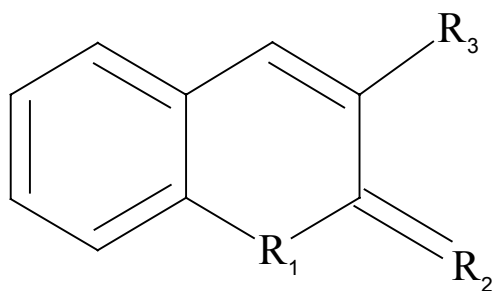


# Supporting Information

## Charge density based classification of intermolecular interactions in molecular crystals

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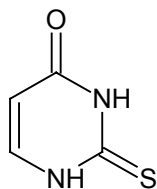
$R_1 = R_2 = O, R_3 = H$ ; Coumarin

$R_1 = S, R_2 = O, R_3 = H$ ; 1-thiocoumarin

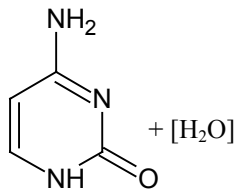
$R_1 = O, R_2 = S, R_3 = H$ ; 2-thiocoumarin

$R_1 = R_2 = S, R_3 = H$ ; dithiocoumarin

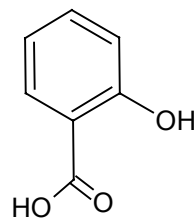
$R_1 = R_2 = O, R_3 = COCH_3$ ; 3-acetylcoumarin



2-thiouracil



Cytosine monohydrate



Salicylic acid

**Scheme S1**

**Table S1.** The parameters characterizing the intermolecular interactions, the values from the periodic calculation using the B3LYP/6-31G\*\* method are given in italics.

<b>Coumarin</b>							
<b>Interactions</b>	<b><math>R_{ij}</math></b>	<b><math>\Delta r_D - \Delta r_A</math></b>	<b><math>\Delta r_D + \Delta r_A</math></b>	<b><math>\rho_b</math></b>	<b><math>\nabla^2 \rho_b</math></b>	<b><math>G(\mathbf{r}_{CP})</math></b>	<b><math>V(\mathbf{r}_{CP})</math></b>
H(4)-X2_O(1)	2.434	0.121	0.306	0.045	0.915	18.39	-11.87
(x+1,y-1/2,-z+3/2)	<i>2.414</i>	<i>0.096</i>	<i>0.326</i>	<i>0.051</i>	<i>0.924</i>	<i>18.97</i>	<i>-12.78</i>
H(3)-X2_O(1)	2.310	0.123	0.230	0.036	0.775	15.30	-9.49
(x+1,y-1/2,-z+3/2)	<i>2.458</i>	<i>0.119</i>	<i>0.282</i>	<i>0.041</i>	<i>0.831</i>	<i>16.61</i>	<i>-10.59</i>
H(6)-X3_O(1)	2.725	-0.041	0.015	0.032	0.520	10.45	-6.74
(-x,y,z-1/2)	<i>2.698</i>	<i>-0.018</i>	<i>0.042</i>	<i>0.036</i>	<i>0.561</i>	<i>11.41</i>	<i>-7.55</i>
H(6)-X4_O(2)	2.834	-0.098	-0.094	0.033	0.518	10.47	-6.83
(-x,y-1/2,-z+1)	<i>2.771</i>	<i>-0.084</i>	<i>-0.031</i>	<i>0.035</i>	<i>0.552</i>	<i>11.19</i>	<i>-7.35</i>
H(5)-X4_C(8)	2.828	-0.046	0.222	0.036	0.408	8.64	-6.16
(-x+1,y-1/2,-z+1)	<i>2.764</i>	<i>-0.042</i>	<i>0.286</i>	<i>0.031</i>	<i>0.438</i>	<i>8.91</i>	<i>-5.89</i>
H(7)-X4_C(5)	3.013	-0.086	0.037	0.027	0.237	5.06	-3.67
(-x,y+1/2,-z+1)	<i>2.993</i>	<i>-0.157</i>	<i>0.057</i>	<i>0.031</i>	<i>0.244</i>	<i>4.82</i>	<i>-2.99</i>
H(2)-X2_C(4)	<i>3.021</i>	-0.054	0.029	0.031	0.319	6.75	-4.81
(x,y+1/2,-z+3/2)	3.009	<i>-0.245</i>	<i>0.041</i>	<i>0.020</i>	<i>0.255</i>	<i>5.09</i>	<i>-3.24</i>
H(5)-X4_C(7)	<i>3.057</i>	-0.187	-0.007	0.025	0.239	5.01	-3.51
(-x+1,y-1/2,-z+1)	3.042	<i>-0.126</i>	<i>0.008</i>	<i>0.022</i>	<i>0.277</i>	<i>5.57</i>	<i>-3.60</i>
H(2)-X2_C(9)	<i>3.131</i>	-0.291	-0.081	0.015	0.229	4.44	-2.65
(x,y+1/2,-z+3/2)	3.081	<i>-0.331</i>	<i>-0.031</i>	<i>0.023</i>	<i>0.278</i>	<i>5.63</i>	<i>-3.69</i>
H(4)-X1_C(7)	3.150	-0.311	-0.100	0.014	0.200	3.89	-2.32
(x+1,y,z)	<i>3.156</i>	<i>-0.282</i>	<i>-0.106</i>	<i>0.021</i>	<i>0.244</i>	<i>4.82</i>	<i>-2.99</i>
H(7)-X1_C(4)	3.200	-0.262	-0.150	0.017	0.184	3.69	-2.37
(x-1,y,z)	<i>3.156</i>	<i>-0.435</i>	<i>-0.106</i>	<i>0.018</i>	<i>0.247</i>	<i>5.77</i>	<i>-3.63</i>
H(4)-X4_C(7)	3.208	-0.279	-0.158	0.025	0.211	4.50	-3.25
(-x+1,y-1/2,-z+1)	<i>3.134</i>	<i>-0.184</i>	<i>-0.084</i>	<i>0.022</i>	<i>0.253</i>	<i>5.13</i>	<i>-3.38</i>
H(7)-X1_C(5)	3.231	-0.066	-0.181	0.012	0.174	3.36	-1.97
(x-1,y,z)	<i>3.221</i>	<i>-0.286</i>	<i>-0.171</i>	<i>0.014</i>	<i>0.193</i>	<i>3.76</i>	<i>-2.26</i>

