Accessory publication

Adsorption of polyaromatic heterocycles on pyrophyllite surface by means of different theoretical approaches

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Preliminary calculations have been performed for SIESTA and CASTEP in order to tune the best calculation conditions including this cut-off energy. Total energy calculations of the mineral + thiophene complex were performed with different cut-off energy values (from 100 to 500 Ry in steps of 50 Ry for SIESTA, and from 310 to 450 eV in steps of 30 eV for CASTEP) in the Γ point. In both cases, the energy decreases with the increase of the cut-off energy reaching asymptotically to a constant value. Hence the decrease of total energy is practically negligible for cut-off energy values higher than 400 Ry in SIESTA and 380 eV in CASTEP. The same behaviour was found with 2 and 3 *k*-points of the Brillouin zone. The optimisations of pyrophyllite with cut-off energy higher than 150 Ry in SIESTA and 310 eV in CASTEP do not yield geometries closer to the experimental values. Further total energy calculations were performed with cut-off energy of 150 Ry in SIESTA and 310 eV in CASTEP for different *k*-points of the Brillouin zone, 1–3 *k*-points in SIESTA and 1–9 *k*-points in CASTEP and no significant decrease of energy was observed with more than 2 *k*-points. Therefore, we will perform optimisations in the Γ point with cut-off energy of 150 Ry in SIESTA and 310 eV in CASTEP and the total energy of the optimised structures will be performed with 2 *k*-points and using cut-off energies of 500 Ry in SIESTA and 450 eV in CASTEP.

Table A1. Main geometrical features (bond lengths in Å and angles in degrees) of calculated molecular structure of benzothiophene

Previous authors' data were from previous calculations (Hinchliffe et al. 1995). All MP2 electrons data calculations based on LCAO at MP2/6-311G** level. All PBE-GGA data were based on LCAO with pseudopotentials with SIESTA. All PW-GGA and PW-LDA data were based on plane-wave approximation. All CVFFH and PCFFH data were based on empirical force fields optimised by Heinz et al. (2005)

Features	Previous authors' data	MP2	PBE-GGA	PW-GGA	PW-LDA	CVFFH	PCFFH
S_1–C_2	1.743	1.730	1.742	1.727	1.723	1.728	1.827
C_2–C_3	1.335	1.369	1.374	1.364	1.365	1.384	1.364
C_3–C_4	1.450	1.434	1.440	1.431	1.429	1.393	1.430
C_4–C_5	1.398	1.412	1.416	1.406	1.408	1.419	1.463
C_4–C_9	1.396	1.421	1.429	1.421	1.422	1.386	1.342
C_5–C_6	1.375	1.389	1.396	1.386	1.386	1.399	1.394
C_6–C_7	1.399	1.412	1.414	1.405	1.406	1.401	1.412
C_7–C_8	1.376	1.391	1.396	1.389	1.389	1.397	1.443
C_8–C_9	1.392	1.406	1.405	1.398	1.399	1.431	1.362
C_9–S_1	1.749	1.736	1.741	1.734	1.729	1.699	1.732
C_2–H	1.072	1.083	1.096	1.086	1.096	1.083	1.102
C_3–H	1.074	1.085	1.098	1.089	1.098	1.080	1.096
C_5–H	1.076	1.087	1.100	1.091	1.100	1.076	1.095
C_6–H	1.076	1.086	1.099	1.090	1.099	1.082	1.103
C_7–H	1.076	1.086	1.099	1.090	1.098	1.082	1.100
C_8–H	1.075	1.087	1.100	1.090	1.099	1.081	1.098
S_1–C_2–C_3	113.39	113.46	113.35	113.03	113.16	112.53	113.69
C_2 –S_1–C_9	90.80	91.25	90.12	91.67	91.76	90.43	84.52
C_2–C_3–C_4	112.79	112.26	112.51	112.70	112.42	111.65	112.56
C_3–C_4–C_5	128.97	129.43	130.45	129.66	129.60	127.98	135.11
C_3–C_4–C_9	111.83	111.63	111.33	111.68	111.77	112.41	109.17
C_4–C_5–C_6	119.48	119.50	119.51	119.70	119.56	119.22	117.72
C_5–C_4–C_9	119.21	118.94	118.22	118.67	118.63	119.61	115.72
C_5–C_6–C_7	120.63	120.82	121.18	120.78	120.95	120.66	121.78
C_6–C_7–C_8	120.80	120.90	120.73	120.93	120.87	121.27	120.99
C_7–C_8–C_9	118.44	118.37	118.05	118.36	118.28	117.54	112.59
C_8–C_9–S_1	127.35	127.13	126.00	127.53	127.39	125.32	108.74
C_8–C_9–C_4	121.45	121.46	122.32	121.55	121.70	121.70	131.21
C_4–C_9–S_1	111.20	111.41	111.69	110.92	110.90	112.98	120.05

