Supporting information for

Thermal stability of phenolic resin: new insights based on bond dissociation energy and reactivity of functional groups

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Contents

Ⅰ. Details of bond order calculation for the PR models with different size 2

Ⅱ. Details for the BDE calculation 4

Ⅲ. BDEs of C-C and C-O bonds calculated at the levels of BPW91/6-311G(d,p), etc. 6

Ⅳ. HOMO/LUMO energy levels of PR models 10

Ⅴ. Condensed Fukui indices for radical attack 11

References 14

Ⅰ. Details of bond order calculation for the PR models with different size

i) 100 conformations were randomly generated through 10 ns molecular dynamics simulation at 500 K. The temperature will be high enough to provide the necessary energy to overcome the rotational barrier of C-C bonds in methylene bridge[1]. The molecular dynamics simulation were performed with LAMMPS[2].

ii) The 100 conformations were all optimized at PM7 level through MOPAC software[3]. The PM7 method is reliable for the introduction of weak interaction correction.

iii) 10 conformations with relatively low energy and different geometry were screened out by a software named molclus[4].

iv) The 10 conformations were optimized at B3LYP/6-311G(d,p) through Gaussian 09[5]. The DFT-D3 dispersion correction method[6] was used to further improve the accuracy of hydrogen bonds or p-π interaction description.

v) The BOs of C-C, C-O bonds were calculated by Multiwfn software[7]. Since there are so many definitions of BO, here we only calculated Mayer BO and Laplacian BO, which have good correlation with bond strength[8].

