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Structural, electronic and vibrational properties of sulfated β–5 lignin model compounds: a DFT investigation

Aleksandr S. Kazachenko, Feride Akman, Utkirjon Holikulov, Abduvakhid Jumabaev and Yuriy N. Malyar

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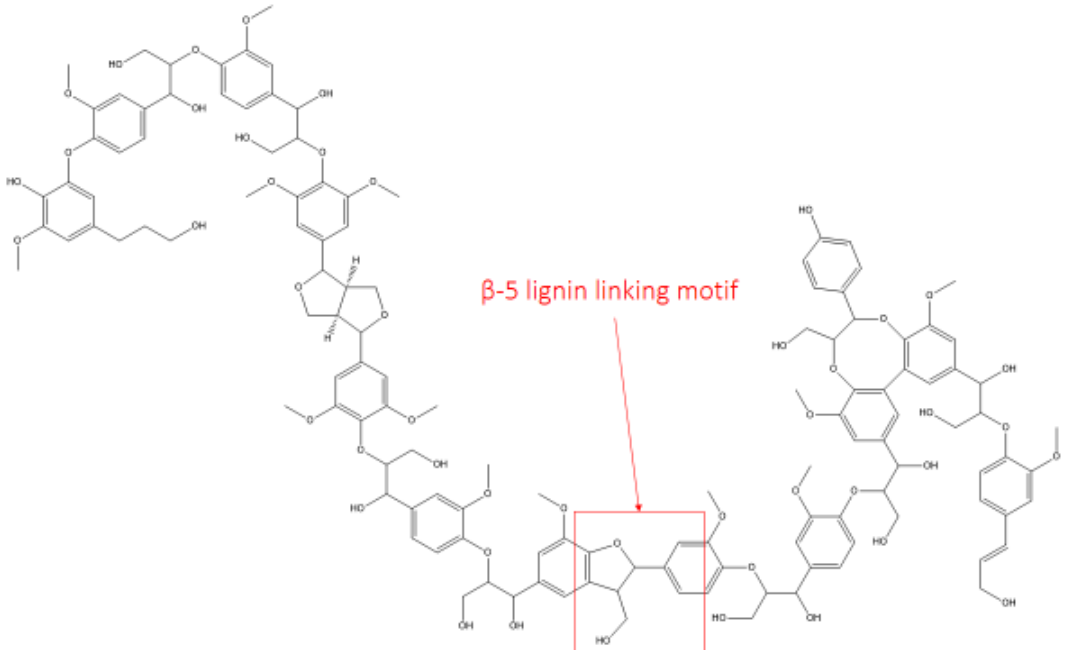
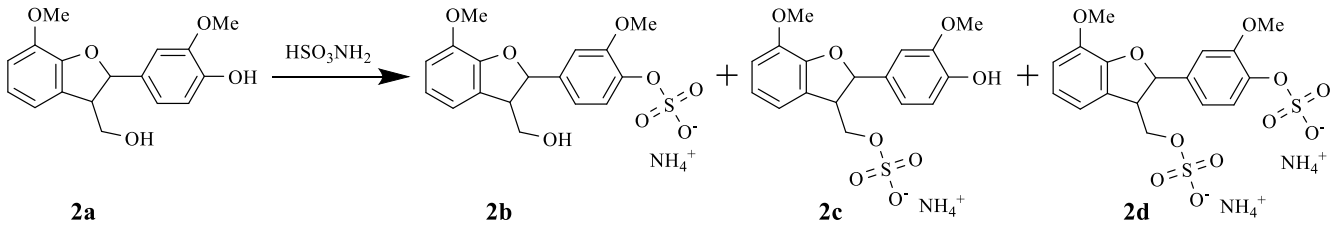


Figure S1 Fragment of lignin molecule with indicated β–5 linking.