1-thiocoumarin							
Interactions	$R_{ij}$	$\Delta r_D - \Delta r_A$	$\Delta r_D + \Delta r_A$	$\rho_b$	$\nabla^2 \rho_b$	$G(r_{CP})$	$V(r_{CP})$
H(6)-X1_O(1)	2.477	0.134	0.263	0.046	0.768	15.79	-10.67
(x,y-1,z)	2.470	0.110	0.270	0.043	0.831	16.74	-10.85
H(3)-X2_O(1)	2.555	0.198	0.185	0.024	0.680	12.97	-7.42
(x,-y+2,z+1/2)	2.478	0.109	0.262	0.042	0.818	16.44	-10.60
H(4)-X2_O(1)	2.603	0.144	0.137	0.027	0.590	11.47	-6.88
(x,-y+2,z+1/2)	2.546	0.096	0.194	0.035	0.691	13.72	-8.62
H(7)-X2_C(4)	2.832	-0.045	0.218	0.031	0.359	7.48	-5.17
(x,-y+1,z-1/2)	2.847	-0.169	0.203	0.032	0.423	8.69	-5.86
H(7)-X2_C(5)	2.987	-0.095	0.063	0.019	0.207	4.18	-2.73
(x,-y+1,z-1/2)	3.015	-0.282	0.035	0.018	0.281	5.49	-3.32
H(6)-X1_C(2)	3.048	-0.034	0.002	0.027	0.290	6.03	-4.15
(x,y-1,z)	3.085	-0.230	-0.035	0.024	0.291	5.91	-3.89