Table A2. Main geometrical features (bond lengths in Å and angles in degrees) of calculated and experimental molecular structure of dibenzothiophene

Experimental data were from of X-ray diffraction (Soscun et al 2001). All MP2 electrons data calculations based on LCAO, at MP2/6-311G** level. All PBE/GGAc and PW/GGAc data are based on LCAO with pseudopotentials with SIESTA. All PW-LDA data are based on plane-wave approximation. All CVFFHe and PCFFHe data are based on empirical force fields optimised by Heinz et al. (2005)

	Experimental data	MP2	PBE/GGA	PW/GGA	PW-LDA	CVFFH	PCFFH
S_1–C_2	1.749	1.748	1.749	1.747	1.739	1.715	1.851
C_2–C_3	1.392	1.403	1.398	1.396	1.396	1.429	1.361
C_3–C_4	1.385	1.393	1.394	1.390	1.391	1.394	1.450
C_4–C_5	1.394	1.409	1.407	1.402	1.404	1.399	1.412
C_5–C_6	1.387	1.392	1.393	1.388	1.390	1.396	1.395
C_6–C_7	1.397	1.407	1.408	1.402	1.400	1.426	1.459
C_7–C_8	1.450	1.448	1.442	1.445	1.444	1.405	1.414
C_7–C_2	1.413	1.415	1.423	1.415	1.417	1.401	1.335
C_8–C_9	1.400	1.407	1.408	1.402	1.400	1.427	1.459
C_9–C_{10}	1.382	1.392	1.393	1.387	1.390	1.396	1.395
C_{10}–C_{11}	1.403	1.409	1.407	1.403	1.404	1.400	1.412
C_{11}–C_{12}	1.378	1.393	1.394	1.391	1.391	1.395	1.450
C_{12}–C_{13}	1.391	1.403	1.398	1.397	1.396	1.429	1.362
C_{13}–S_1	1.749	1.748	1.749	1.746	1.739	1.715	1.851
C_3–H	0.950	1.087	1.100	1.090	1.100	1.080	1.097
C_4–H	0.950	1.086	1.088	1.089	1.099	1.081	1.099
C_5–H	0.950	1.086	1.100	1.089	1.099	1.082	1.101
C_6–H	0.950	1.087	1.100	1.90	1.100	1.080	1.097
S_1–C_2–C_7	112.15	112.73	112.15	112.07	112.25	114.68	123.10
S_1–C_2 –C_3	126.17	126.01	126.69	126.61	126.18	124.03	104.91
C_2–C_3–C_4	118.60	118.54	118.36	118.62	118.38	118.05	112.23
C_2–C_7–C_6	118.94	119.23	118.74	118.91	118.93	119.27	115.37
C_3–C_4–C_5	120.51	120.80	121.08	120.81	120.80	121.22	120.57
C_3–C_2–C_7	121.68	121.26	121.52	121.32	121.16	121.29	131.99
C_4–C_5–C_6	120.99	120.59	120.45	120.49	120.67	120.99	121.99
C_5–C_6–C_7	119.26	119.57	119.06	119.85	119.65	119.18	117.86
C_8–C_7–C_2	112.12	111.73	112.16	112.06	111.84	110.86	109.01
C_{13}–S_1–C_2	91.79	91.09	91.79	91.74	91.80	89.05	75.99