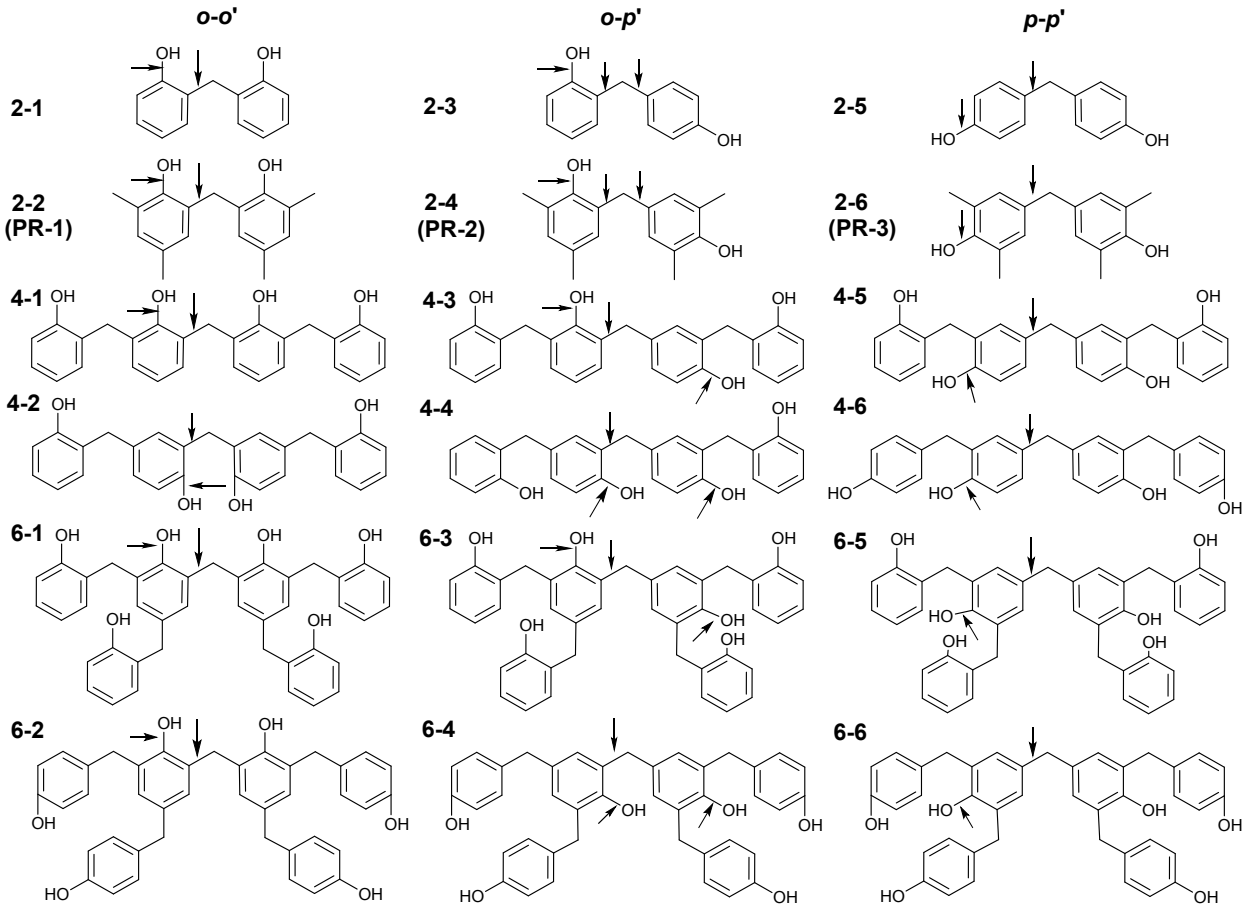


Fig. S1 PR models used for models size- bond strength relationship study. BOs of the C-C bonds in the middle methyl bridges and the C-O bonds in the tri-methyl substituted phenol are calculated.

Ⅱ. Details for the BDE calculation

The BDE for a molecule A-B is calculated as the difference in the enthalpies of formation of the products and reactants for hemolysis,

$$\mathrm{AB} \rightarrow \mathrm{A}\cdot + \mathrm{B}\cdot \tag{1}$$

$$\mathrm{BDE} = \Delta H_T(\mathrm{A}\text{-}\mathrm{B}) = H_T(\mathrm{B}\cdot) + H_T(\mathrm{A}\cdot) - H_T(\mathrm{A}B) \tag{2}$$

Officially, the IUPAC definition of bond dissociation energy (IUPAC, Compendium of Chemical Terminology, 2nd ed., the "Gold Book", 1997) refers to the energy change that occurs at 0 K, and the symbol is Do. However, it is commonly referred to as BDE, the bond dissociation energy, and it is generally used, albeit imprecisely, interchangeably with the bond dissociation enthalpy, which generally refers to the enthalpy change at room temperature (298K).

According to quasi-harmonic approximation (McQuarrie, Molecular Thermodynamics, 1999), the enthalpy (H) at certain temperature,

$$H_T = U + k_B \cdot T \tag{3}$$

$$U = E(el) + E(ZPE) + E(vib) + E(rot) + E(trans) \tag{4}$$

k_B, Boltmann's constant; U, the inner energy; $E(el)$, the total energy from the electronic structure calculation; E(ZPE), the zero temperature vibrational energy from the frequency calculation; E(vib), the finite temperature correction to $E(ZPE)$ due to population of excited vibrational states; $E(rot)$, the rotational thermal energy; $E(trans)$ is the translational thermal energy.

After the optimization and frequency calculation, the scaled enthalpy and zero-point vibrational energy at 298 K can be calculated with a shell script like this,

```
1  #!/bin/sh
2  # One should change the scale factor in line 6 before running this shell script.
3    for j in `ls *.fchk`
4    do
5      echo scaling ${j} ...
```

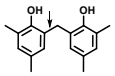
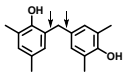
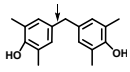
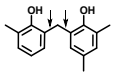
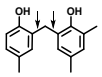
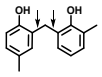
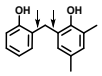
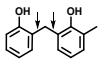
```
    freqchk ${j} -np 8 -o ${j%.*}.tmp N 298.15 1 0.983
    ZPE=`awk '/Zero-point vibrational energy/{print $4}' ${j%.*}.tmp`
    echo ${j%.*}" "${Z} >> ZPE.txt
    dH=`awk '/Thermal correction to Enthalpy=/{print $5}' ${j%.*}.tmp`
    echo ${j%.*}" "${H}def >> dH.txt
  done
  rm *.tmp
```

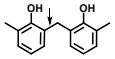
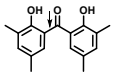
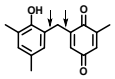
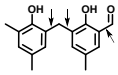
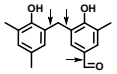
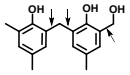
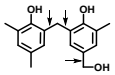
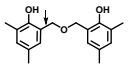
H_T for each species is E_{total}+dH, where E_{total} can be extract from the *.out/*.log files with a shell script like this,

```
#!/bin/sh
  for j in `ls *.out *.log`
  do
    echo extracting ${j} ...
    Etotal=`grep "SCF Done:" ${j} | tail -n 1 | awk '{print $5}'`
    echo ${j%.*}" "${Z} >> Etotal.txt
  done
```

Ⅲ. BDEs of C-C and C-O bonds calculated at the levels of BPW91/6-311G(d,p), etc.