Scheme S1 Sulfation of β–5 lignin model compound, 4-[3-(hydroxymethyl)-7-methoxy-2,3-dihydrobenzofuran-2-yl]-2-methoxyphenol **2a**, yields its aromatic monosulfate, ammonium 4-[3-(hydroxymethyl)-7-methoxy-2,3-dihydrobenzofuran-2-yl]-2-methoxyphenyl sulfate **2b**, aliphatic monosulfate, ammonium [2-(4-hydroxy-3-methoxyphenyl)-7-methoxy-2,3-dihydrobenzofuran-3-yl]methyl sulfate **2c**, and disulfate, diammonium 2-methoxy-4-{7-methoxy-3-[(sulfonatooxy)methyl]-2,3-dihydrobenzofuran-2-yl}phenyl sulfate **2d**.

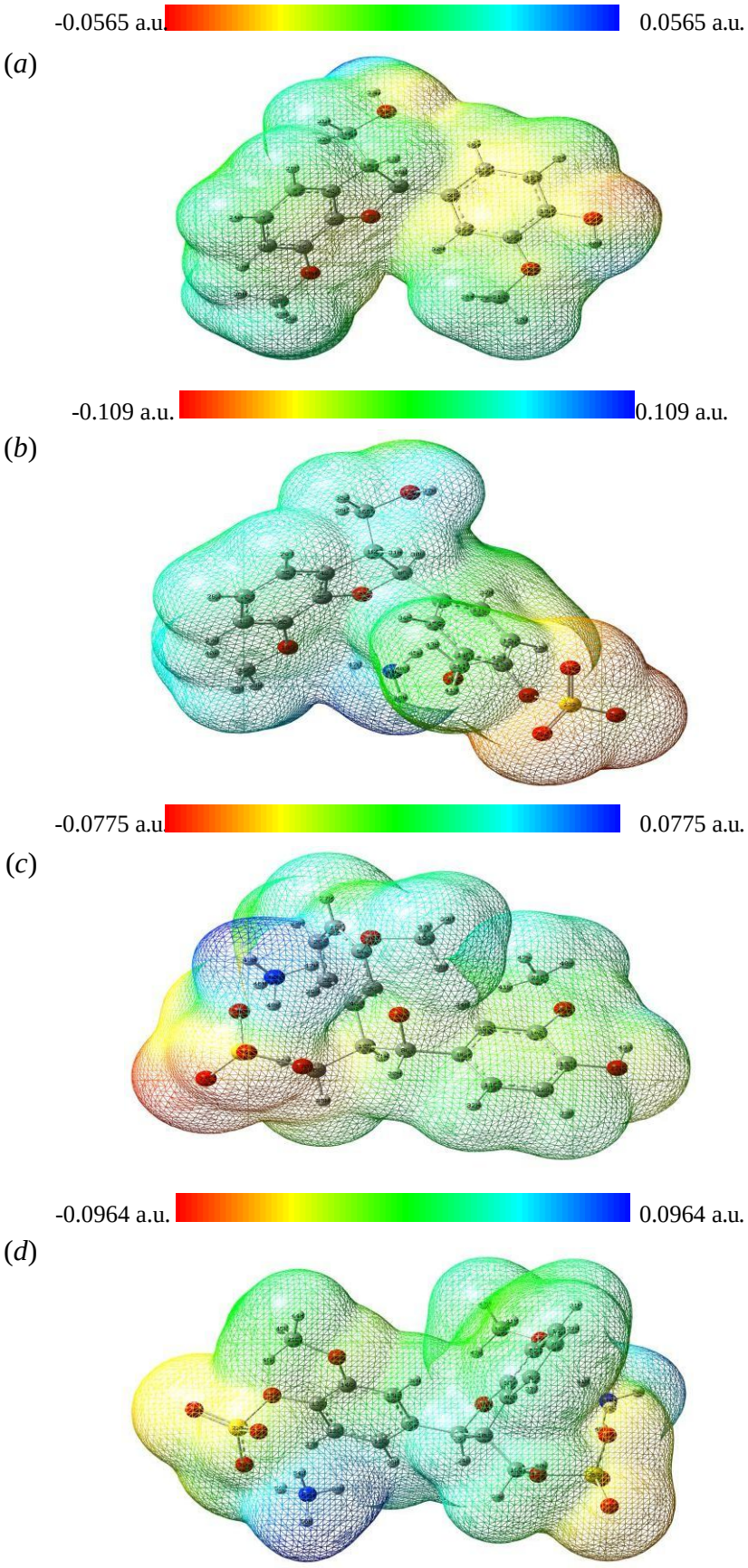


Figure S2 3D MEP surface maps of (*a*) the β–5 lignin model compound **2a**, as well as its (*b*) aromatic monosulfate **2b**, (*c*) aliphatic monosulfate **2c** and (*d*) disulfate **2d**.

