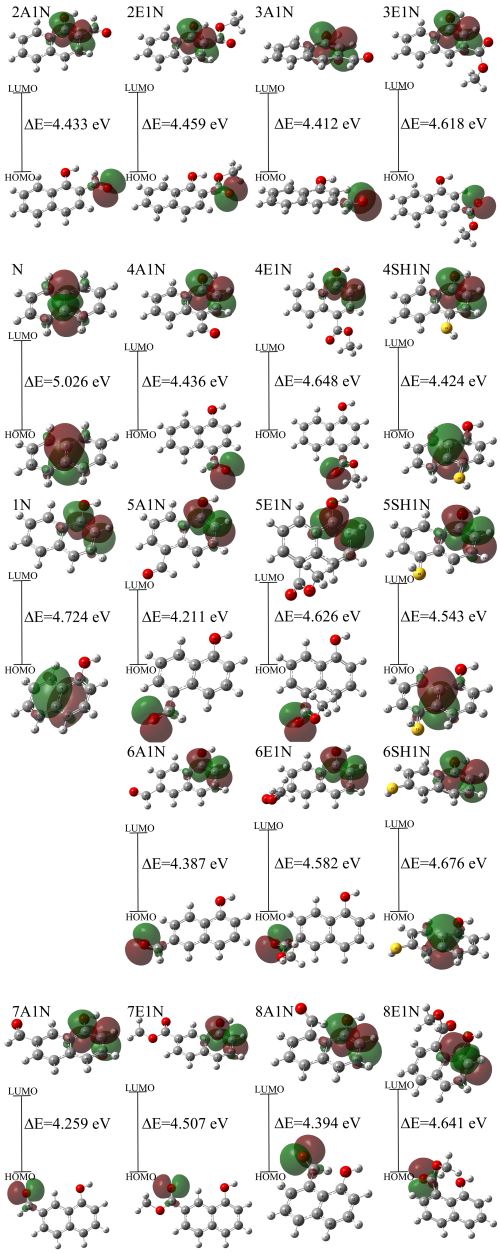
Supplementary Information

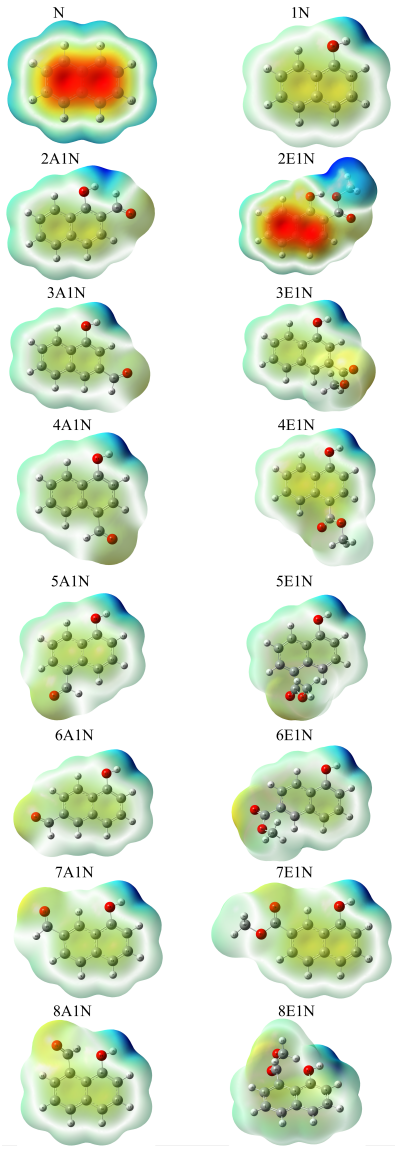
1-Naphthols as Components for Multifunctional Material Systems (MFMS) – the Molecular Modeling Approach

Ilona Radkowska,[*,1] Piotr Bragiel[1]

[1] *Faculty of Science and Technology, Jan Dlugosz University, Czestochowa, Poland*

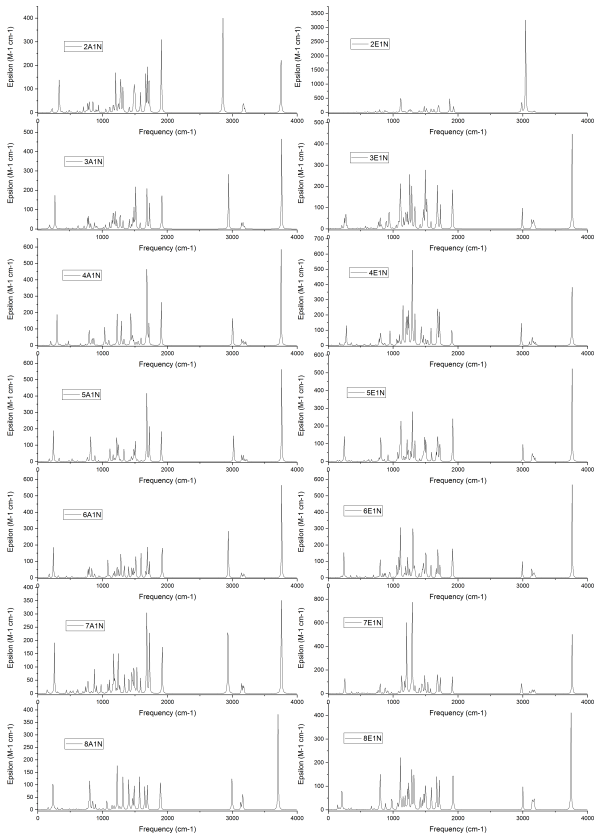


(a) The frontier orbitals of all studied compounds.

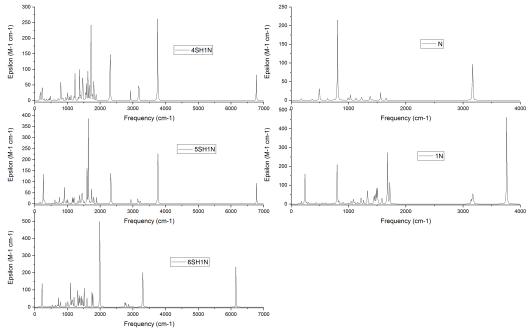


(b) The MEPs of all studied compounds

Figure S1: The examples of global descriptors of reactivity calculated with NBO population analysis.



(a) The infrared spectra for 1-naphthol derivatives having substituent as EWG or EDG groups.



(b) The infrared spectra for naphthalene, 1-naphthol and thio derivatives of 1-naphthol.

Figure S2: The simulated IR spectra for all studied molecules

Table S1: The structural parameters of studied compounds; bond lengths in Å, valence angles inside the aromatic ring in °.