3-acetylcoumarin							
Form A							
Interactions	$R_{ij}$	$\Delta r_D - \Delta r_A$	$\Delta r_D + \Delta r_A$	$\rho_b$	$\nabla^2 \rho_b$	$G(r_{CP})$	$V(r_{CP})$
H(6)-X1_O(2A)	2.433	0.117	0.307	0.048	0.926	18.80	-12.37
(x-1,y-1,z)	2.408	0.114	0.332	0.047	0.930	18.80	-12.27
H(5A)-X1_O(1A)	2.442	0.188	0.298	0.038	0.927	18.18	-11.10
(x,y-1,z)	2.427	0.141	0.313	0.042	0.868	17.35	-11.06
H(6A)-X1_O(2)	2.445	0.128	0.295	0.044	0.885	17.78	-11.47
(x+1,y,z)	2.408	0.110	0.332	0.048	0.933	18.92	-12.44
H(5)-X1_O(1)	2.499	0.220	0.242	0.030	0.827	15.92	-9.32
(x,y-1,z)	2.439	0.143	0.301	0.040	0.849	16.88	-10.63
H(4A)-X1_O(3)	2.518	0.178	0.222	0.031	0.734	14.28	-8.58
(x,y,z+1)	2.522	0.182	0.218	0.028	0.684	13.23	-7.83
H(4)-X1_O(3A)	2.552	0.148	0.188	0.032	0.690	13.54	-8.28

(x,y-1,z-1)	2.534	0.137	0.206	0.033	0.677	13.35	-8.27
H(7A)-X1_O(1)	2.645	0.235	0.095	0.020	0.560	10.52	-5.79
(x+1,y,z)	2.626	0.100	0.114	0.030	0.567	11.20	-6.96
H(7)-X1_O(1A)	2.664	0.167	0.077	0.025	0.530	10.29	-6.15
(x-1,y-1,z)	2.664	0.076	0.076	0.029	0.533	10.53	-6.55
H(6A)-X2_C(5)	3.174	-0.230	-0.124	0.011	0.197	3.75	-2.13
(-x+1,-y,-z)	3.162	-0.328	-0.112	0.016	0.223	4.37	-2.66
H(6A)-X2_C(4)	3.177	-0.198	-0.127	0.014	0.248	4.76	-2.76
(-x+1,-y,-z)	3.158	-0.338	-0.108	0.017	0.234	4.60	-2.83
H(4A)-X2_C(3A)	3.189	-0.319	-0.139	0.013	0.220	4.22	-2.45
(-x+1,-y+1,-z+1)	3.189	-0.319	-0.139	0.012	0.170	3.28	-1.94
H(4)-X2_C(6A)	3.244	-0.312	-0.194	0.011	0.168	3.22	-1.87
(-x+1,-y,-z)	3.244	-0.319	-0.194	0.015	0.188	3.70	-2.28
H(6A)-X1_C(1)	3.381	0.117	-0.331	0.005	0.110	2.04	-1.09
(x+1,y,z)	3.389	0.026	-0.339	0.007	0.117	2.20	-1.22
H(6)-X1_C(7A)	3.382	0.312	-0.332	0.005	0.175	3.22	-1.68
(x-1,y-1,z)	3.269	0.072	-0.218	0.013	0.194	3.75	-2.21
H(6)-X1_C(1A)	3.409	0.109	-0.359	0.006	0.107	2.00	-1.10
(x-1,y-1,z)	3.398	0.034	-0.348	0.006	0.114	2.13	-1.16
H(5A)-X1_C(1A)	3.726	0.376	-0.676	0.005	0.106	1.97	-1.05
(x,y-1,z)	3.600	0.302	-0.550	0.006	0.123	2.30	-1.24
H(7A)-X2_C(1)	3.835	-0.373	-0.785	0.006	0.074	1.41	-0.80
(-x+1,-y+1,-z)	3.842	-0.390	-0.792	0.005	0.070	1.32	-0.73
C(10)···C(8A)	3.337	0.049	0.363	0.032	0.348	7.33	-5.18
(-x+1,-y+1,-z)	3.342	-0.108	0.358	0.030	0.309	6.52	-4.62
C(3)···C(8)	3.366	0.068	0.334	0.038	0.310	6.97	-5.5
(-x+1,-y,-z)	3.382	0.087	0.318	0.040	0.398	8.69	-6.54
C(6)···C(10)	3.380	-0.103	0.320	0.024	0.295	5.98	-3.93
(-x+1,-y,-z)	3.383	-0.056	0.317	0.042	0.354	8.02	-6.39
C(3A)···C(8A)	3.386	0.109	0.314	0.036	0.330	7.22	-5.45
(-x+2,-y+1,-z+1)	3.384	-0.050	0.316	0.032	0.315	6.73	-4.88