Table A3. Net atomic charges of thiophene used for the PCFFH and CVFFH calculations

All Mulliken and ESP_A data are based on MP2/6-311G** calculations. All ESP_B data are based on BHandHLYP/6-311G** calculations. All Qeq data are based on the empirical equilibration method

Atoms	Mulliken	ESP_A	ESP_B	Qeq
S_1	0.2704	0.0598	0.05441	–0.382
C_2	–0.2889	–0.2816	–0.2595	0.040
C_3	–0.1008	–0.1293	–0.2595	–0.098
C_4	–0.1008	–0.1293	–0.1242	–0.096
C_5	–0.2889	–0.2816	–0.1242	0.043
H_{C2}	0.1429	0.2266	0.2119	0.129
H_{C3}	0.1115	0.1543	0.2119	0.114
H_{C4}	0.1115	0.1543	0.1445	0.120
H_{C5}	0.1429	0.2266	0.1445	0.130

Table A4. Net atomic charges of benzothiophene used in the PCFFH and CVFFH calculations

All Mulliken and ESP_A data are based on MP2/6-311G** calculations. All ESP_B data are based on BHandHLYP/6-311G** calculations. All Qeq data are based on the empirical equilibration method

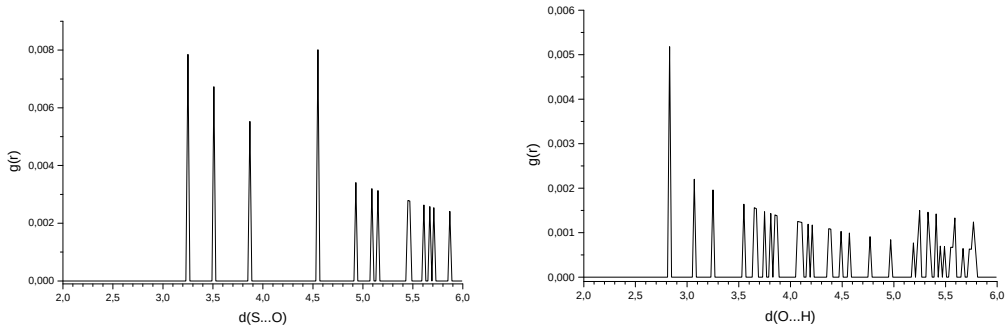
Atoms	Mulliken	ESP_A	ESP_B	Qeq
S_1	0.2461	–0.0297	–0.0346	–0.395
C_2	–0.2756	–0.2169	–0.1782	0.002
C_3	–0.0515	–0.3817	–0.3899	–0.123
C_4	–0.0232	0.3678	0.3487	0.059
C_5	–0.0478	–0.3523	–0.3364	–0.116
C_6	–0.1084	–0.1103	–0.0793	–0.116
C_7	–0.0879	–0.2191	–0.2074	–0.127
C_8	–0.0601	–0.1761	–0.1795	–0.086
C_9	–0.2292	–0.0448	–0.0251	0.179
H_{C2}	0.1385	0.2397	0.2189	0.137
H_{C3}	0.1017	0.2105	0.2068	0.105
H_{C5}	0.0934	0.1928	0.1769	0.110
H_{C6}	0.1008	0.1545	0.1360	0.120
H_{C7}	0.1018	0.1658	0.1534	0.119
H_{C8}	0.1015	0.2000	0.1896	0.131

Table A5. Net atomic charges of dibenzothiophene used in the PCFFH and CVFFH calculations