Compound	C1-C2	C2-C3	C3-C4	C4-C5	C5-C6	C6-C7	C7-C8	C8-C9	C9-C10	C5-C10	C1-O	C-subst
N	1.375	1.414	1.375	1.416	1.416	1.375	1.414	1.375	1.416	1.428	-	-
1N	1.380	1.407	1.372	1.413	1.415	1.375	1.412	1.376	1.414	1.427	1.350	-
2A1N	1.392	1.415	1.362	1.416	1.412	1.377	1.410	1.377	1.413	1.423	1.345	1.461
3A1N	1.374	1.408	1.373	1.411	1.414	1.376	1.411	1.378	1.412	1.426	1.348	1.473
4A1N	1.381	1.394	1.379	1.426	1.418	1.376	1.408	1.375	1.414	1.431	1.345	1.479
5A1N	1.378	1.403	1.373	1.415	1.428	1.381	1.401	1.376	1.411	1.433	1.349	1.481
6A1N	1.381	1.406	1.372	1.412	1.412	1.376	1.414	1.370	1.416	1.426	1.349	1.474
7A1N	1.380	1.407	1.373	1.411	1.415	1.373	1.412	1.379	1.405	1.429	1.347	1.475
8A1N	1.380	1.405	1.371	1.414	1.414	1.373	1.406	1.381	1.424	1.431	1.354	1.490
4SH1N	1.374	1.400	1.334	1.367	1.420	1.374	1.413	1.377	1.406	1.413	1.350	1.493
5SH1N	1.380	1.408	1.372	1.418	1.370	1.337	1.402	1.371	1.398	1.411	1.347	1.492
6SH1N	1.376	1.405	1.367	1.407	1.392	1.341	1.370	1.359	1.384	1.401	1.346	1.464
2E1N	1.403	1.412	1.363	1.417	1.412	1.378	1.410	1.378	1.410	1.423	1.319	1.464
3E1N	1.377	1.407	1.372	1.411	1.415	1.375	1.412	1.377	1.413	1.426	1.349	1.490
4E1N	1.378	1.400	1.376	1.423	1.417	1.375	1.408	1.375	1.414	1.430	1.347	1.485
5E1N	1.380	1.405	1.372	1.413	1.418	1.375	1.409	1.375	1.412	1.426	1.349	1.495
6E1N	1.380	1.407	1.372	1.413	1.412	1.375	1.412	1.373	1.413	1.426	1.349	1.490
7E1N	1.380	1.407	1.373	1.411	1.414	1.373	1.416	1.377	1.407	1.426	1.348	1.487
8E1N	1.379	1.406	1.372	1.414	1.414	1.373	1.408	1.378	1.417	1.429	1.354	1.501

Compound	C1-C2-C3	C2-C3-C4	C3-C4-C5	C4-C5-C6	C5-C6-C7	C6-C7-C8	C7-C8-C9	C8-C9-C10	C4-C5-C10	C5-C10-C1	C6-C5-C10	C5-C10-C9
N	120.2	120.2	120.9	122.1	120.9	120.2	120.2	120.9	118.9	118.9	118.9	118.9
1N	121.4	120.5	120.0	121.9	121.4	120.1	120.1	120.8	119.8	119.0	118.3	119.4
2A1N	119.5	122.0	120.0	122.2	121.3	120.1	120.0	120.7	119.4	119.4	118.4	119.5
3A1N	121.9	119.8	120.6	121.9	121.2	120.0	120.2	120.7	119.6	118.9	118.5	119.3
4A1N	120.8	122.4	118.5	123.3	121.9	120.5	119.5	121.0	119.6	119.5	117.1	120.0
5A1N	120.8	121.0	120.5	123.4	119.8	121.9	119.5	120.8	118.6	119.6	118.0	119.9
6A1N	121.5	120.4	119.9	121.9	122.0	119.3	120.5	120.8	120.1	118.9	118.1	119.3
7A1N	121.3	120.7	119.9	122.0	121.1	120.8	119.2	121.4	119.8	119.0	118.1	119.4
8A1N	121.5	120.5	120.3	120.9	121.2	119.7	121.7	119.3	120.3	117.8	118.9	119.3
4SH1N	123.2	114.3	126.2	116.7	117.4	120.3	121.8	119.9	119.9	115.4	122.8	117.3
5SH1N	123.2	120.5	116.0	116.3	127.2	114.3	121.8	122.1	124.8	116.6	118.3	116.1
6SH1N	120.9	120.2	120.3	121.4	117.9	126.0	115.6	122.3	120.0	119.2	118.7	119.5
2E1N	120.0	121.9	120.0	122.3	121.3	120.2	119.9	120.8	119.5	119.9	118.2	119.7
3E1N	122.1	119.5	120.6	121.7	121.2	120.1	120.1	120.7	119.9	118.7	118.4	119.4
4E1N	121.0	122.1	118.4	122.9	121.8	120.5	119.5	121.0	119.9	119.5	117.2	120.0
5E1N	121.2	120.6	120.2	121.8	120.3	120.9	120.1	120.5	119.6	119.1	118.6	119.6
6E1N	121.4	120.5	119.9	121.8	122.0	119.1	120.7	120.8	119.9	119.1	118.3	119.1
7E1N	121.3	120.6	119.9	122.3	121.7	120.7	118.5	122.0	120.0	119.1	117.7	119.4
8E1N	121.1	120.3	120.3	121.4	120.9	120.0	121.2	119.5	119.9	118.2	118.7	119.6

Optimized structure - more detailed description

Molecules with the substituent in the position 2 have the shortest C-O and C-subst bonds, while 8E1N has the longest ones.

As can be expected, the presence of the EDG group causes elongation of the C-subst bond (it is seen especially for the bonds having the same substituent positions with the exception of 6SH1N molecule). For EWG group (aldehyde substituent) the C-subst bond lengths are listed as follows:

$$8A > 5A > 4A > 7A > 6A > 3A > 2A$$

for EDG group (ester substituent):

$$8E > 5E > 3E = 6E > 7E > 4E > 2E$$

and for thio substituent: 4SH > 5SH > 6SH. Thereby some conclusions can be made based on the order of the bond lengths (thio derivatives are omitted). The longest C-subst bond is found for the substituent in the position 8 and the shortest in the position 2; bond in the position 5 is always the second-longest; we assume the shortest bonds are due to the *ortho-para* directing influence of the hydroxyl group – electron density is increased in the positions thereby the substituents are strongly "connected" to the naphthalene ring.

For C-O bond length there is almost no influence of type of electron directing group. The bonds for EDG are as follows:

$$8E > 5E = 6E = 3E > 7E > 4E > 2E$$

for EWG:

$$8A > 5A = 6A > 3A > 7A > 4A = 2A$$

and for thio substituent: 4SH > 5SH > 6SH (the same order as previous). The longest bond is also observed for position 8, the shortest for position 2. Here, the influence of directing to *orto-* and *para-* positions of OH group is very strong: the shortest bonds are in positions 2 and 4, whereas the order of the rest of bonds is very similar to the order observed for C-subst bonds for EDG substituent.

Table S2: The total (in hartree) and relative (in kcal/mol) energy of molecules differing in substituent position in relation to naphthalene ring.