C(6A)···C(10A)	3.400	-0.113	0.300	0.026	0.270	5.62	-3.88
(-x+2,-y+1,-z+1)	3.409	-0.113	0.291	0.033	0.242	5.46	-4.32
C(2A)···C(5A)	3.498	-0.010	0.202	0.030	0.336	7.01	-4.86
(-x+2,-y+1,-z+1)	3.633	-0.008	0.067	0.037	0.342	7.49	-5.68
C(1)···C(4)	3.503	0.079	0.197	0.028	0.260	5.53	-3.98
(-x+1,-y,-z)	3.567	0.015	0.133	0.037	0.348	7.60	-5.73
C(2)···C(4)	3.609	0.069	0.091	0.029	0.300	6.30	-4.44
(-x+1,-y,-z)	3.678	-0.097	0.021	0.037	0.348	7.60	-5.73
C(10A)···C(11A)	3.817	0.534	-0.117	0.039	0.306	6.96	-5.58
(-x+1,-y+2,-z+1)	3.778	0.215	-0.078	0.026	0.214	4.60	-3.37
O(1A)···C(3)	3.405	-0.364	-0.015	0.021	0.350	6.86	-4.18
(-x+1,-y+1,-z)	3.391	-0.302	-0.001	0.021	0.344	6.75	-4.12
O(1)···C(5)	3.466	-0.071	-0.076	0.030	0.369	7.61	-5.16
(x,y+1,z)	3.469	0.056	-0.079	0.034	0.399	8.36	-5.85
O(1A)···C(5A)	3.475	-0.043	-0.085	0.030	0.375	7.72	-5.22
(x,y+1,z)	3.465	0.064	-0.075	0.034	0.407	8.51	-5.93
O(1)···C(11)	3.556	0.031	-0.166	0.029	0.203	4.54	-3.56
(-x+1,-y+1,-z)	3.438	-0.009	-0.048	0.032	0.386	8.02	-5.52
O(1A)···C(11A)	3.631	0.133	-0.241	0.035	0.187	4.57	-4.04
(-x+2,-y+2,-z+1)	3.506	0.036	-0.116	0.031	0.362	7.53	-5.2
<b>Form B</b>							
<b>Interactions</b>	<b><math>R_{ij}</math></b>	<b><math>\Delta r_D - \Delta r_A</math></b>	<b><math>\Delta r_D + \Delta r_A</math></b>	<b><math>\rho_b</math></b>	<b><math>\nabla^2 \rho_b</math></b>	<b><math>G(\mathbf{r}_{CP})</math></b>	<b><math>V(\mathbf{r}_{CP})</math></b>
H(3)···O(3)	2.354	0.131	0.386	0.061	1.091	22.77	-15.82
(-x+2,-y+3,-z)	2.362	0.109	0.378	0.058	1.036	21.53	-14.84
H(7)···O(2)	2.386	0.213	0.354	0.041	1.035	20.32	-12.45
(-x+1,-y+1,-z)	2.382	0.121	0.358	0.055	1.016	20.94	-14.2

H(4)···O(3)	2.546	0.104	0.194	0.038	0.731	14.62	-9.32
(-x+2,-y+3,-z)	2.538	0.109	0.202	0.038	0.705	14.14	-9.09
C(4)···C(8)	3.551	-0.022	0.149	0.032	0.341	7.20	-5.11
(x,y+1,z)	3.531	-0.040	0.169	0.048	0.385	8.97	-7.46
C(5)···C(7)	3.562	-0.149	0.138	0.03	0.346	7.19	-4.95
(x,y+1,z)	3.549	-0.035	0.151	0.045	0.38	8.68	-7.01
O(1)···C(2)	3.300	-0.326	0.09	0.038	0.489	10.22	-7.13
(x,y-1,z)	3.479	-0.094	-0.089	0.021	0.263	5.28	-3.39
O(1)···C(11)	3.516	-0.151	-0.126	0.016	0.266	5.15	-3.05
(-x+3/2,y-1/2,-z+1/2)	3.301	-0.252	0.089	0.040	0.542	11.30	-7.85