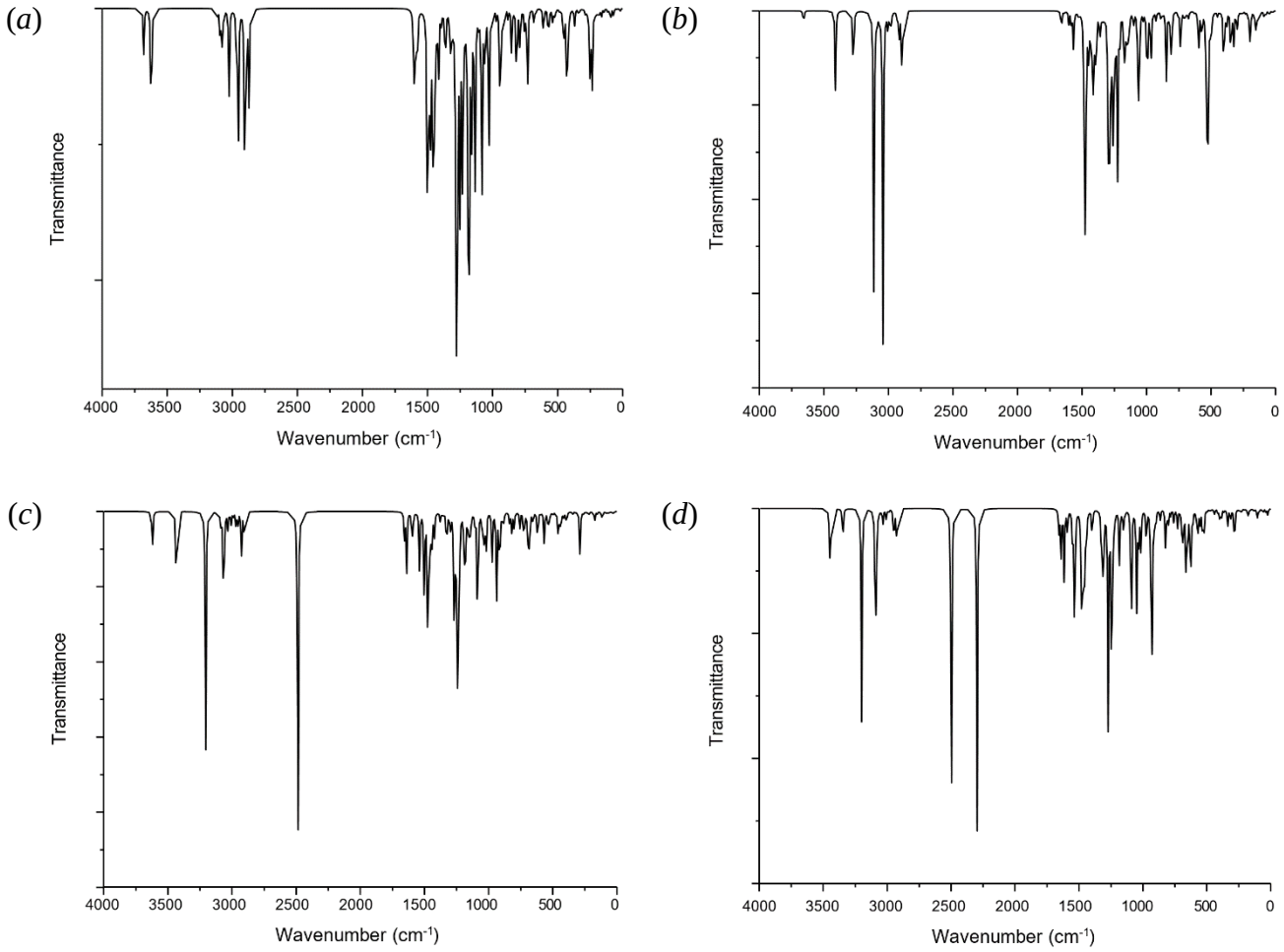


Figure S3 Theoretical FTIR spectral analysis of (a) the β–5 lignin model compound **2a**, as well as its (*b*) aromatic monosulfate **2b**, (*c*) aliphatic monosulfate **2c** and (*d*) disulfate **2d**.