	E+ZPE (hartree)	relative energy (kcal/mol)
2A1N	−572.421 417 3	0.65
3A1N	−572.422 455 8	0.00
4A1N	−572.419 087 1	2.11
5A1N	−572.416 941 4	3.46
6A1N	−572.421 736 0	0.45
7A1N	−572.421 322 1	0.71
8A1N	−572.412 541 7	6.22
4SH1N	−844.710 040 4	1.17
5SH1N	−844.711 904 1	0.00
6SH1N	−844.652 490 1	37.28
2E1N	−686.473 829 1	0.00
3E1N	−686.445 180 5	17.98
4E1N	−686.453 697 9	12.63
5E1N	−686.448 256 1	16.05
6E1N	−686.444 891 6	18.16
7E1N	−686.455 887 1	11.26
8E1N	−686.448 151 7	16.11

Table S3: The analysis of IR vibrations (expressed in cm^{-1}) for the vibrations having $\varepsilon > 5M^{-1}cm^{-1}$ performed using APF-D/NLO-V method for free molecules. Part 1.

	aromatic ring																						
	carbon ring																						
N	1034	1561																					
1N	810	1044	1085	1445	1464	1506	1580	1681	1720														
2A1N	221	485	1500	1583	1664	1688	1716																
3A1N	190	1469	1585	1686	1727																		
4A1N	198	471	1031	1093	1435	1460	1683	1713															
5A1N	177	326	527	878	1444	1680	1719																
6A1N	177	316	1470	1593	1665	1690	1720																
7A1N	735	904	977	1584	1671	1679	1722																
8A1N	157	1586	1671	1710																			
4SH1N	169	1558	1579	1626	1665	1723																	
5SH1N	162	296	618	848	1453	1475	1517	1594	1639	1740													
6SH1N	1491	1501	1557	1590	1635	1675	1730																
2E1N	565	605	636	730	768	875	900	1050	1110	1260	1283	1399	1463	1479	1515	1587	1628	1689	1700				
3E1N	895	933	946	1046	1084	1109	1413	1454	1470	1497	1518	1582	1659	1682	1729								
4E1N	176	806	953	1098	1532	1585	1685	1685	1714														
5E1N	623	667	792	814	921	1070	1594	1665	1684	1717													
6E1N	697	866	941	1057	1471	1512	1581	1665	1691	1722													
7E1N	748	916	1487	1535	1576	1672	1684	1726															
8E1N	145	882	1478	1498	1589	1656	1673	1712															

	aromatic ring																						
	carbon ring-H atoms																						
N	491	807	1379	3164	3171																		
1N	800	1108	1220	1263	1331	1489	3140	3169	3177	3189													
2A1N	705	770	794	852	935	1051	1108	1165	1200	1243	1277	1314	1411	1477	1490	3170	3178						
3A1N	628	718	774	791	822	882	1051	1112	1150	1172	1198	1224	1276	1322	1416	1447	1488	1515	3143	3160	3170	3189	
4A1N	789	837	864	1060	1222	1225	1288	1381	1459	1477	1516	1589	3144	3167	3190	3207							
5A1N	806	814	878	1101	1111	1161	1219	1243	1329	1444	1483	1504	3145	3167	3186	3221							
6A1N	773	795	834	876	1081	1108	1165	1196	1221	1248	1282	1333	1399	1448	1505	1513	3142	3179					
7A1N	765	773	872	1081	1105	1153	1169	1188	1240	1266	1338	1404	1451	1464	1484	1530	3143	3163	3179				
8A1N	782	802	844	884	1073	1144	1228	1319	1416	1473	1497	3142	3172	3179									
4SH1N	794	802	848	1007	1061	1112	1199	1334	1374	1463	1759	1809	1880	2927	3174	3182	3193						
5SH1N	752	899	908	932	983	1010	1149	1173	1325	1377	1768	1804	1893	2944	3146	3171	3227						
6SH1N	621	724	793	835	897	1086	1097	1148	1161	1303	1308	1336	1378	1822	2000	2032	3150	3181	3279				
2E1N	188	440	792	837	873	1161	1243	1283	1479	3159	3169	3183	3188										
3E1N	774	798	820	889	1119	1159	1189	1203	1222	1256	1287	1333	1413	1454	3148	3170	3189						
4E1N	753	805	1056	1075	1149	1222	1227	1240	1295	1336	1421	1431	1440	1465	3144	3166	3191						
5E1N	811	1095	1107	1118	1163	1193	1215	1231	1270	1297	1335	1451	1460	1469	1488	1506	3143	3166					
6E1N	798	841	881	955	1086	1109	1113	1176	1194	1224	1226	1255	1307	1331	1402	1447	1509	1511	3142	3166	3179		
7E1N	770	798	879	882	1085	1131	1178	1209	1268	1339	1404	1453	3142	3179									
8E1N	789	802	980	1068	1101	1112	1152	1184	1226	1290	1323	1415	1447	3144	3171	3178							

	substituents in naphthalene																						
	additional															OH							
N																							
1N																238	1263	3762					
2A1N	1500	1906	2854													330	1200	3748					
3A1N	1416	1469	1512	1916	2942											271	1276	3759					
4A1N	198	837	1516	1548	1904	3003										296	1225	3751					
5A1N	765	1504	1905	3019												241	1219	3760					
6A1N	1491	1513	1917	2938												240	1221	3760					
7A1N	1917	2932														256	1240	3757					
8A1N	1908	3014														209	1228	3742					
4SH1N	1374	1404	2304	6774												231	1232	3756					
5SH1N	1435	2329	6779													268	1207	3761					
6SH1N	1256	2270	7024													258	1247	3771					
2E1N	1116	1284	1434	1478	1931	2978										1184	1874	1931	2978	3043			
3E1N	250	268	798	1460	1470	1497	1500	1915	2991	3136						1287	3758						
4E1N	211	868	1070	1202	1421	1431	1440	1447	1502	1908	2976	3102				278	3757						
5E1N	243	247	1193	1215	1231	1297	1451	1460	1469	1476	1488	1506	1509	1918	3001	1297	3759						
6E1N	697	1057	1194	1226	1461	1471	1479	1500	1509	1915	2992	3136				1255	3760						
7E1N	358	800	1131	1206	1293	1404	1442	1449	1503	1911	2979	3107				253	1209	1268	3759				
8E1N	1112	1242	1290	1468	1506	1924	3000	3149	3155							212	3742						

vibrations grouped into two categories: aromatic ring and substituent vibrations.

For a more detailed analysis see table S4;

values unscalled due to the lack of scaling factors for the method.

Table S4: The analysis of IR vibrations (expressed in cm^{-1}) for the vibrations having $\varepsilon > 5M^{-1}cm^{-1}$ performed using APF-D/NLO-V method for free molecules. Part 2.

	CH stretching					CH bending								CH_2=CH_2								
N	3164	3171				1379								1034								
1N	3140	3169	3177	3188		1331	1445	1464	1489	1506				1044	1085	1108	1220	1263				
2A1N	2854	3170	3178			1411	1477	1490	1500	1583				936	1051	1108	1165	1200	1243	1277	1314	
3A1N	2942	3142	3160	3170	3189	1322	1416	1447	1469	1488	1512	1515		1051	1112	1150	1172	1198	1224	1276		
4A1N	3003	3144	3167	3190	3207	1288	1331	1435	1460	1477	1516			1031	1060	1093	1222	1225				
5A1N	3019	3145	3167	3168	3221	1329	1443	1483	1504					1101	1111	1161	1219	1243				
6A1N	2938	3142	3179			1282	1333	1399	1448	1470	1491	1505	1513	1081	1108	1165	1186	1221	1248			
7A1N	2932	3143	3164	3179		1338	1404	1451	1464	1484				1081	1105	1153	1169	1188	1240	1266		
8A1N	3014	3142	3172	3179		1320	1416	1473	1497					1073	1144	1228						
4SH1N	2927	3174	3182	3193		1334	1374	1404	1463					1007	1061	1112	1199	1232				
5SH1N	2944	3146	3171	3227		1325	1377	1435	1453	1476	1517			1010	1149	1173	1207					
6SH1N	3150	3181	3279			1303	1308	1336	1378	1491	1501			1087	1097	1148	1162	1247	1256			
2E1N	3159	3169	3183	3188		1283	1399	1463	1479	1515				1050	1110	1116	1161	1243	1260			
3E1N	3148	3170	3189			1287	1333	1413	1454	1470	1497	1518		1046	1084	1109	1119	1159	1189	1203	1223	1256
4E1N	3144	3166	3191			1296	1336	1421	1432	1465	1532			1056	1075	1098	1149	1222	1227	1240		
5E1N	3143	3166				1271	1297	1335	1451	1460	1488	1506		1070	1095	1107	1118	1163	1193	1215	1231	
6E1N	3142	3166	3179			1331	1402	1447	1471	1497	1503	1512		1057	1086	1109	1113	1176	1194	1224	1226	1255 1307
7E1N	3142	3179				1268	1293	1339	1404	1453	1487	1536		1085	1131	1178	1209					
8E1N	3144	3149	3171	3178		1290	1323	1415	1447	1478	1498			1068	1101	1112	1152	1184	1226	1242		