2-thiouracil							
Interaction	$\Delta r_D - \Delta r_A$	$\Delta r_D + \Delta r_A$	$R_{ij}$	$\rho_b$	$\nabla^2 \rho_b$	$G(r_{CP})$	$V(r_{CP})$
H(3)-X2_O(4)	0.259	0.942	1.798	0.160	3.972	86.87	-65.56
-x,-y+1,-z	0.229	0.944	1.796	0.182	4.061	92.02	-73.44
H(1)-X2_S(2)	0.242	0.654	2.286	0.082	1.626	34.37	-24.45
-x+1,-y+2,-z+1	0.301	0.653	2.287	0.091	1.703	36.68	-26.98
H(5)-X2_O(4)	0.21	0.446	2.294	0.057	1.297	26.19	-17.06
-x-1,-y+2,-z	0.216	0.448	2.293	0.052	1.295	25.78	-16.29
H(6)-X1_S(2)	0.033	0.086	2.854	0.042	0.534	11.28	-8.02
x-1,+y+1,z	0.163	0.085	2.855	0.052	0.632	13.74	-10.27
H(6)-X1_S(2)	-0.022	-0.083	3.023	0.041	0.513	10.84	-7.71
x,+y+1,z	0.088	-0.067	3.007	0.052	0.573	12.67	-9.73
O(4)-X2_C(5)	-0.238	0.175	3.215	0.039	0.536	11.14	-7.67
-x,-y+2,-z	-0.273	0.174	3.216	0.035	0.497	10.2	-6.86
C(2)-X1_C(5)	0.132	0.335	3.365	0.036	0.447	9.34	-6.51
x+1,+y,z	0.079	0.279	3.421	0.038	0.415	8.88	-6.45

N(1)-X2_N(1)	0	-0.207	3.407	0.031	0.444	9.02	-5.94
-x,-y+2,-z+1	0	-0.207	3.407	0.032	0.459	9.34	-6.19
O(4)-X2_O(4)	0	-0.352	3.431	0.018	0.292	5.69	-3.42
-x-1,-y+1,-z	0	-0.351	3.431	0.016	0.265	5.13	-3.04
S(2)-X1_N(3)	0.041	-0.285	3.625	0.03	0.391	8.01	-5.36
x+1,+y,z	-0.064	-0.307	3.647	0.037	0.45	9.46	-6.66
S(2)-X2_S(2)	0	-0.156	3.636	0.031	0.357	7.44	-5.16
-x+1,-y+1,-z+1	0	-0.156	3.636	0.047	0.44	9.9	-7.82

Cytosine monohydrate							
Interaction	$\Delta r_D - \Delta r_A$	$\Delta r_D + \Delta r_A$	$R_{ij}$	$\rho_b$	$\nabla^2 \rho_b$	$G(r_{CP})$	$V(r_{CP})$
H(1A)-X4_O(2)	0.256	0.87	1.87	0.124	3.37	70.84	-49.89
x,-y+1/2,z-1/2	0.196	0.876	1.864	0.183	3.353	79.33	-67.35
H(1)-X2_N(3)	0.25	0.884	1.916	0.154	2.943	67.28	-54.4
-x,y-1/2,-z+3/2	0.266	0.885	1.915	0.185	3.267	78.11	-67.24
H(4B)-X4_O(1)	0.273	0.791	1.949	0.113	2.896	60.85	-42.82
x-1,-y+1/2,z+1/2	0.217	0.794	1.946	0.117	2.977	62.81	-44.54
H(4A)-X2_O(2)	0.298	0.782	1.958	0.08	2.982	58.79	-36.37
-x,y+1/2,-z+3/2	0.235	0.792	1.948	0.11	2.975	61.92	-42.81
H(5)-X4_O(1)	0.107	0.332	2.408	0.065	1.089	23.06	-16.46
x-1,-y+1/2,z+1/2	0.097	0.369	2.371	0.07	1.099	23.67	-17.42
H(6)-X2_O(1)	0.205	0.328	2.412	0.05	1.078	21.7	-14.03
-x,y-1/2,-z+3/2	0.185	0.352	2.388	0.061	1.084	22.64	-15.76
H(6)-X3_O(1)	-0.041	-0.002	2.742	0.055	0.771	16.49	-11.98
-x,-y,-z+1	-0.065	0.022	2.718	0.059	0.783	17.01	-12.7
N(1)-X3_N(1)	0.000	-0.109	3.309	0.04	0.513	10.78	-7.58
-x,-y,-z+2	0.000	-0.109	3.309	0.039	0.541	11.23	-7.72
N(3)-X4_C(4)	-0.251	0.064	3.386	0.038	0.403	8.66	-6.35
x,-y+1/2,z-1/2	-0.276	0.089	3.361	0.037	0.397	8.49	-6.17