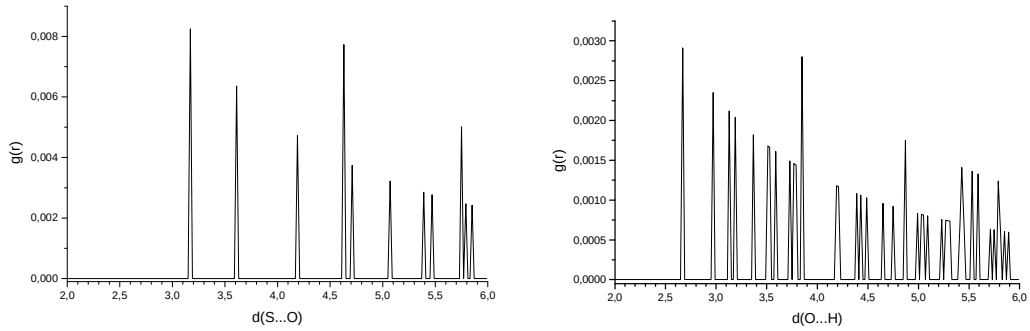
All Mulliken and ESP_A data are based on MP2/6-311G** calculations. All ESP_B data are based on BHandHLYP/6-311G** calculations. All Qeq data are based on the empirical equilibration method

Atoms	Mulliken	ESP_A	ESP_B	Qeq
S_1	0.2452	–0.1586	–0.1428	–0.437
C_2	–0.2272	0.0683	0.0577	0.138
C_3	–0.0843	–0.1673	–0.1387	–0.071
C_4	–0.0748	–0.2066	–0.1922	–0.123
C_5	–0.1107	–0.0747	–0.0741	0.113
C_6	–0.0281	–0.2513	–0.2014	–0.120
C_7	0.0052	0.0788	0.0563	0.025
C_8	0.0052	0.0732	0.0513	0.025
C_9	–0.0281	–0.2644	–0.2144	–0.120
C_{10}	–0.1107	–0.0529	–0.0559	0.113
C_{11}	–0.0748	0.1940	–0.2001	–0.123
C_{12}	–0.0842	–0.1731	–0.1468	–0.071
C_{13}	–0.2272	0.0764	0.0679	0.138
H_{C3}	0.1013	0.1887	0.1698	0.145
H_{C4}	0.1021	0.1513	0.1372	0.114
H_{C5}	0.1006	0.1277	0.1162	0.116
H_{C6}	0.0931	0.1644	0.1402	0.108
H_{C9}	0.0931	0.1695	0.1455	0.108
H_{C10}	0.1006	0.1222	0.1117	0.116
H_{C11}	0.1021	0.1523	0.1377	0.114
H_{C12}	0.1013	0.1940	0.1750	0.145

TM1



TM2



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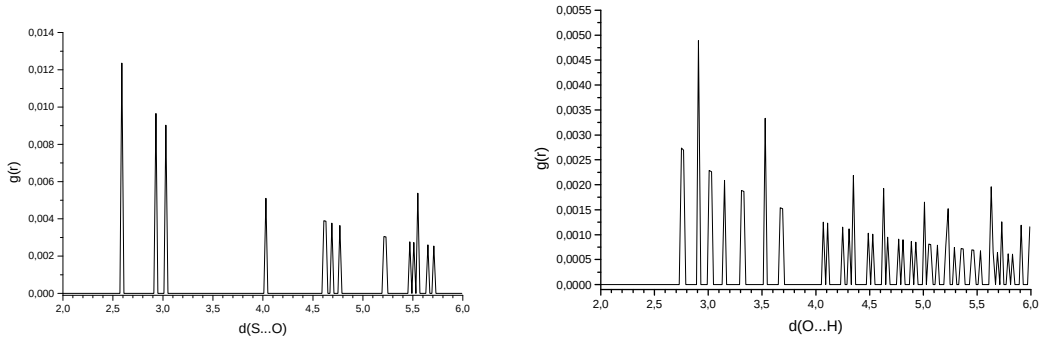
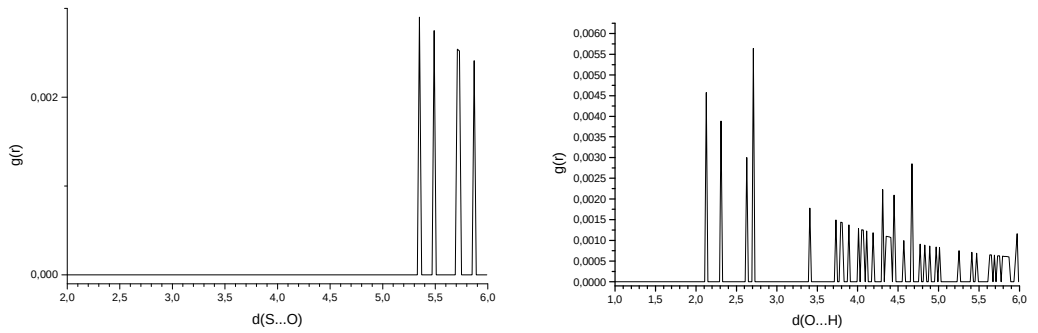


