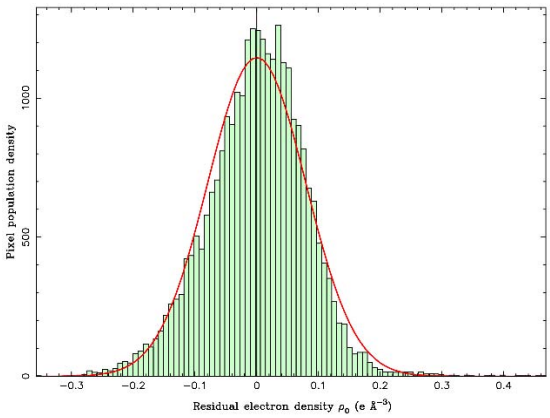
S2.2. Residual density analysis of compound 2

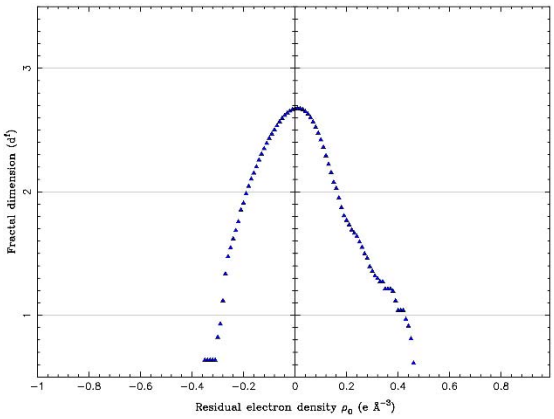


S2.3. Residual density analysis of compound 3



S2.4. Residual density analysis of compound 4





S3. Topological analysis of hydrogen bonds

Topological investigation [Blatov, A. P., Shevchenko, A. P. & Prosepio, D. M. (2014). *Cryst. Growth Des.*, **14**, 3576-3586] of the hydrogen bonds in compounds **1**-**4** was performed using the *ToposPro* software. The most important intermolecular hydrogen bonds were considered in network extension and in all cases the nets were simplified in two steps. In the first one, the H atoms involved in hydrogen bonds were chosen as central atoms, thus generating an intermediary topological arrangement. For compounds **1** and **3**, in which crystallization water molecules are present, the molecules were grouped in four kinds of nodes: one corresponding to the cation molecule, one associated to the pyromellitate ion, one for the H atoms involved in the hydrogen bonds, and one for O atoms in water molecules. Of course, for the anhydrous compounds **2** and **4**, only three kinds of nodes were defined. However, this simplification did not provide an adequate description of the network. In a further step, nodes associated to the pyromellitate anions was chosen as "central atoms". The obtained underlying networks are displayed in Fig. S2.

After the simplification, all structures could be classified as three-dimensional (3D) uninodal nets, but the connectivity is different. The structure of **1** is described as a (14)-connected system with a point symbol ($3^{36}.4^{48}.5^{7}$). The net is of type ***bcu-x***, with cubic symmetry $Im\bar{3}m$, transitivity [1211] and signature [3^4]. The nets for **3** and **4** are identical, and classified as ***fcu*** with cubic symmetry $Im\bar{3}m$, transitivity [1112] and showing two different tiles with signature 2[3^4] + [3^8]. Compound **2** reveals an unprecedented topological net type.