	C=C									C=CH_2, CH=CH							C-H out-of-plane					O-H out-of-plane	
N	1561																491	807					
1N	1580	1681	1720							794												238	
2A1N	1664	1688	1717							794							484					330	
3A1N	1585	1686	1727							718	791						190	628	774	822	882	271	
4A1N	1548	1589	1683	1713						471	837						198	789	864			295	
5A1N	1680	1719								326	527	765	806	878			177	814				241	
6A1N	1593	1664	1690	1720						316	794						177	774	834	876		240	
7A1N	1530	1584	1671	1679	1722					735	765	904	977				773	872				256	
8A1N	1587	1671	1710														157	782	802	844	884	209	
4SH1N	1558	1579	1626	1665	1729	1759	1809	1880		794	802						169	849				231	
5SH1N	1594	1639	1740	1768	1804	1893				618	848	908	932	983			162	297	752	899		268	297
6SH1N	1557	1590	1635	1675	1730	1822	2000	2032		621	724	897					793	835				258	
2E1N	1587	1628	1689	1700						565	605	636	730	768	875	900	440	793	837	873		1184	
3E1N	1582	1659	1682	1729						895	933	946					774	798	820	889		250	268
4E1N	1585	1685	1714							806	953						783	804	868			278	
5E1N	1594	1665	1684	1717						667	782	814	921				811					243	247
6E1N	1581	1665	1691	1722						697	866	941					798	841	881	955		242	
7E1N	1575	1672	1684	1726						358	748	800	873	916			770	798	882			253	
8E1N	1589	1657	1673	1712						146	980						789	801	882			212	

	CH_3									SH				CO	OH				
N																			
1N															3762				
2A1N														1906	3748				
3A1N														1916	3759				
4A1N														1904	3751				
5A1N														1905	3760				
6A1N														1917	3760				
7A1N														1917	3757				
8A1N														1908	3742				
4SH1N										2304	6772				3756				
5SH1N										1435	2329	6779			3761				
6SH1N										1256	1336	2270	7024		3771				
2E1N	1184	1434	1478	2978										1931	1874	1931	2978	3043	
3E1N	210	250	1460	1470	1497	1500	2991	3136						1109	1915	1287	3758		
4E1N	176	355	1202	1440	1447	1502	2976	3102						1075	1907	1227	3757		
5E1N	243	247	1297	1460	1469	1477	1506	1510	3001					1918		1215	1297	1488	3759
6E1N	1461	1471	1479	1500	2992	3136								1915		1224	3760		
7E1N	253	1206	1404	1441	1449	1503	2979	3107						1911		1209	1453	3759	
8E1N	1226	1242	1468	1506	3000	3149	3155							1924		1226	1478	3742	

The vibrations are divided into categories due to the characteristic IR band positions;

values unscalled due to the lack of scaling factors for the method.

Table S5: The reactivity descriptors calculated from the energies of neutral and ionic forms of each molecule.

Compound	HOMO	LUMO	Δ	I	A	η	χ	ω	S
N	−6.747 88	−1.722 21	5.026	8.520	−0.019	4.269	4.251	2.116	0.234
1N	−6.133 72	−1.409 55	4.724	7.897	−0.312	4.105	3.792	1.752	0.244
2A1N	−6.457 27	−2.024 53	4.433	8.146	0.380	3.883	4.263	2.340	0.258
3A1N	−6.397 40	−1.985 62	4.412	8.095	0.343	3.876	4.219	2.296	0.258
4A1N	−6.388 15	−1.952 42	4.436	8.069	0.308	3.880	4.188	2.260	0.258
5A1N	−6.339 98	−2.128 75	4.211	8.048	0.463	3.792	4.256	2.388	0.264
6A1N	−6.374 27	−1.987 52	4.387	8.078	0.330	3.874	4.204	2.281	0.258
7A1N	−6.335 90	−2.076 77	4.259	8.034	0.440	3.797	4.237	2.364	0.263
8A1N	−6.318 21	−1.923 85	4.394	8.028	0.261	3.884	4.145	2.212	0.257
4SH1N	−6.099 71	−1.675 68	4.424	7.801	0.016	3.893	3.908	1.962	0.257
5SH1N	−6.187 06	−1.643 57	4.543	7.873	−0.010	3.942	3.932	1.961	0.254
6SH1N	−6.282 84	−1.606 56	4.676	7.959	−0.044	4.002	3.957	1.957	0.250
2E1N	−6.092 90	−1.634 32	4.459	7.730	0.052	3.839	3.891	1.972	0.260
3E1N	−6.347 88	−1.729 56	4.618	8.013	0.126	3.943	4.069	2.099	0.254
4E1N	−6.235 76	−1.588 06	4.648	7.879	−0.018	3.948	3.931	1.957	0.253
5E1N	−6.309 51	−1.683 30	4.626	7.975	0.054	3.961	4.014	2.034	0.252
6E1N	−6.326 92	−1.744 52	4.582	8.011	0.138	3.936	4.074	2.109	0.254
7E1N	−6.213 18	−1.706 15	4.507	7.883	0.131	3.876	4.007	2.071	0.258
8E1N	−6.317 94	−1.676 77	4.641	7.977	0.043	3.967	4.010	2.027	0.252

Values expressed in eV (only in the case of S the values are in eV^{-1}); for more details see Computational details section in the main text.

Table S6: The analysis of an influence of the substituent position on the reactivity of molecules.

	EWG														EDG													
Δ	5	>	7	>	6	>	8	>	3	>	2	>	4		2	>	7	>	6	>	3	>	5	>	8	>	4	
MEP	8	>	7	>	6	>	5	>	2	>	3	>	4		2	>	7	>	3	>	4	>	6	>	8	>	5	
I	8	>	7	>	5	>	4	>	6	>	3	>	2		2	>	4	>	7	>	5	>	8	>	6	>	3	
A	8	>	4	>	6	>	3	>	2	>	7	>	5		4	>	8	>	2	>	5	>	3	>	7	>	6	
η	5	>	7	>	6	>	3	>	4	>	2	>	8		2	>	7	>	6	>	3	>	4	>	5	>	8	
S	5	=	7	>	2	=	3	=	4	=	6	=	8		2	>	7	>	3	=	4	=	6	>	5	=	8	
χ	2	>	5	>	7	>	3	>	6	>	4	>	8		6	>	3	>	5	>	8	>	7	>	4	>	2	
ω	5	>	7	>	2	>	3	>	6	>	4	>	8		6	>	3	>	7	>	5	>	8	>	2	>	4	
	electrophile												nucleophile		electrophile												nucleophile	

	the most reactive	the least reactive	the most reactive	the least reactive
position	times of occur.	times of occur.	times of occur.	times of occur.
2	1	4	5	1
3	0	4	1	1
4	1	4	2	2
5	4	1	0	3
6	0	1	1	2
7	6	1	4	1
8	3	3	1	4

The reactivity is ordered according to definitions of the used descriptors; the first two maximal values are taken into account and the times of occurrence is shown in the table for each tested positions of the substituents.