TM4

Fig. A1. Radial distribution function (RDF) profiles of the distances between the S and H atoms of thiophene and the O atoms of pyrophyllite for the main configurations of minimal energy for the thiophene–mineral complexes optimised with SIESTA



TM5

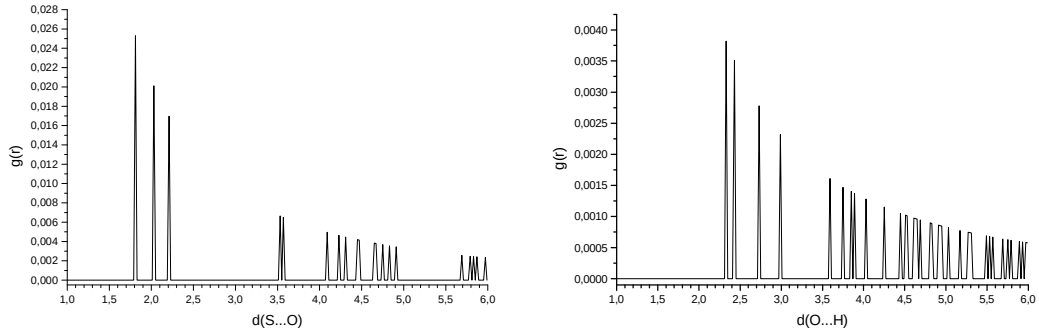
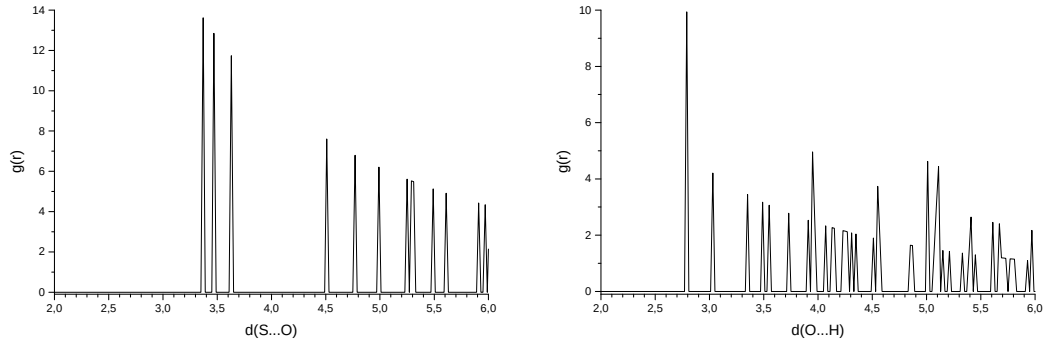
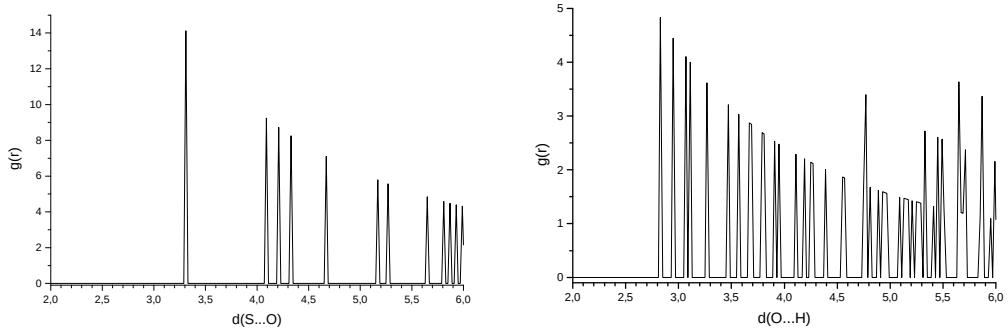