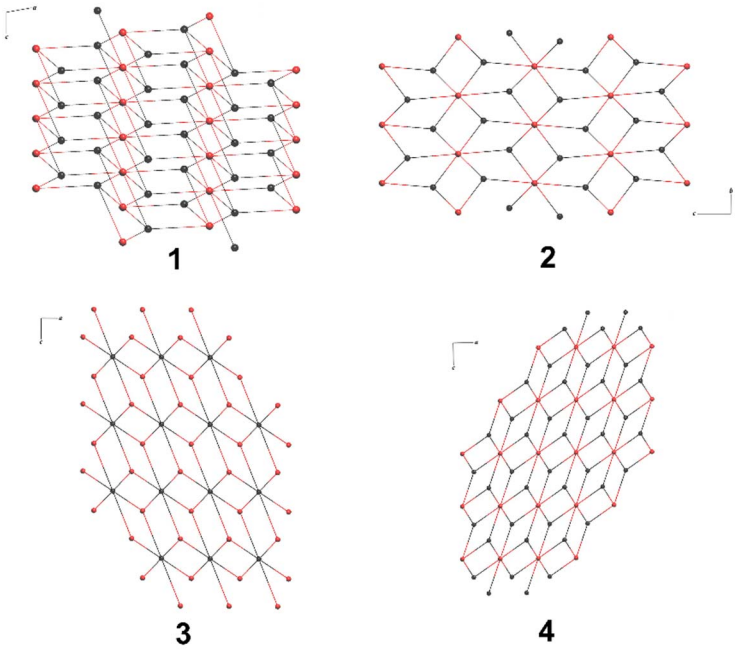
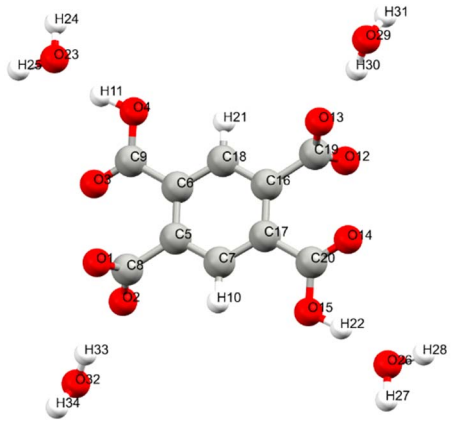


Figure S2 Simplified nets for compounds **1**-**4**. Red spheres denote nodes obtained from simplification of pyromellitate anions whereas black spheres denote nodes obtained from either the cations or crystallization water molecules.

S4. Diagonalized atomic polarizability tensor components (in au) for aggregates

S4.1. Aggregate extracted from compound 1 (corresponding to interactions 1 and 2)



Atom	α_{11}	α_{22}	α_{33}	α_{ISO}
O1	3.140	7.012	10.036	6.730
O2	2.661	3.388	20.225	8.758
O3	2.761	5.168	9.299	5.743
O4	2.458	3.628	11.977	6.021
C5	2.388	7.915	10.905	7.069
C6	2.567	9.861	10.696	7.708
C7	2.942	5.421	10.901	6.421
C8	1.839	3.489	10.720	5.349
C9	1.176	4.384	6.577	4.045
H10	0.538	0.744	3.203	1.495
H11	-0.032*	0.062	1.702	0.577
O12	3.144	6.945	10.019	6.703
O13	2.658	3.359	20.200	8.739
O14	2.734	5.101	9.306	5.714
O15	2.465	3.554	11.870	5.963
C16	2.388	7.954	10.905	7.082
C17	2.554	9.549	10.670	7.591
C18	2.921	5.407	10.978	6.436
C19	1.807	3.498	10.811	5.372