Table S7: The analysis of f^+: the list of atoms in studied molecules, for which the f^+ descriptor is dominant.

N		2	3	4	5	6	7	8	9	10				
1N	1	2	3	4	5	6	7	8	9	10	O^{OH}			
2A1N		2	3	4	5	6	7	8	9		O^{OH}	O^{CHO}		
3A1N		2	3	4	5	6	7	8	9	10	O^{OH}	O^{CHO}		
4A1N		2	3	4	5	6	7		9		O^{OH}	O^{CHO}		
5A1N		2	3	4	5	6	7	8	9		O^{OH}	O^{CHO}		
6A1N		2	3	4	5	6	7	8	9	10	O^{OH}	O^{CHO}		
7A1N		2	3	4	5	6	7	8	9		O^{OH}	O^{CHO}		
8A1N		2	3	4	5	6	7	8	9	10	O^{OH}	O^{CHO}		
2E1N		2	3	4	5	6	7	8	9		O^{OH}	E2	O^{E2}	O^{E1}
3E1N		2	3	4	5	6	7	8	9	10	O^{OH}	E2	O^{E2}	O^{E1}
4E1N		2	3	4	5	6	7	8	9	10	O^{OH}	E2	O^{E2}	O^{E1}
5E1N		2	3	4	5	6	7	8	9	10	O^{OH}	E2	O^{E2}	O^{E1}
6E1N		2	3	4	5	6	7	8	9	10	O^{OH}	E2	O^{E2}	O^{E1}
7E1N		2	3	4	5	6	7	8	9		O^{OH}	E2	O^{E2}	O^{E1}
8E1N		2	3	4	5	6	7	8	9	10	O^{OH}	E2	O^{E2}	O^{E1}

The atom numeration in accordance with figure 1;

in ester substituent carbon atoms are numbered as E1 (carboxyl substituent) and E2 (methyl substituent); hydrogen atoms are listed as H-carbon atom number, e.g.H7 means hydrogen atom associated with C7 of the naphthalene ring;

for complete analysis the table S7 should be juxtaposed with table S8.

Table S8: The analysis of f^-: the list of atoms in studied molecules, for which the f^- descriptor is dominant.

N							H1	H2	H3	H4	H5	H6	H7	H8					
1N	1							H2	H3	H4	H5	H6	H7	H8	H^{OH}				
2A1N	1			10	C^{CHO}				H3	H4	H5	H6	H7	H8	H^{OH}	H^{CHO}			
3A1N	1				C^{CHO}			H2		H4	H5	H6	H7	H8	H^{OH}	H^{CHO}			
4A1N	1		8	10	C^{CHO}			H2	H3		H5	H6	H7	H8	H^{OH}	H^{CHO}			
5A1N	1			10	C^{CHO}			H2	H3	H4		H6	H7	H8	H^{OH}	H^{CHO}			
6A1N	1				C^{CHO}			H2	H3	H4	H5		H7	H8	H^{OH}	H^{CHO}			
7A1N	1			10	C^{CHO}			H2	H3	H4	H5	H6		H8	H^{OH}	H^{CHO}			
8A1N	1				C^{CHO}			H2	H3	H4	H5	H6	H7		H^{OH}	H^{CHO}			
2E1N	1			10		E1			H3	H4	H5	H6	H7	H8	H^{OH}	H^{CH_3}	H^{CH_3}	H^{CH_3}	
3E1N	1					E1		H2		H4	H5	H6	H7	H8	H^{OH}	H^{CH_3}	H^{CH_3}	H^{CH_3}	
4E1N	1					E1		H2	H3		H5	H6	H7	H8	H^{OH}	H^{CH_3}	H^{CH_3}	H^{CH_3}	
5E1N	1					E1		H2	H3	H4		H6	H7	H8	H^{OH}	H^{CH_3}	H^{CH_3}	H^{CH_3}	
6E1N	1					E1		H2	H3	H4	H5		H7	H8	H^{OH}	H^{CH_3}	H^{CH_3}	H^{CH_3}	
7E1N	1			10		E1		H2	H3	H4	H5	H6		H8	H^{OH}	H^{CH_3}	H^{CH_3}	H^{CH_3}	
8E1N	1					E1		H2	H3	H4	H5	H6	H7		H^{OH}	H^{CH_3}	H^{CH_3}	H^{CH_3}	

The atom numeration in accordance with figure 1;

in ester substituent carbon atoms are numbered as E1 (carboxyl substituent) and E2 (methyl substituent); hydrogen atoms are listed as H-carbon atom number, e.g.H7 means hydrogen atom associated with C7 of the naphthalene ring;

for complete analysis the table S8 should be juxtaposed with table S7.

Table S9: The analysis of relative electrophilicity s^+/s^-: the list of atoms in studied molecules, for which the s^+/s^- descriptor is dominant.

N		2	3			6	7		9	10								
1N	1	2	3	4		6	7			10	O^{OH}							
2A1N		2	3	4	5		7		9	10	O^{OH}							
3A1N	1	2						8	9	10	O^{OH}							
4A1N	1	2		4	5	6	7				O^{OH}							
5A1N	1	2	3	4			7				O^{OH}							
6A1N	1	2		4			7	8	9	10	O^{OH}							
7A1N	1	2		4			7			10	O^{OH}							
8A1N	1	2	3	4		6	7			10	O^{OH}							
2E1N		2	3	4	5		7		9	10	O^{OH}	E1	O^{E2}	E2				
3E1N	1	2				6	7			10	O^{OH}		O^{E2}	O^{E1}			H^{CH_3}	
4E1N	1	2	3				7			10	O^{OH}	E1	O^{E2}	O^{E1}	E2			
5E1N	1	2	3	4		6	7			10	O^{OH}	E1	O^{E2}	O^{E1}	E2		H^{CH_3}	
6E1N	1	2	3	4		6	7			10	O^{OH}		O^{E2}	O^{E1}			H^{CH_3}	
7E1N	1	2		4						10	O^{OH}		O^{E2}	O^{E1}	E2			
8E1N	1	2	3	4		6	7			10	O^{OH}	E1	O^{E2}	O^{E1}	E2		H^{CH_3}	H^{CH_3}

The atom numeration in accordance with figure 1;

in ester substituent carbon atoms are numbered as E1 (carboxyl substituent) and E2 (methyl substituent); hydrogen atoms are listed as H-carbon atom number, e.g.H7 means hydrogen atom associated with C7 of the naphthalene ring;

for complete analysis the table S9 should be juxtaposed with table S10.

Table S10: The analysis of relative nucleophilicity s^-/s^+: the list of atoms in studied molecules, for which the s^-/s^+ descriptor is dominant.