Table S1 Global reactivity descriptor values of β–5 lignin model compound **2a**, as well as its aromatic monosulfate **2b**, aliphatic monosulfate **2c** and disulfate **2d**.

	2a	**2b**	**2c**	**2d**
E_{HOMO}	-5.2679	-5.4760	-5.7971	-6.1114
E_{LUMO}	0.1771	-1.0661	-0.3976	-0.9170
E_g	5.4450	4.4099	5.3996	5.1944
IP	5.2679	5.4760	5.7971	6.1114
EA	-0.1771	1.0661	0.3976	0.9170
χ	2.5454	3.2711	3.0973	3.5142
μ	-2.5454	-3.2711	-3.0973	-3.5142
η	2.7225	2.2049	2.6998	2.5972
ζ	0.3673	0.4535	0.3704	0.3850
ω	1.1899	2.4264	1.7767	2.3775
ΔN_{max}	0.9349	1.4835	1.1473	1.3531
$\sigma_{\circ}$	0.1837	0.2268	0.1852	0.1925
N	0.8404	0.4121	0.5628	0.4206

Table S2 Theoretical and experimental[S1] frequencies of β–5 lignin model compound **2a**, as well as its aromatic monosulfate **2b**, aliphatic monosulfate **2c** and disulfate **2d**.

β–5 lignin model compound **2a**			Aromatic monosulfate **2b**		
Assignment	Theory	Experiment	Assignment	Theory	Experiment
$\nu_{O–H}$	3679, 3622	3400–3600	$\nu_{O–H}$	3657	3400–3600
			$\nu_{N–H}$	3409–3112, 3041	3450–3300
$\nu_{C–H}$ (aromatic)	3112–3060	2950–2900	$\nu_{C–H}$ (aromatic)	3097–3068, 3046	2950–2900
$\nu_{C–H}$ (aliphatic)	3024–2871	2950–2900	$\nu_{C–H}$ (aliphatic)	3050, 3034–2891	2950–2900
$\nu_{C=C}$	1604–1479	1600–1500	$\nu_{C=C}$	1601–1478	1600–1500
			$\nu_{S–O}$	1256, 1223, 965, 524	1250–1245
Aliphatic monosulfate **2c**			Disulfate **2d**		
Assignment	Theory	Experiment	Assignment	Theory	Experiment
$\nu_{O–H}$	3620	3400–3600			
$\nu_{N–H}$	3436, 3204, 3064, 2485	3450–3300	$\nu_{N–H}$	3449–3198, 3091, 3085, 2497, 2296	3450–3300
$\nu_{C–H}$ (aromatic)	3091–3063	2950–2900	$\nu_{C–H}$ (aromatic)	3097, 3088, 3084–3061	2950–2900
$\nu_{C–H}$ (aliphatic)	3034–2905	2950–2900	$\nu_{C–H}$ (aliphatic)	3042–2918	2950–2900
$\nu_{C=C}$	1601–1500	1600–1500	$\nu_{C=C}$	1593–1481	1600–1500
$\nu_{S–O}$	1244, 1084, 936, 615	1250–1245	$\nu_{S–O}$	1272, 1244, 1089, 1049, 939, 927, 684, 627	1250–1245

Table S3 Cartesian coordinates of optimized structures **2a–d**.