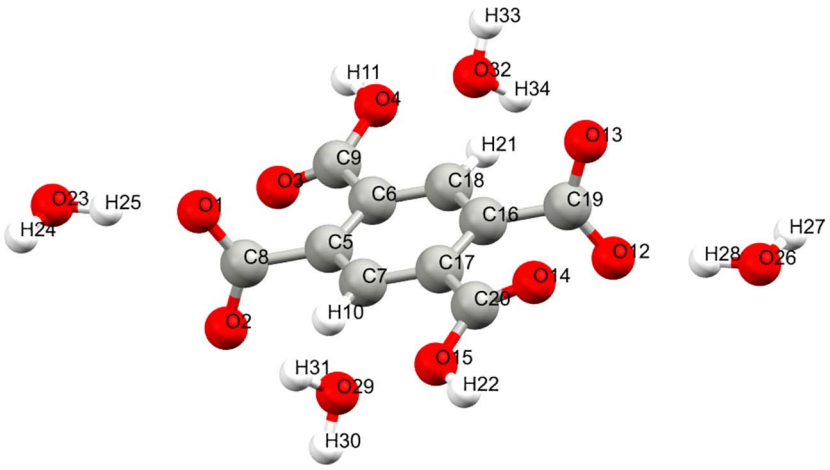
C20	1.138	4.312	5.918	3.789
H21	0.534	0.744	3.200	1.493
H22	-0.021*	0.058	1.617	0.551
O23	3.485	5.277	9.038	5.933
H24	0.209	0.285	1.950	0.815
H25	0.175	0.367	1.290	0.610
O26	3.481	5.164	8.964	5.870
H27	0.213	0.271	1.894	0.793
H28	0.176	0.367	1.226	0.590
O29	4.001	4.565	12.520	7.029
H30	0.155	0.212	3.324	1.230
H31	0.321	0.383	1.923	0.876
O32	4.033	4.580	12.520	7.044
H33	0.153	0.211	3.334	1.233
H34	0.318	0.391	1.953	0.887

***** In general, QTAIM integration inside an atomic basin implies that eventual regions that would respond counterintuitively to the applied electric field (i.e. potentially generating negative atomic diagonal tensor components) are typically overwhelmed by those of positive polarizability, thus producing the expected result that on average the overall electron density responds intuitively to the applied field. Therefore, atoms in molecular systems may in principle have negative atomic tensor components. In practice, this is unlike to occur for atoms with an electronic core, which implies a sufficiently large basin, but it could eventually be observed for H atoms, especially when involved in moderate-to-strong hydrogen bonds, for which they tend to exhibit smaller and irregular atomic basins. For detailed discussion, see:

(1) Dos Santos, L. H. R. & Macchi, P. (2016). *Crystals* **6**, 43.

(2) Otero, N., Van Alsenoy, C., Pouchan, C. & Karamanis, P. (2015). *J. Comput. Chem.* **36**, 1831-1843.

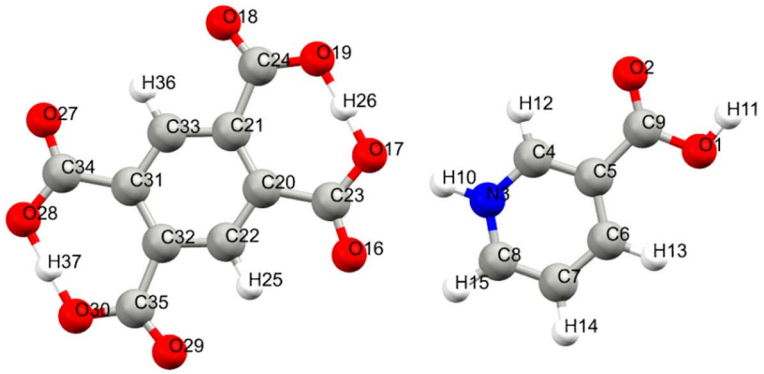
S4.2. Aggregate extracted from compound 1 (corresponding to interactions 3 and 4)



Atom	α_{11}	α_{22}	α_{33}	α_{ISO}
O1	5.201	7.360	19.128	10.563
O2	5.101	8.395	16.409	9.969
O3	4.713	7.333	13.433	8.493
O4	4.642	5.033	14.388	8.021
C5	3.730	12.854	15.489	10.691
C6	3.936	12.851	17.822	11.536
C7	4.543	7.341	18.511	10.132
C8	3.413	5.452	13.299	7.388
C9	2.162	4.688	11.204	6.018
H10	1.025	1.136	4.426	2.196
H11	0.266	0.428	3.399	1.364
O12	5.180	7.354	19.114	10.549
O13	5.099	8.376	16.430	9.968
O14	4.714	7.347	13.427	8.496
O15	4.694	5.037	14.448	8.060
C16	3.731	12.869	15.412	10.671
C17	3.926	12.863	17.916	11.568
C18	4.543	7.266	18.461	10.090