N	1		4	5			8							H1	H2	H3	H4	H5	H6	H7	H8				
1N				5			8	9							H2	H3	H4	H5	H6	H7	H8	H^{OH}			
2A1N	1				6		8	9		C^{CHO}	O^{CHO}					H3	H4	H5	H6	H7	H8	H^{OH}	H^{CHO}		
3A1N		3	4	5	6	7				C^{CHO}	O^{CHO}				H2		H4	H5	H6	H7	H8	H^{OH}	H^{CHO}		
4A1N		3					8	9	10	C^{CHO}	O^{CHO}				H2	H3		H5	H6	H7	H8	H^{OH}	H^{CHO}		
5A1N				5	6		8	9	10	C^{CHO}	O^{CHO}				H2	H3	H4		H6	H7	H8	H^{OH}	H^{CHO}		
6A1N		3		5	6					C^{CHO}	O^{CHO}				H2	H3	H4	H5		H7	H8	H^{OH}	H^{CHO}		
7A1N		3		5	6		8	9		C^{CHO}	O^{CHO}					H3	H4	H5	H6		H8	H^{OH}	H^{CHO}		
8A1N				5			8	9		C^{CHO}	O^{CHO}				H2	H3	H4	H5	H6	H7		H^{OH}	H^{CHO}		
2E1N	1				6		8						O^{E1}			H3	H4	H5	H6	H7	H8	H^{OH}	H^{CH_3}	H^{CH_3}	H^{CH_3}
3E1N		3	4	5			8	9				E1	O^{E1} E2		H2		H4	H5	H6	H7	H8	H^{OH}	H^{CH_3}	H^{CH_3}	
4E1N			4	5			8	9							H2	H3		H5	H6	H7	H8	H^{OH}	H^{CH_3}	H^{CH_3}	H^{CH_3}
5E1N				5			8	9							H2	H3	H4		H6	H7	H8	H^{OH}	H^{CH_3}	H^{CH_3}	
6E1N				5			8	9				E1	C^{CH_3}		H2	H3	H4	H5		H7	H8	H^{OH}	H^{CH_3}	H^{CH_3}	
7E1N		3		5	6	7	8	9				E1			H2	H3	H4	H5	H6		H8	H^{OH}	H^{CH_3}		
8E1N				5			8	9							H2	H3	H4	H5	H6	H7		H^{OH}	H^{CH_3}		

The atom numeration in accordance with figure 1;

in ester substituent carbon atoms are numbered as E1 (carboxyl substituent) and E2 (methyl substituent); hydrogen atoms are listed as H-carbon atom number, e.g.H7 means hydrogen atom associated with C7 of the naphthalene ring;

for complete analysis the table S10 should be juxtaposed with table S9.

Table S11: The analysis of dual Δf and Δs local descriptors.

	$\Delta f > 0$ (electrophilic)										$\Delta f < 0$ (nucleophilic)													
N	1	2	3	4	5	6	7	8	9	10						H1	H2	H3	H4	H5	H6	H7	H8				
1N		2	3	4	5	6	7	8	9	10	O^{OH}				1				H2	H3	H4	H5	H6	H7	H8	H^{OH}			
2A1N		2	3	4	5	6	7	8	9		O^{OH}	O^{CHO}			1	10	C^{CHO}		H3	H4	H5	H6	H7	H8	H^{OH}	H^{CHO}		
3A1N		2	3	4	5	6	7	8	9	10	O^{OH}	O^{CHO}			1		C^{CHO}	H2		H4	H5	H6	H7	H8	H^{OH}	H^{CHO}		
4A1N		2	3	4	5	6	7	8	9		O^{OH}	O^{CHO}			1	10	C^{CHO}	H2	H3		H5	H6	H7	H8	H^{OH}	H^{CHO}		
5A1N		2	3	4	5	6	7	8	9		O^{OH}	O^{CHO}			1	10	C^{CHO}	H2	H3	H4		H6	H7	H8	H^{OH}	H^{CHO}		
6A1N		2	3	4	5	6	7	8	9	10	O^{OH}	O^{CHO}			1		C^{CHO}	H2	H3	H4	H5		H7	H8	H^{OH}	H^{CHO}		
7A1N		2	3	4	5	6	7	8	9		O^{OH}	O^{CHO}			1	10	C^{CHO}		H3	H4	H5	H6		H8	H^{OH}	H^{CHO}		
8A1N		2	3	4	5	6	7	8	9	10	O^{OH}	O^{CHO}			1		C^{CHO}	H2	H3	H4	H5	H6	H7		H^{OH}	H^{CHO}		
2E1N		2	3	4	5	6	7	8	9		O^{OH}	O^{E2}	E2	O^{E1}	1	10	E1		H3	H4	H5	H6	H7	H8	H^{OH}	H^{CH_3}	H^{CH_3}	H^{CH_3}
3E1N		2	3	4	5	6	7	8	9	10	O^{OH}	O^{E2}	E2	O^{E1}	1		E1	H2		H4	H5	H6	H7	H8	H^{OH}	H^{CH_3}	H^{CH_3}	H^{CH_3}
4E1N		2	3	4	5	6	7	8	9	10	O^{OH}	O^{E2}	E2	O^{E1}	1		E1	H2	H3		H5	H6	H7	H8	H^{OH}	H^{CH_3}	H^{CH_3}	H^{CH_3}
5E1N		2	3	4	5	6	7	8	9	10	O^{OH}	O^{E2}	E2	O^{E1}	1		E1	H2	H3	H4		H6	H7	H8	H^{OH}	H^{CH_3}	H^{CH_3}	H^{CH_3}
6E1N		2	3	4	5	6	7	8	9	10	O^{OH}	O^{E2}	E2	O^{E1}	1		E1	H2	H3	H4	H5		H7	H8	H^{OH}	H^{CH_3}	H^{CH_3}	H^{CH_3}
7E1N		2	3	4	5	6	7	8	9		O^{OH}	O^{E2}	E2	O^{E1}	1	10	E1	H2	H3	H4	H5	H6		H8	H^{OH}	H^{CH_3}	H^{CH_3}	H^{CH_3}
8E1N		2	3	4	5	6	7	8	9	10	O^{OH}	O^{E2}	E2	O^{E1}	1		E1	H2	H3	H4	H5	H6	H7		H^{OH}	H^{CH_3}	H^{CH_3}	H^{CH_3}

The analysis is presented for Δf descriptor;

the list of atoms in studied molecules, for which the Δf is positive (the selectivity toward nucleophilic attack) and Δf is negative (the selectivity toward electrophilic attack);

Δs has the same order of atoms; the atom numeration in accordance with figure 1; in ester substituent carbon atoms are numbered as E1 (carboxyl substituent) and E2 (methyl substituent); hydrogen atoms are listed as H-carbon atom number, e.g.H7 means hydrogen atom associated with C7 of the naphthalene ring.

Naphthalene/1-Naphthol description

1. **Frontier Orbitals**

   In the case of naphthalene molecule, the HOMO orbital is localized mainly in the region of C9-C10 bond with small influence from surrounding atoms and the LUMO orbital is very similar in its localization (the only difference is a change of the main shape – here, the orbital is formed in the regions of C9 and C10 atoms separately, not C9-C10 bond) – hence small reactivity of the molecule.

2. **MEP**

   The MEP surface of naphthalene (see fig. S1b) shows a high electronegative center of the ring and positively charged margins of the molecule. Thereby the delocalized electrons within both benzene rings are present equally in the molecule and as the consequence, the molecule is not very reactive. The situation is completely different when the hydroxyl group is present. The group represents the most positive potential region (thereby it is the nucleophilic center) due to the charge transfer from high electronegative OH group to the naphthalene ring resulting in more charge scattering seen as the change of the color of the center of the molecule from red to yellow and slightly positive charged margins of the molecule.