O(1)-X1_C(5)	-0.169	-0.255	3.645	0.016	0.213	4.19	-2.57
x+1,y,z	-0.124	-0.262	3.652	0.017	0.211	4.18	-2.62
N(4)-X4_C(5)	-0.243	-0.264	3.714	0.019	0.247	4.91	-3.09
x,-y+1/2,z-1/2	-0.219	-0.277	3.727	0.017	0.265	5.16	-3.11
<b>Salicylic acid</b>							
<b>Interaction</b>	$\Delta r_D - \Delta r_A$	$\Delta r_D + \Delta r_A$	$R_{ij}$	$\rho_b$	$\nabla^2 \rho_b$	$G(r_{CP})$	$V(r_{CP})$
H(1)-X3O(2)	0.325	1.113	1.627	0.23	5.783	132.01	-106.52
-x+2,-y,-z	0.233	1.113	1.627	0.288	5.794	144.49	-131.19
H(3)-X4_O(1)	0.05	0.235	2.505	0.048	0.82	16.87	-11.41
x-1,-y+1/2,z+1/2	0.045	0.217	2.523	0.046	0.781	16.03	-10.79
H(6)-X4_O(3)	0.042	0.087	2.653	0.042	0.674	13.83	-9.29
x,-y+1/2,z-1/2	0.029	0.085	2.655	0.041	0.644	13.22	-8.9
O(2)-X3_C(7)	-0.283	0.224	3.166	0.035	0.5	10.25	-6.88
-x+1,-y,-z	-0.227	0.14	3.25	0.036	0.506	10.42	-7.05
O(2)-X3_O(2)	-0.001	-0.289	3.369	0.033	0.502	10.18	-6.68
-x+1,-y,-z	0.000	-0.288	3.368	0.034	0.544	10.99	-7.17
O(1)-X3_O(3)	0.000	-0.297	3.376	0.023	0.36	7.12	-4.43
-x+1,-y,-z	-0.002	-0.296	3.376	0.024	0.375	7.43	-4.65
O(2)-X1_C(3)	-0.318	-0.129	3.519	0.025	0.353	7.08	-4.54
x-1,y,z	-0.25	-0.113	3.503	0.029	0.383	7.81	-5.19
O(3)-X2_C(4)	-0.297	-0.147	3.537	0.023	0.35	6.94	-4.34
-x+1,y-1/2,-z+1/2	-0.297	-0.147	3.537	0.023	0.35	6.94	-4.34
O(1)-X1_C(5)	-0.155	-0.172	3.562	0.021	0.289	5.75	-3.62
x+1,y,z	-0.159	-0.162	3.552	0.025	0.301	6.13	-4.07

C(1)-X1_C(3)	-0.127	0.134	3.566	0.026	0.334	6.78	-4.46
x+1,y,z	-0.125	0.098	3.602	0.034	0.401	8.4	-5.87
O(1)-X1_C(1)	-0.181	-0.195	3.585	0.022	0.298	5.95	-3.79
x+1,y,z	-0.139	-0.183	3.573	0.026	0.34	6.89	-4.51

## Experimental

The high-resolution single-crystal X-ray diffraction data were collected on a Bruker AXS SMART APEX CCD diffractometer using MoK $\alpha$  radiation (50 kV, 40 mA). To achieve the final temperature the ramp rate was set to 40K/hr. During the data collection the temperature was maintained at 90.0(2) K by using the Oxford Cryo systems with N<sub>2</sub> flows. Suitable crystals with reasonable sizes were mounted in a Lindeman capillary and allowed to stabilize at final temperature for an hour. The unit-cell parameters were determined repeatedly until the estimated standard deviations in cell dimensions did not vary beyond acceptable limits. The data were collected in three steps with different scan times to cover the full-sphere of reciprocal space with different  $2\theta$  settings of the detector ( $-25^\circ$ ,  $-50^\circ$ , and  $-75^\circ$ ) and  $\varphi$  settings ( $0^\circ$ ,  $90^\circ$ ,  $180^\circ$ , and  $270^\circ$ ) of the goniometer and the scanning angle  $\omega$  was set to  $0.3^\circ$  for each 606 frames. Additional 60 frames were collected with  $2\theta$  settings of the detector at  $-25^\circ$  and  $\varphi$  settings at  $0^\circ$  at the end of the data collection to perform the crystal decay correction. The crystal-to-detector distance was kept at 6.03cm. This strategy<sup>1</sup> provides high resolution, large redundancy, and appropriate completeness in data sets, which are the key factors for multipole refinement modeling. The data collection was monitored and reduced with the packages SMART<sup>2</sup> and SAINTPLUS<sup>2</sup> respectively. Sorting, scaling, merging, and empirical correction for absorption of the set of intensities were performed with SORTAV.<sup>3</sup> The structures were solved by direct methods using SHELXS97<sup>4</sup> and refined in the spherical atom approximation (based on  $F^2$ ) by using SHELXL97<sup>4</sup> included in a complete package WinGX.<sup>5</sup>