C19	3.439	5.417	13.309	7.388
C20	2.160	4.701	11.265	6.042
H21	1.024	1.135	4.431	2.197
H22	0.266	0.428	3.397	1.364
O23	7.596	8.797	13.426	9.940
H24	0.576	0.612	2.856	1.348
H25	0.219	0.294	3.553	1.355
O26	7.605	8.801	13.417	9.941
H27	0.577	0.613	2.858	1.349
H28	0.212	0.292	3.551	1.352
O29	6.777	7.694	11.204	8.559
H30	0.551	0.599	3.274	1.474
H31	0.265	0.285	2.508	1.019
O32	6.770	7.703	11.204	8.559
H33	0.552	0.598	3.276	1.475
H34	0.264	0.285	2.508	1.019

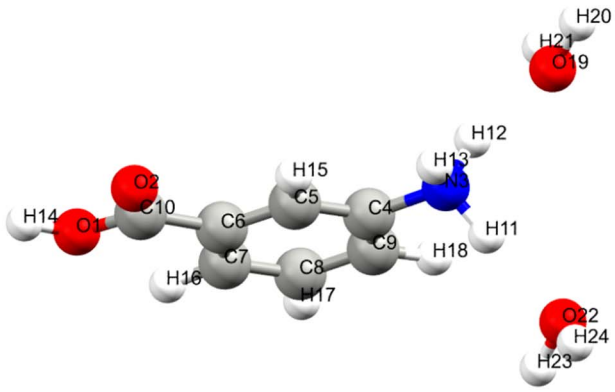
S4.3. Aggregate extracted from compound 2 (corresponding to interaction 5)



Atom	α_{11}	α_{22}	α_{33}	α_{ISO}
O1	2.319	3.488	9.228	5.012
O2	2.472	4.887	6.201	4.520
N3	2.975	6.719	10.751	6.815
C4	2.536	2.866	8.721	4.708
C5	3.122	5.531	10.281	6.311
C6	3.245	5.159	6.841	5.081
C7	3.768	4.379	8.983	5.710
C8	2.915	3.240	7.966	4.707
C9	1.633	2.403	6.394	3.477
H10	0.328	0.410	5.009	1.916
H11	0.065	0.227	1.442	0.578
H12	0.409	0.763	1.565	0.912
H13	0.461	0.782	2.890	1.377
H14	0.547	1.071	2.556	1.392
H15	0.719	1.033	3.379	1.710
O16	2.442	3.422	8.945	4.936
O17	3.028	5.866	13.343	7.412
O18	2.586	4.694	8.862	5.381
O19	3.806	5.065	11.932	6.934
C20	3.257	4.773	14.043	7.358

C21	3.117	5.994	10.626	6.579
C22	2.709	3.736	11.820	6.088
C23	1.236	3.283	8.759	4.426
C24	1.204	3.147	5.586	3.312
H25	0.712	1.593	2.312	1.539
H26	0.131	0.183	2.159	0.825
O27	2.566	4.322	9.979	5.623
O28	3.778	6.371	8.708	6.286
O29	3.362	5.680	7.990	5.677
O30	3.888	4.874	11.297	6.686
C31	3.029	5.592	10.274	6.299
C32	3.095	5.341	10.096	6.177
C33	2.855	3.736	12.151	6.247
C34	1.596	2.550	7.656	3.934
C35	1.577	3.276	5.621	3.491
H36	0.279	0.679	1.675	0.878
H37	0.156	0.233	1.736	0.708