Global reactivity descriptors - more detailed data

Ionisation Energy (I) is the ability of an atom to form a positive ion and is defined as the work done in removing an electron at zero temperature, whereas the ionization potential is the electric potential required to separate an electron from the orbital system in free space with the kinetic energy remaining unchanged [28].

The ionisation energy calculated for EWG (based on results from the table 1; all the data is collected in table S5) has the following order:

$$2A > 3A > 6A > 4A > 5A > 7A > 8A$$

As it is seen, the best ability to form positive ion (the smallest values of I) have substituents having neighboring positions in relation to the OH group in the other benzene ring whereas the greatest values of the I descriptor are found for the substituents lying near the hydroxyl group in the same benzene ring.

Quite different situation is observed when EDG is added:

$$3E > 6E > 8E > 5E > 7E > 4E > 2E$$

Here, the greatest potential of forming cation is observed for 1-naphthol derivatives having the substituents in *ortho* and *para* positions, whereas the worst results (the greatest values of I) are for both *meta* positions in relation to the hydroxyl group.

Electron Affinity (A) is the ability of an atom to accept an electron and is defined as the change in energy of a neutral atom (in the gaseous phase) when an electron is added to the atom to form a negative ion [39].

The order of the calculated values of A in the case of EWG are listed below:

$$5A > 7A > 2A > 3A > 6A > 4A > 8A$$

Inversely in comparison to the case of I descriptor, the most reactive compounds are the molecules with the greatest values of A descriptor: 5A1N and 7A1N while the least reactive are 4A1N and 8A1N. A very similar situation is observed for EDG:

$$6E > 7E > 3E > 5E > 2E > 8E > 4E$$

The least reactive are the substituents with the same position as for EWG, for the most reactive compounds there is small change – substituent in position 6 causes much more reactivity than for molecule with a substituent in the position 5.

Absolute hardness (η) is the measure of the escaping tendency of electrons from the species. The idea of chemical hardness and softness was introduced in connection with the behavior of Lewis acids and bases [47]. Thereby, in this classification, soft systems are large and easy to polarise, while hard systems are quite small and much less polarizable [61].

The order of values of hardness for molecules with substituent with EWG/EDG group respectively (calculated as shown in eq. 1):

$$8A > 2A > 4A > 3A > 6A > 7A > 5A$$
$$8E > 5E > 4E > 3E > 6E > 7E > 2E$$

The order of η is very similar for both types of substituents – the only difference is the change of 5 and 2 substituent positions; the most "hard" molecule is the compound with substituent in the position 8.

Softness (S) as the inverse of global hardness [67] is the ability of a molecule to accept electrons [62].

$$5A = 7A > 2A = 3A = 4A = 6A = 8A$$
$$2E > 7E > 3E = 4E = 6E > 5E = 8E$$

The least reactive are 1-naphthol derivatives for both substituents in position 8.

Electronegativity (χ) is the power of an atom in a molecule to attract electrons to itself. The difference in electronegativity between the atoms X and Y could be perceived as a measure of the degree of electron transfer from atom X to atom Y on forming the chemical bond between them [49].

In the case of non-metals, the reactivity increases with the electronegativity. Thereby, for the order of molecules with EWG/EDG groups respectively:

$$2A > 5A > 7A > 3A > 6A > 4A > 8A$$
$$6E > 3E > 5E > 8E > 7E > 4E > 2E$$

the most reactive position of EWG is the least reactive position of EDG. The least reactive position substituent for EWG is 8 and the most reactive position of the substituent for EDG is 6. Position 4 in both cases likewise is not very reactive.

Electrophilicity (ω) is a descriptor, which involves two other descriptors: hardness and chemical potential to express the property of species to accept an electron [58] and to determine the stabilization energy of the species [62]. Low values of ω indicate a good nucleophile whereas greater values specify the existence of a good electrophile [58].

Among tested compounds the best nucleophiles are 8A1N and 4E1N whereas the best electrophiles are 5A1N and 6E1N. The order of the values for EWG and EDG groups is as follows:

$$5A > 7A > 2A > 3A > 6A > 4A > 8A$$
$$6E > 3E > 7E > 5E > 8E > 2E > 4E$$

Local Reactivity Descriptors – detailed analysis:

Fukui functions

The analysis of the Fukui functions is divided into three parts: nucleophilic, electrophilic and radical Fukui functions description.

The electrophilic Fukui function (f^+) (calculated as in eq. 5) is associated with the situation the electron was added to the system after a nucleophilic attack. The most reactive are the C2 carbon atom, oxygen from the hydroxyl group and E2 carbon atom (the second carbon atom of the ester substituent which is not directly connected to the aromatic ring); the least reactive is the hydrogen atom from the hydroxyl group, C1 (the exception is 6A1N) and E1 (the carbon atom of the ester substituent directly connected with the aromatic ring) carbon atoms.

The nucleophilic Fukui function (f^-) (see eq. 6) is used to describe the system with the lack of an electron due to the electrophilic attack. The order of atoms also does not depend on the substitution. The most reactive are the hydrogen atom from the hydroxyl group, H8 (the hydrogen atom connected with C8 atom) and E1 carbon atom; the least reactive are the oxygen atom from the hydroxyl group, C2, C4 atoms and E2 carbon atom in the case of EDG substituent.

The radical Fukui function (f^0) is calculated (as in eq. 7) to predict the most reactive places for the reactions involving radicals. Here, the most reactive are C9 (the exception is 6A1N) and C10 atoms; the least reactive are C4, C5 (the exception is the position 2) and C8 atoms.

The analysis of the dominant contribution (for a more detailed analysis see tables: S7 and S8) showed that all the tested compounds do not exhibit radical character. The electrophilic character is shown by the carbon atoms of the ring (the exception is C1 and C10 for substituted 1-naphthol: the positions 2 and 7 for both substituents and 5A1N, 6A1N), all the oxygen atoms regardless of the type of substituent and the carbon atoms of substituent less bonded to the ring (E2). The nucleophilic character is observed for all the hydrogen atoms and the substituent carbon atoms closely connected to the naphthalene ring.

Relative electrophilicity and nucleophilicity

According to collected data (table S9 for s^+/s^- and table S10 for s^-/s^+), in all the cases, the hydrogen atoms in the aromatic ring are nucleophilic (the dominant influence of s^-/s^+ descriptor, see table S10), while the oxygen atom from the hydroxyl group is electrophilic site (thereby it is present in table S9). Nucleophilic places in the N molecule are 1, 4, 5, 8 positions, in 1N the situation is similar with a few differences – the nucleophilic site in position 1 has changed to hydrogen atom from the hydroxyl group, position 4 has disappeared and the position 9 has shown up.

In the case of derivatives with EWG, the most reactive places for the electrophilic attack are similar to 1N: the position 8 is dominating (it does not show only in 3A1N and 6A1N molecules), all the substituent atoms are nucleophilic, the most reactive are the positions 3 (*2A1N, 5A1N, 8A1N), 5 (*2A1N, 4A1N), 6 (*4A1N and 8A1N) and 9 (*2A1N, 3A1N and 6A1N). There is no tendency in the substituent position on the electrophilicity of the site (e.g. for 2A1N the position 2 is not nucleophilic whereas in 6A1N the position 6 is nucleophilic): the positions 1 (*2A1N), 2, 4 (*3A1N) and 7 (*3A1N) are electrophilic. The position 10 is also electrophilic with the exceptions for 4A1N and 5A1N molecules. In the case of additional EDG, the most reactive for an electrophilic attack are the positions 5 (*2A1N), 8 and 9 (*2E1N) while for the nucleophilic attack are the positions 1 (*2E1N), 2, 3 (*3E1N, 7E1N), 6 (*2E1N, 7E1N), 7 (*7E1N) and 10. The positions indicated by the substituent are generally nucleophilic (except 2E1N and 6E1N). The substituent atoms are generally electrophilic, however, hydrogen atoms are mostly nucleophilic, and E1 carbon atom is almost equally probable for both attacks (in four cases is nucleophilic: 2E1N, 3E1N, 6E1N and 7E1N).