Table S1 Calculated BDEs (298K, kJ/mol) of C-C bonds in methylene bridges of PR models

Models		BPW91/ 6-311G(d,p)	B3PW91/ 6-311G(d,p)	B3LYP/ 6-311G(d,p)	B3LYP/ def2-TZVP	M06-2X/ 6-311G(d,p)	M06-2X/ def2-TZVP
Ref.[a9]		397.46	345.17	401.05	326.97	377.64	379.19
PR-1		341.59	350.25	347.18	328.87	397.62	387.78
PR-2		348.83	348.22	350.47	332.31	403.45	386.17
		345.66[b]	343.50	346.00	329.03	395.34	379.11
PR-3		346.36	343.89	345.23	321.52	392.92	378.16
PR-4		339.40	334.12	341.37	306.21	397.88	372.71
		348.47	342.30	351.68	312.53	410.19	380.93
PR-5		350.69	351.13	351.52	327.61	402.70	388.19
		349.60	353.21	347.03	323.04	401.21	386.02
PR-6		346.39	340.91	347.89	316.61	409.71	380.55
		355.05	348.33	356.64	322.89	418.47	386.89
PR-7		343.98	344.84	345.33	322.20	396.43	382.27
		351.81	350.77	351.07	327.96	402.44	388.16
PR-8		348.26	341.92	350.35	309.64	409.92	380.76
		347.02	339.66	345.79	309.08	403.62	378.43
PR-9		348.54	349.28	348.67	322.42	403.04	387.56

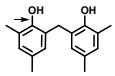
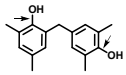
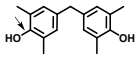
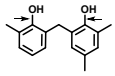
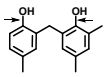
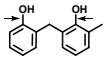
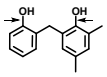
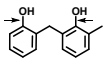
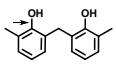
		355.95	354.45	352.86	328.15	405.50	391.58
PR-10		346.09	333.56	349.52	309.25	414.31	373.64
PR-11		332.54	351.12	358.29	331.21	399.73	386.84
PR-12		331.22	330.84	330.99	316.21	381.40	371.80
		353.12	351.06	350.71	333.87	405.35	393.10
PR-13		343.29	354.99	344.10	320.03	395.68	384.56
		364.94	351.88	355.08	328.93	404.09	393.29
		411.80[c]	421.00	399.63	404.06	443.75	433.93
PR-14		354.00	355.67	355.88	330.72	406.88	394.68
		355.84	355.65	356.34	330.93	405.79	393.51
		426.93[c]	433.73	414.19	419.70	455.40	447.71
PR-15		336.48	353.64	363.05	336.96	413.80	399.62
		317.20	357.07	352.97	328.85	404.48	389.83
		407.59[c]	459.69	434.16	352.17	476.77	469.07
PR-16		325.77	352.96	351.27	326.27	402.61	389.49
		326.29	353.30	351.71	326.85	402.79	389.61
		414.70[c]	463.64	440.84	362.07	480.98	471.91
PR-17		394.92	392.08	397.45	379.42	441.33	423.09

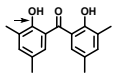
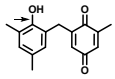
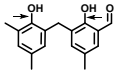
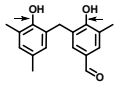
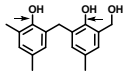
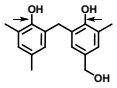
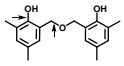
[a] The reported BDE of C-C bond in the methylene bridge of diphenylmethane is 378.2±8.4 kJ/mol[9].

[b] The BDE of the C-C bonds in Both sides of the methylene bridge were calculated, if the model is asymmetric.

[c] The BDE of the C-C bonds that linked to the aldehydes (PR-13, PR-14) or hydroxymethyls (PR-15, PR-16).

Table S2 Calculated BDEs (298K, kJ/mol) of C-O bonds in hydroxyls of PR models

Models		BPW91/ 6-311G(d,p)	B3PW91/ 6-311G(d,p)	B3LYP/ 6-311G(d,p)	B3LYP/ def2-TZVP	M06-2X/ 6-311G(d,p)	M06-2X/ def2-TZVP
Ref.[a]		445.67	430.42	447.21	421.28	457.89	449.15
PR1		440.56	440.65	421.21	449.37	465.12	457.07
PR-2		447.03	448.62	426.12	460.15	469.03	458.52
		447.80	448.34	429.44	457.53	469.56	460.57
PR-3		449.67	441.96	421.76	448.10	468.16	459.67
PR-4		446.60	444.81	420.25	445.42	466.87	458.2
		449.08	447.40	422.16	447.09	468.86	461.00
PR-5		448.62	441.48	420.64	448.72	467.45	459.27
		448.62	441.48	420.64	448.72	467.45	459.27
PR-6		452.05	459.72	432.34	454.37	477.23	467.20
		443.62	452.40	428.02	454.17	468.77	459.10
PR-7		449.02	433.31	420.71	445.80	467.69	459.56
		449.02	433.31	420.71	445.80	467.69	459.56
PR-8		455.53	440.02	428.34	454.63	475.87	468.37
		443.72	451.74	420.03	459.49	466.42	458.96
PR-9		443.13	439.98	420.92	451.88	462.85	456.81
		464.86	449.90	425.12	451.88	474.44	466.62
PR-10		442.58	451.37	433.57	455.19	466.52	459.03