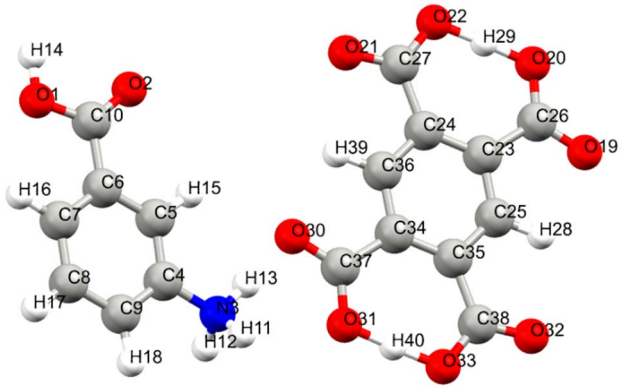
S4.4. Aggregate extracted from compound 3 (corresponding to interactions 6 and 7)



Atom	α_{11}	α_{22}	α_{33}	α_{ISO}
O1	4.436	4.745	12.662	7.281
O2	4.810	5.106	13.211	7.709
N3	4.562	6.267	13.012	7.947
C4	4.348	9.500	12.139	8.662
C5	4.891	6.879	14.664	8.811
C6	4.322	10.658	15.246	10.075
C7	4.965	7.586	12.991	8.514
C8	5.337	8.591	12.566	8.832
C9	5.243	8.728	11.584	8.518
C10	2.404	4.049	11.787	6.080
H11	0.359	0.457	2.817	1.211
H12	0.350	0.443	2.728	1.174
H13	0.411	0.440	1.881	0.911
H14	0.183	0.298	2.213	0.898
H15	0.873	1.090	4.110	2.024
H16	0.848	1.016	4.234	2.033
H17	1.020	1.164	5.091	2.425
H18	1.095	1.181	5.061	2.445
O19	6.619	6.866	10.847	8.111
H20	0.320	0.349	1.947	0.872
H21	0.320	0.381	1.721	0.807

O22	6.439	6.611	10.999	8.016
H23	0.307	0.395	1.619	0.774
H24	0.314	0.348	1.858	0.840

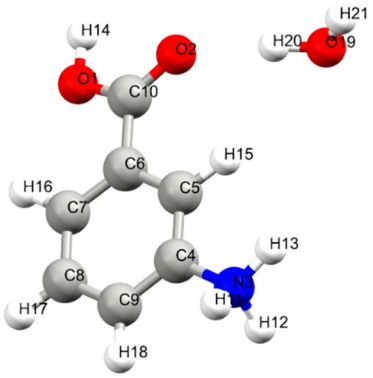
S4.5. Aggregate extracted from compound 3 (corresponding to interaction 8)



Atom	α_{11}	α_{22}	α_{33}	α_{ISO}
O1	2.709	4.736	10.991	6.145
O2	2.902	4.994	10.671	6.189
N3	3.461	5.472	11.146	6.693
C4	3.061	5.650	11.432	6.715
C5	3.209	6.175	12.572	7.318
C6	3.162	8.120	15.093	8.791
C7	3.474	6.489	12.108	7.357
C8	3.862	7.416	11.540	7.606
C9	3.865	8.863	9.177	7.302
C10	1.764	3.021	10.438	5.075
H11	0.249	0.460	1.815	0.841
H12	0.281	0.405	1.990	0.892
H13	0.516	0.630	3.524	1.557
H14	0.115	0.313	2.307	0.912
H15	0.794	1.343	4.104	2.081
H16	0.678	0.976	3.370	1.675
H17	0.732	1.205	4.325	2.087
H18	0.638	1.278	5.346	2.420
O19	4.718	7.189	9.952	7.286
O20	4.054	6.698	14.369	8.374
O21	3.350	5.901	11.683	6.978