Dual descriptors

The most nucleophilic places in the case of N, 1N and derivatives with both tested groups are hydrogen atoms of naphthalene ring and the hydroxyl group. The most electrophilic are the carbon atoms (without position 1) of the naphthalene ring (with some exceptions for the position 10) and the oxygen atom from the hydroxyl group. The C1, C9, C10 and atoms

from substituent are not reactive – they are placed in the middle of the series. In the case of the substituents with the two EDG groups, the order is slightly modified: the E1 carbon atom is added to the most nucleophilic atoms, and the E2 carbon atom is added to the most electrophilic atoms.

Table S12: The NLO parameters of studied molecules.

						static		dynamic for 532 nm		
Compound	μ	μ_x	μ_y	μ_z	α	β	γ	α	β	γ
N	0.000	0.000	0.000	0.000	15.894	0.000	1.814	16.930	0.000	2.741
1N	1.610	−1.357	0.866	0.000	16.697	1.248	2.125	17.891	2.148	3.547
2A1N	1.817	−0.632	1.704	0.000	19.469	2.952	6.026	21.248	5.246	11.304
3A1N	1.806	−0.243	1.789	0.000	19.499	4.143	6.920	21.263	8.226	16.063
4A1N	3.238	−2.154	−2.417	0.000	19.139	3.630	3.978	20.768	6.509	7.773
5A1N	3.598	−3.054	−1.902	0.000	19.002	2.948	4.024	20.648	7.130	10.022
6A1N	3.488	1.560	3.119	0.000	19.494	5.718	7.554	21.211	12.433	20.812
7A1N	2.514	−0.807	2.381	0.000	19.477	5.774	7.294	21.278	12.663	17.276
8A1N	2.126	1.863	−0.977	0.307	18.839	1.159	3.636	20.309	2.885	7.660
4SH1N	45.810	42.919	5.695	−14.969	20.545	4.875	0.559	17.664	9.801	−16.778
5SH1N	44.677	−35.308	−22.285	−15.898	20.333	3.309	4.949	16.855	158.277	−1728.924
6SH1N	3.164	2.928	−1.181	0.206	19.417	1.064	5.789	20.923	1.179	10.075
2E1N	2.230	−1.302	1.810	0.000	22.303	2.989	7.161	24.201	4.266	13.223
3E1N	2.468	−1.664	0.628	−1.712	21.475	1.580	6.464	23.023	2.796	11.084
4E1N	2.465	0.816	−2.273	0.497	21.635	3.019	5.606	23.195	4.906	9.862
5E1N	3.974	−3.481	−0.031	1.916	20.868	0.850	3.498	22.272	1.869	6.556
6E1N	3.918	3.507	0.383	−1.706	21.490	1.291	6.606	23.034	2.374	11.149
7E1N	1.078	−1.010	0.375	0.000	22.262	4.398	10.338	24.081	9.067	20.362
8E1N	2.583	−1.598	−1.180	1.651	20.806	1.969	3.227	22.176	3.277	5.957
urea	2.733	0.000	0.000	−2.733	3.662	0.177	0.156	3.728	0.206	0.175

The dipole moment expressed in Debye, the polarizability and hyperpolarizability tensors in ESU units; values for α, β and γ should be multiplied by 10^{-24}, 10^{-30} and 10^{-36} respectively.

NLO properties – more detailed description

Dipole moment

The dipole moment is a measure of molecular polarisation. Due to the symmetric charge distribution with only two types of atoms, the N molecule has no dipole moment. The presence of the hydroxyl group causes uneven charge distribution and as the consequence, the 1N has the dipole moment of 1.610 Debye. The addition of the EWG increases molecule polarisation more than 15% and the order of the molecules is as follows:

$$3A < 2A < 8A < 7A < 4A < 6A < 5A$$

As it is expected, the greatest values have compounds, in which the hydroxyl group (EDG) and aldehyde group (EWG) are possibly far away from each other (5 and 6 positions) due to the bigger influence on charge distribution. The difference between the biggest and the smallest dipole moments is almost two times. The change of EWG to EDG generally increases polarisation. Only in 7E1N molecule, the dipole moment is decreased and is the smallest among all the studied compounds.

$$7E < 2E < 4E < 3E < 8E < 6E < 5E$$

The largest values are obtained when the same positions are substituted as previous – to allow electron transfer within the whole molecule. The smallest polarisation could be observed when there is a possibility of forming O–H–O interaction.

Polarizability and hyperpolarizability tensors

As in the case of dipole moment, the addition of hydroxyl group to the naphthalene ring slightly improves its NLO properties. The introduction of the second substituent further improves the NLO properties (the exception is beta for 5E1N). The order of derivatives with EWG due to the increasing NLO features is following:

$$\alpha: \quad 8A < 5A < 4A < 2A < 7A < 6A < 3A$$
$$\beta: \quad 8A < 5A < 2A < 4A < 3A < 6A < 7A$$
$$\gamma: \quad 8A < 4A < 5A < 2A < 3A < 7A < 6A$$

The order of derivatives with EDG is presented below:

$$\alpha: \quad 8E < 5E < 3E < 6E < 4E < 7E < 2E$$
$$\beta: \quad 5E < 6E < 3E < 8E < 2E < 4E < 7E$$
$$\gamma: \quad 8E < 5E < 4E < 3E < 6E < 2E < 7E$$

The values of α for EWG are maximally 17% greater than in unsubstituted 1N, whereas for EDG is 34% respectively. It is worth to note, the smallest value for EDG is about 7% bigger than the greatest value for EWG. For both groups, the maximal values are obtained when the substituent is in the same benzene ring as the hydroxyl group while the minimal values are found for the substituent in the second benzene ring at the same position as the OH group. The second maximal value connected with the substituent is localized symmetrically in regard to the C9-C10 axis and the second minimal value for the molecule with the substituent is localized symmetrically in the direction perpendicular to the axis. In all the cases of studied positions, the EDG gives greater values of α.

While alpha values are at a comparable level, beta values are strictly associated with the position and type of substituent. For EWG the values are more than 2.4 times bigger than in 1N (the exception is the 8A1N molecule, which value is slightly less than in 1N). For EDG the values are also greater than in 1N (with the exception for 5E1N), but smaller than for EWG – the maximal value stands for about 75% maximal value of EWG and the minimal value is 36% smaller than in EWG. For both groups the maximal and minimal values are associated with the substituent localized in the second benzene ring positions; the maximum is in position 7 in both cases.

Gamma value increases with the presence of additional substituents: the addition of OH group increases its NLO behavior more than 15%, and further substitution improves the second-order hyperpolarizability value more than 70/50% for EWG/EDG groups respectively. The maximal and minimal values of gamma can be found, as in the case of beta, for the second benzene ring positions. Both the extreme values of γ are obtained for the EDG group; the greatest value is almost 5 times larger than for 1N and more than 35% larger than the greatest value for EWG.