Fig. A1. (*Cont.*)

TM1C



TM2C



TM3C

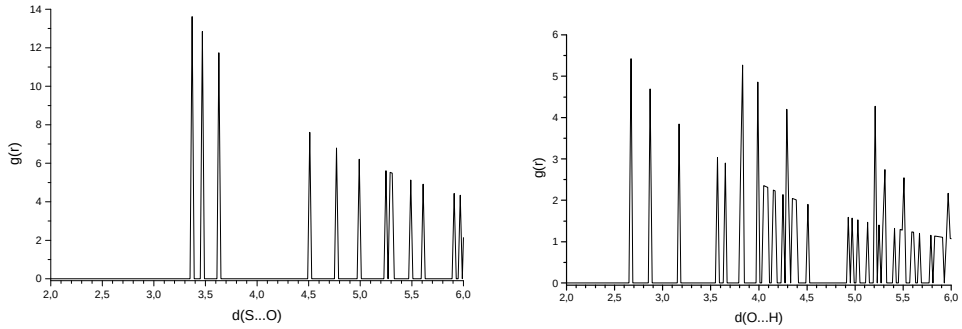
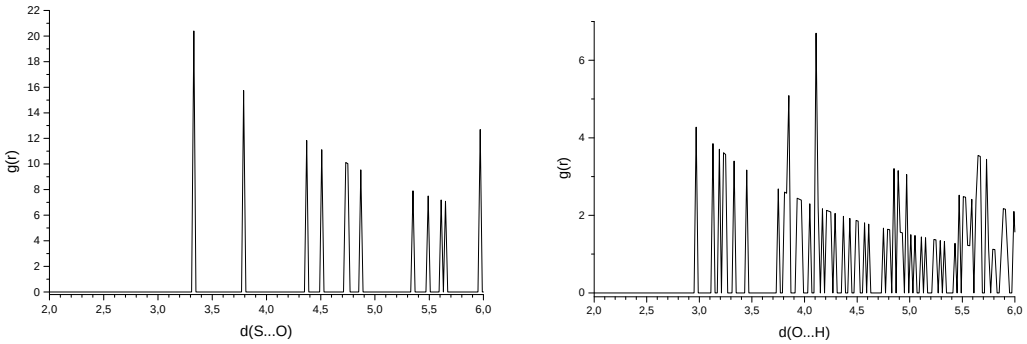


Fig. A2. RDF of configurations of thiophene on pyrophyllite optimised with CVFFH.

BM1C



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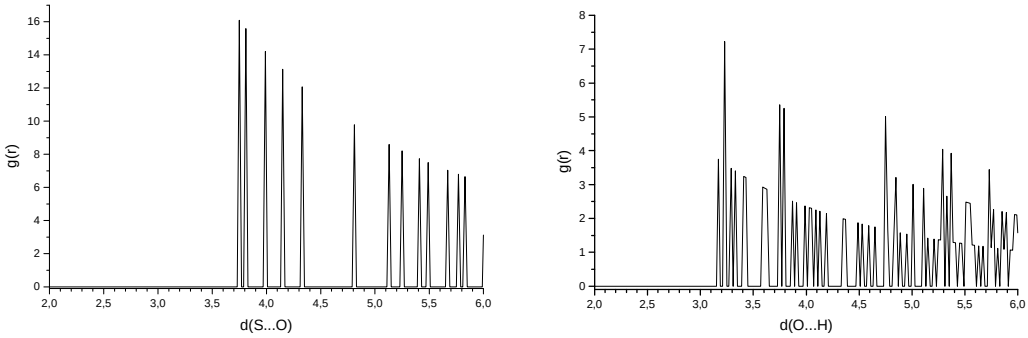

Fig. A3. RDF of configurations of benzothiophene on pyrophyllite optimised with CVFFH.