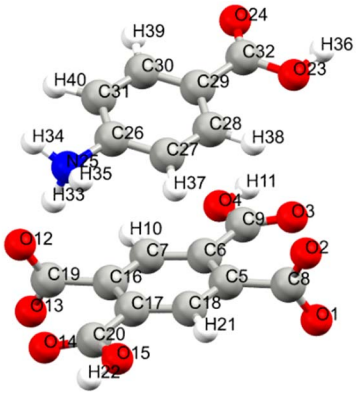
O22	4.397	7.387	11.808	7.864
C23	3.490	6.952	12.792	7.745
C24	3.542	7.227	14.416	8.395
C25	2.937	5.095	15.775	7.936
C26	1.899	3.982	7.835	4.572
C27	1.862	3.146	10.471	5.160
H28	0.801	2.110	2.288	1.733
H29	0.181	0.332	2.105	0.872
O30	3.369	6.470	12.853	7.564
O31	3.879	6.801	13.484	8.054
O32	3.017	5.635	12.419	7.024
O33	4.458	8.312	11.188	7.986
C34	3.727	8.162	14.203	8.698
C35	3.590	7.636	14.641	8.622
C36	3.032	5.233	15.690	7.985
C37	1.654	4.773	6.009	4.145
C38	1.875	3.347	9.768	4.997
H39	0.701	1.647	2.466	1.605
H40	0.174	0.328	2.360	0.954

S4.6. Aggregate extracted from compound 3 (corresponding to interaction 9)



Atom	α_{11}	α_{22}	α_{33}	α_{ISO}
O1	4.555	4.652	12.670	7.292
O2	4.797	5.399	15.328	8.508
N3	4.365	4.917	11.885	7.056
C4	4.417	9.870	11.946	8.744
C5	4.708	6.611	13.989	8.436
C6	4.313	10.847	14.803	9.988
C7	4.848	7.351	13.358	8.519
C8	5.247	8.623	12.154	8.675
C9	5.195	9.058	11.204	8.486
C10	2.338	4.432	12.592	6.454
H11	0.336	0.410	2.003	0.916
H12	0.337	0.414	2.023	0.924
H13	0.325	0.363	1.677	0.789
H14	0.175	0.283	2.060	0.840
H15	0.856	1.004	3.597	1.819
H16	0.838	0.985	4.076	1.966
H17	0.968	1.117	5.014	2.366
H18	1.064	1.197	5.332	2.531
O19	7.294	7.709	10.786	8.596
H20	0.039	0.154	2.134	0.776
H21	0.389	0.444	2.334	1.056

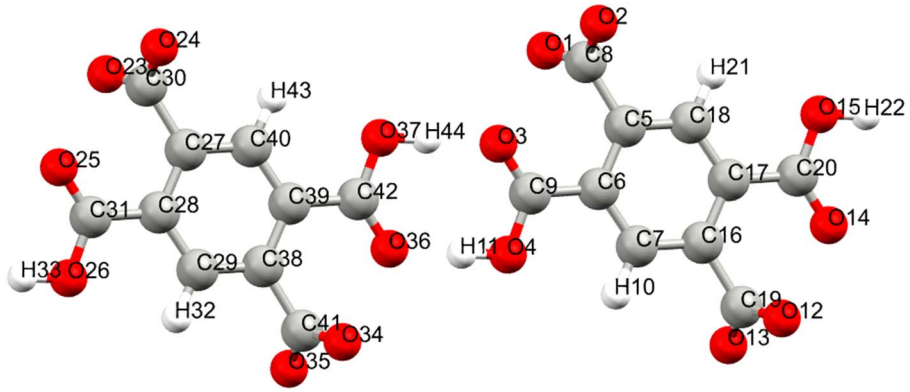
S4.7. Aggregate extracted from compound 4 (corresponding to interaction 10)