(a) Stoichiometry $C_{17}H_{18}O_5$ (β–5 lignin model compound **2a**)

Framework group C1[X($C_{17}H_{18}O_5$)]

Deg. of freedom 114

Full point group C1 NOp 1

Largest Abelian subgroup C1 NOp 1

Largest concise Abelian subgroup C1 NOp 1

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.973230	-0.887033	0.830001
2	6	0	-4.017341	0.306971	1.564166
3	6	0	-3.035142	1.293465	1.422666
4	6	0	-1.998041	1.069540	0.521603
5	6	0	-1.943078	-0.125718	-0.219421
6	6	0	-2.928745	-1.123398	-0.073971
7	8	0	-0.863197	-0.206261	-1.076572
8	6	0	-0.054324	1.030372	-0.888467
9	6	0	1.331898	0.640121	-0.451427
10	6	0	-0.805419	1.912208	0.160013
11	6	0	2.283573	1.649249	-0.267909
12	6	0	3.590242	1.331861	0.120219
13	6	0	3.931135	-0.006215	0.320254
14	6	0	2.961492	-1.030379	0.132923
15	6	0	1.665075	-0.710647	-0.251861
16	6	0	-1.205474	3.273279	-0.416439
17	8	0	0.050603	3.950977	-0.636260
18	8	0	-2.745688	-2.247429	-0.847699
19	6	0	-3.775303	-3.264305	-0.783852
20	8	0	3.469433	-2.294974	0.379270
21	6	0	2.576886	-3.414676	0.163303
22	8	0	5.221651	-0.279314	0.700008
23	1	0	-4.755233	-1.627370	0.973330
24	1	0	-4.837667	0.464593	2.263281
25	1	0	-3.078558	2.208864	2.005585
26	1	0	-0.044934	1.478250	-1.906215
27	1	0	-0.153619	2.082004	1.055444
28	1	0	2.003073	2.696324	-0.424119
29	1	0	4.341645	2.105618	0.267355
30	1	0	0.900674	-1.474497	-0.405265
31	1	0	-1.810592	3.855862	0.300741
32	1	0	-1.742365	3.187660	-1.377808
33	1	0	-0.107648	4.849905	-0.981257
34	1	0	-3.394962	-4.004841	-1.500197
35	1	0	-3.833024	-3.686161	0.223239
36	1	0	-4.735604	-2.859056	-1.114725
37	1	0	3.222978	-4.267031	0.406906
38	1	0	1.724838	-3.354529	0.847457
39	1	0	2.255401	-3.446365	-0.882358
40	1	0	5.357954	-1.261406	0.807814

(b) Stoichiometry $C_{17}H_{21}NO_8S$ (aromatic monosulfate **2b**)

Framework group C1[X($C_{17}H_{21}NO_8S$)]

Deg. of freedom 138

Full point group C1 NOp 1

Largest Abelian subgroup C1 NOp 1

Largest concise Abelian subgroup C1 NOp 1

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.088761	-1.931333	1.127207
2	6	0	-4.284452	-0.984162	2.140512
3	6	0	-3.795013	0.319588	2.016457
4	6	0	-3.133012	0.674890	0.843592
5	6	0	-2.991439	-0.252107	-0.184787
6	6	0	-3.415496	-1.575140	-0.044714
7	8	0	-2.346733	0.223542	-1.286565
8	6	0	-1.701894	1.516082	-0.879488
9	6	0	-0.235739	1.207264	-0.751278
10	6	0	-2.480802	1.964269	0.387230
11	6	0	0.575092	1.292656	-1.893461
12	6	0	1.849548	0.725211	-1.908244
13	6	0	2.370292	0.033652	-0.794533
14	6	0	1.555205	-0.028497	0.380859
15	6	0	0.283591	0.558711	0.384682
16	6	0	-3.515384	3.060846	0.059801
17	8	0	-2.925647	4.206236	-0.530962
18	8	0	-3.069975	-2.437425	-1.075926
19	6	0	-3.654442	-3.742600	-1.070042
20	8	0	1.982478	-0.787944	1.426926
21	6	0	2.191099	-0.127619	2.685813
22	8	0	3.527816	-0.596517	-0.909686
23	16	0	4.937506	-0.144191	0.235203
24	8	0	5.979078	0.018248	-0.778804
25	8	0	4.408946	1.090140	0.846870
26	8	0	5.020952	-1.321688	1.103080
27	1	0	-4.446173	-2.944409	1.269738
28	1	0	-4.805966	-1.282621	3.043769
29	1	0	-3.919353	1.031679	2.826382
30	1	0	-1.876605	2.204390	-1.707789
31	1	0	-1.783537	2.354968	1.138521
32	1	0	0.202987	1.804004	-2.778611
33	1	0	2.490683	0.804686	-2.780195
34	1	0	-0.320177	0.449939	1.281059
35	1	0	-4.081229	3.311270	0.969523
36	1	0	-4.231427	2.679255	-0.675096
37	1	0	-2.359491	4.631975	0.127068
38	1	0	-3.340181	-4.220941	-1.998457
39	1	0	-3.307114	-4.335063	-0.215866
40	1	0	-4.746488	-3.673922	-1.048469
41	1	0	2.599893	-0.890081	3.348986