## Multipole Refinement

The package XD<sup>6</sup> was used to perform the detail analysis of charge density distribution in all the compounds. The module XDLSM,<sup>6</sup> which is a full-matrix least squares program, was used to carry out the multipolar refinement. The residual bonding density, not modeled in the conventional spherical refinement, is taken into account in this multipolar refinement. Scattering factors were derived from the Clementi and Roetti<sup>7</sup> wave functions for all atoms. The function minimized in the least-squares refinement is  $\sum w(|F_0|^2 - K|F_c|^2)^2$  for all reflections with  $I > 3\sigma(I)$ . Similar refinement procedure as described earlier by us<sup>1,8</sup> was followed for all the compounds. Initially only the scale factor was refined with all reflections. Next, to determine the accurate positional and thermal parameters the higher order ( $\sin\theta/\lambda \geq 0.8 \text{ \AA}^{-1}$ ) refinements were performed for non H-atoms. The positional and isotropic thermal parameters of the H-atoms were then refined using the lower angle data ( $\sin\theta/\lambda \leq 0.8 \text{ \AA}^{-1}$ ). Due to unavailability of the neutron data the positions of the H-atoms in this refinement as well as in the subsequent refinements were fixed to average bond distance value obtained from reported neutron diffraction studies.<sup>9</sup> In the next stage monopole, dipole, quadrupole, octapole, and hexadecapole (whenever required) populations were allowed to refine in a stepwise manner. Next, only single  $\kappa$  parameters and then single  $\kappa'$  parameters together with  $\kappa$  for all non H-atoms were refined. Finally, all the multipole parameters (including the isotropic thermal parameters of H-atoms) were refined to reach the final model of charge density distribution. For all H-atom the multipole expansion was truncated at  $l_{\max} = 1$  (dipole, bond-directed) level. For chemically different group of non-hydrogen atoms separate  $\kappa$  and  $\kappa'$  were allowed while for H-atoms the corresponding values were fixed at 1.2. No chemical restraints were applied but the molecular electro-neutrality constraint was applied and the scale factor was allowed to refine throughout all refinements. The module XDPROP<sup>6</sup> of the package XD was used for topological analysis of the electron densities.

## Theoretical Calculations

**Calculation of Periodic Wavefunction and Theoretical Structure Factors.** The program CRYSTAL03<sup>10</sup> was used to perform the single-point periodic calculations based on the experimental geometry by using density functional theory (DFT) method at the B3LYP<sup>11</sup> level with 6-31G\*\* basis set.<sup>12</sup> This basis set has been shown to provide reliable and consistent results with respect to studies involving intermolecular interactions.<sup>8,13</sup> The shrinking factors (IS1, IS2, and IS3) along the reciprocal lattice vectors were set at 4 (30 K-points in the irreducible Brillouin zone). For all the three compounds the truncation parameters (ITOL), which control the accuracy of the calculation of the bielectronic Coulomb and exchange series were set as ITOL1 = ITOL2 = ITOL3 = ITOL4 = 6 and ITOL5 = 15. As suggested by Spackman and Mitchell,<sup>14</sup> the exponents of the polarization functions were not scaled due to the large difference between ITOL4 and ITOL5. Rapid convergence was achieved when the level shifter value was set equal to 0.3 Hartree. Upon convergence on energy ( $\sim 10^{-6}$ ) the periodic wavefunction was obtained and used to generate the theoretical structure factors with the option XFAC.

To eliminate an important source of correlation between parameters, the temperature factors and atomic positions were not refined during the multipole refinement of the theoretical structure factors via XD. The same multipoles, as used in the refinement of experimental structure factors, were allowed to refine with separate  $\kappa'$  parameters for each non H-atom. All the theoretical reflections (without any cut off criteria) were included in the refinements.

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