Atom	α_{11}	α_{22}	α_{33}	α_{ISO}
O1	5.434	6.355	20.130	10.640
O2	5.558	8.012	16.824	10.131
O3	5.820	7.187	11.293	8.100
O4	4.085	4.791	12.741	7.206
C5	3.772	12.993	16.423	11.062
C6	6.933	12.540	13.972	11.148
C7	4.847	6.319	15.977	9.048
C8	3.599	4.956	15.989	8.182
C9	2.352	3.975	9.954	5.427
H10	0.836	1.086	3.831	1.918
H11	0.202	0.388	2.795	1.128
O12	3.739	10.435	20.734	11.636
O13	5.318	6.531	18.784	10.211
O14	4.752	7.283	13.529	8.521
O15	4.308	4.895	14.309	7.837
C16	3.778	12.674	14.768	10.407
C17	4.231	12.839	16.934	11.335
C18	4.578	8.803	16.791	10.057
C19	3.604	6.677	10.899	7.060
C20	2.217	4.269	11.847	6.111
H21	0.848	1.059	4.344	2.084

H22	0.215	0.387	3.198	1.267
O23	4.437	6.978	12.111	7.842
O24	4.623	5.109	14.882	8.205
N25	3.598	8.808	16.116	9.507
C26	4.036	8.484	11.763	8.095
C27	6.539	9.432	13.613	9.862
C28	4.271	5.871	14.023	8.055
C29	4.039	9.755	16.311	10.035
C30	4.682	7.983	12.394	8.353
C31	4.743	8.664	13.825	9.077
C32	2.202	4.054	11.823	6.026
H33	0.110	0.991	6.543	2.548
H34	0.379	0.480	2.512	1.124
H35	0.346	0.527	2.049	0.974
H36	0.222	0.349	2.575	1.049
H37	0.579	2.861	4.942	2.794
H38	0.917	1.820	3.459	2.065
H39	0.812	1.137	4.666	2.205
H40	1.056	1.239	5.267	2.521

S4.8. Aggregate extracted from compound 4 (corresponding to interaction 11)



Atom	α_{11}	α_{22}	α_{33}	α_{ISO}
O1	6.976	7.447	18.385	10.936
O2	7.165	7.809	19.087	11.354
O3	3.843	7.001	16.279	9.041
O4	4.318	5.385	14.701	8.135
C5	3.804	13.602	17.219	11.542
C6	3.938	13.148	21.157	12.747
C7	4.671	7.209	19.999	10.626
C8	4.376	5.289	14.023	7.896
C9	1.999	3.672	12.958	6.209
H10	1.040	1.095	4.066	2.067
H11	0.195	0.224	2.874	1.098
O12	6.361	7.924	19.601	11.295
O13	6.726	8.092	19.912	11.577
O14	5.164	7.948	15.444	9.519
O15	4.620	5.332	16.605	8.852
C16	3.865	13.864	16.992	11.574
C17	4.285	13.630	20.619	12.845
C18	5.005	7.784	19.699	10.829
C19	4.091	5.167	14.989	8.082
C20	2.231	4.803	13.583	6.872
H21	1.027	1.257	4.778	2.354

H22	0.282	0.535	4.878	1.898
O23	6.359	7.921	19.599	11.293
O24	6.726	8.093	19.918	11.579
O25	5.162	7.967	15.447	9.526
O26	4.648	5.329	16.637	8.871
C27	3.858	14.000	17.192	11.683
C28	4.283	13.745	20.736	12.921
C29	5.009	7.756	19.937	10.901
C30	4.082	5.253	14.939	8.091
C31	2.233	4.834	13.573	6.880
H32	1.025	1.258	4.776	2.353
H33	0.284	0.535	4.875	1.898
O34	6.978	7.450	18.387	10.939
O35	7.165	7.809	19.081	11.351
O36	3.846	7.029	16.259	9.045
O37	4.313	5.414	14.692	8.140
C38	3.817	13.926	17.375	11.706
C39	3.935	13.275	21.211	12.807
C40	4.664	7.274	20.207	10.715
C41	4.207	5.268	14.209	7.894
C42	2.001	3.717	13.002	6.240
H43	1.040	1.096	4.069	2.068
H44	0.182	0.227	2.859	1.090