42	1	0	2.916546	0.678268	2.561180
43	1	0	1.246797	0.250352	3.100539
44	7	0	-0.277808	-1.827281	-1.602113
45	1	0	-0.223189	-1.015751	-2.231389
46	1	0	0.105003	-1.467957	-0.707241
47	1	0	-1.272642	-2.110897	-1.486187
48	1	0	0.310551	-2.588133	-1.943019

(c) Stoichiometry $C_{17}H_{21}NO_8S$ (aliphatic monosulfate **2c**)

Framework group C1[X($C_{17}H_{21}NO_8S$)]

Deg. of freedom 138

Full point group C1 NOp 1

Largest Abelian subgroup C1 NOp 1

Largest concise Abelian subgroup C1 NOp 1

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.435453	3.209566	1.210186
2	6	0	1.774266	2.404275	2.289106
3	6	0	1.458756	1.040663	2.309965
4	6	0	0.792280	0.500996	1.227107
5	6	0	0.442677	1.309217	0.127771
6	6	0	0.765880	2.667317	0.099537
7	8	0	-0.215778	0.620424	-0.869821
8	6	0	-0.442375	-0.733850	-0.389670
9	6	0	-1.913503	-1.016202	-0.237518
10	6	0	0.311839	-0.894438	0.970969
11	6	0	-2.332634	-2.349498	-0.309230
12	6	0	-3.669915	-2.684897	-0.167080
13	6	0	-4.619949	-1.673404	0.041043
14	6	0	-4.200583	-0.330072	0.104353
15	6	0	-2.847617	-0.006016	-0.026456
16	6	0	1.432843	-1.951875	0.943593
17	8	0	2.177421	-1.907399	-0.235843
18	8	0	0.533653	3.470104	-1.012210
19	6	0	-0.808454	3.895401	-1.126836
20	8	0	-5.142876	0.652640	0.405668
21	6	0	-5.409198	1.528765	-0.668426
22	8	0	-5.915508	-2.083088	0.170373
23	16	0	3.870904	-1.626268	-0.322872
24	8	0	3.950173	-1.194775	-1.758736
25	8	0	4.524637	-2.820133	0.129226
26	8	0	4.062901	-0.353905	0.465480
27	1	0	1.685526	4.276574	1.219549
28	1	0	2.301968	2.843156	3.142647
29	1	0	1.748168	0.410518	3.157730
30	1	0	-0.014805	-1.367900	-1.200064
31	1	0	-0.402061	-1.191891	1.775964
32	1	0	-1.590604	-3.140051	-0.477872

33	1	0	-3.987134	-3.732966	-0.219128
34	1	0	-2.532309	1.044680	0.030029
35	1	0	0.982431	-2.961977	0.960700
36	1	0	2.069488	-1.835543	1.842283
37	1	0	-0.810591	4.435412	-2.076673
38	1	0	-1.511883	3.054197	-1.164099
39	1	0	-1.085421	4.566894	-0.306783
40	1	0	-6.129417	2.228023	-0.236534
41	1	0	-4.510674	2.064755	-0.996573
42	1	0	-5.852796	1.003933	-1.521593
43	1	0	-6.455489	-1.318967	0.331459
44	7	0	3.576200	1.376601	-1.442894
45	1	0	4.217935	2.061863	-1.777485
46	1	0	3.808617	1.107942	-0.473184
47	1	0	2.648171	1.749574	-1.475318
48	1	0	3.637437	0.519213	-2.012405

(d) Stoichiometry $C_{17}H_{24}N_2O_{11}S_2$ (disulfate **2d**)

Framework group C1[X($C_{17}H_{24}N_2O_{11}S_2$)]

Deg. of freedom 162

Full point group C1 NOp 1

Largest Abelian subgroup C1 NOp 1

Largest concise Abelian subgroup C1 NOp 1

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.945747	2.892301	1.046098
2	6	0	3.901631	2.092790	2.180189
3	6	0	3.086800	0.956685	2.239423
4	6	0	2.306962	0.645572	1.142463
5	6	0	2.331378	1.458530	-0.008050
6	6	0	3.165440	2.577281	-0.079855
7	8	0	1.485855	1.022985	-1.004080
8	6	0	0.793739	-0.161580	-0.507718
9	6	0	-0.690675	0.079280	-0.509405
10	6	0	1.344809	-0.480891	0.918527
11	6	0	-1.501854	-0.719678	-1.315545
12	6	0	-2.879903	-0.553830	-1.321667
13	6	0	-3.476627	0.425445	-0.511427
14	6	0	-2.651229	1.254900	0.284309
15	6	0	-1.265949	1.075733	0.279228
16	6	0	1.970797	-1.881973	1.061114
17	8	0	2.682201	-2.273484	-0.073332
18	8	0	3.334425	3.320789	-1.242353
19	6	0	2.275874	4.218162	-1.504879
20	8	0	-3.166093	2.185971	1.180310
21	6	0	-3.625563	3.374313	0.572943
22	8	0	-4.815649	0.653500	-0.561957
23	16	0	-6.031111	-0.473248	-0.065240

24	8	0	-7.206396	0.332046	-0.123884
25	8	0	-5.884910	-1.647810	-0.995190
26	16	0	4.361603	-2.639437	-0.110322
27	8	0	4.629801	-2.341223	-1.556781
28	8	0	4.504548	-3.969891	0.407598
29	8	0	-5.568192	-1.037746	1.245850
30	8	0	5.003517	-1.497876	0.637117
31	1	0	4.590911	3.778038	1.022446
32	1	0	4.520221	2.352512	3.045854
33	1	0	3.079107	0.318014	3.129122
34	1	0	1.062062	-0.945832	-1.253355
35	1	0	0.523820	-0.408871	1.672993
36	1	0	-1.048386	-1.484340	-1.957984
37	1	0	-3.503478	-1.177132	-1.975440
38	1	0	-0.630053	1.717169	0.902644
39	1	0	1.167271	-2.634577	1.164042
40	1	0	2.595882	-1.913243	1.975169
41	1	0	2.587587	4.687796	-2.441065
42	1	0	1.319396	3.700793	-1.638084
43	1	0	2.180853	4.971281	-0.715193
44	1	0	-3.990574	3.950473	1.426899
45	1	0	-2.810991	3.912216	0.074920
46	1	0	-4.438398	3.197051	-0.139859
47	7	0	5.289310	0.185685	-1.354700
48	1	0	5.025598	-0.655914	-1.888161
49	1	0	5.366878	-0.099898	-0.365754
50	1	0	6.159391	0.545126	-1.682083
51	1	0	4.584601	0.890380	-1.447189
52	7	0	-4.800783	-3.432636	0.572321
53	1	0	-5.139552	-3.086335	-0.339209
54	1	0	-4.937491	-2.668350	1.251358
55	1	0	-3.834633	-3.672831	0.512700
56	1	0	-5.318685	-4.238205	0.849986

Reference

S1 A. S. Kazachenko, F. Akman, N. Yu. Vasilieva, Y. N. Malyar, O. Yu. Fetisova, M. A. Lutoshkin, Y. D. Berezhnaya, A. V. Miroshnikova, N. Issaoui and Z. Xiang, *Polymers*, 2022, **14**, 3000; https://doi.org/10.3390/polym14153000.