PR-11		430.16	440.81	413.35	438.02	458.04	451.89
PR-12		423.06	434.97	414.41	444.55	458.52	452.03
PR-13		432.39	438.39	416.49	442.26	460.87	454.62
		441.74	443.89	420.88	447.88	467.83	462.06
PR-14		439.58	441.73	419.62	446.51	466.33	460.83
		445.34	449.13	428.27	454.60	473.61	468.36
PR-15		452.48	440.17	418.42	420.24	462.1	459.59
		445.97	433.66	412.49	414.30	457.93	452.47
PR-16		452.16	440.37	418.63	420.12	465.49	459.32
		453.13	441.80	421.05	422.28	467.88	461.31
PR-17		448.85	451.98	429.57	447.61	469.91	459.23
		256.59	257.84	260.66	248.89	319.11	307.95

[a] The referential BDE of C-O bond in the hydroxyl of phenol is 465.7±4.2 kJ/mol[9].

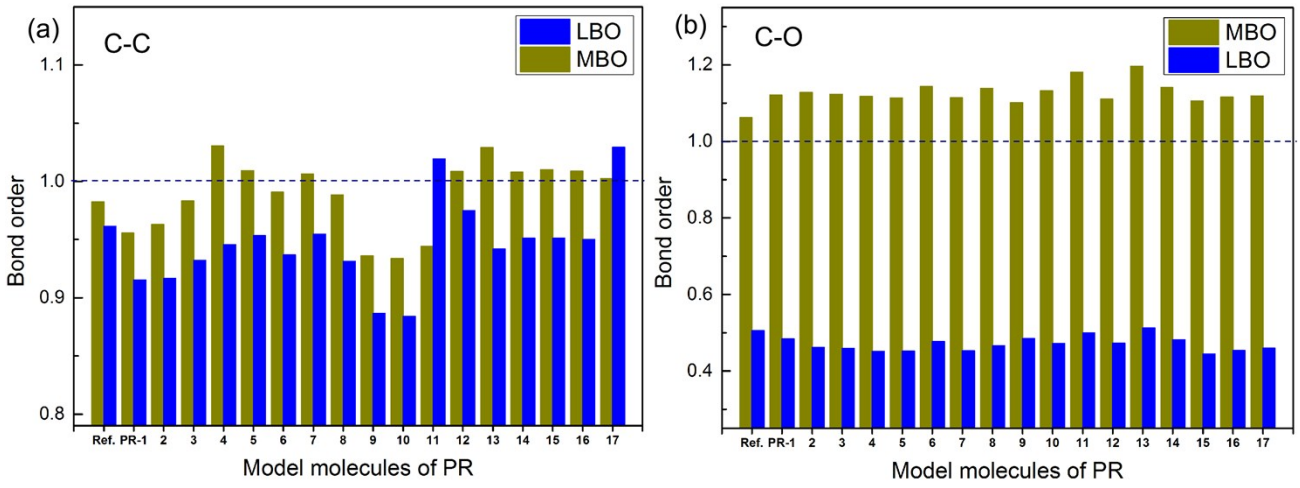


Fig. S2 Bond order of C-C (a) and C-O (b) bonds in PR models calculated at M06-2X/6-311G(d,p) level. The dark yellow and blue bars represent for the Mayer bond order (MBO) and Laplacian bond order (LBO), respectively.

Ⅳ. HOMO/LUMO energy levels of PR models

Table S3 Frontier orbital energy levels of the PR models calculated at M06-2X/6-311G(d,p) level

	HOMO (eV)	LUMO (eV)	Gap between SOMO(β) of HO· and HOMO of PR models
PR-1	-6.973	0.873	3.657
PR-2	-6.962	0.694	3.668
PR-3	-6.952	0.693	3.678
PR-4	-6.945	0.513	3.685
PR-5	-6.991	0.638	3.639
PR-6	-7.365	0.484	3.265
PR-7	-7.007	0.631	3.623
PR-8	-7.566	0.386	3.064
PR-9	-7.363	0.297	3.267
PR-10	-7.443	0.417	3.187
PR-11	-7.296	-0.477	3.334
PR-12	-7.290	-2.347	3.340
PR-13	-7.423	-0.532	3.207
PR-14	-7.313	-0.508	3.317
PR-15	-6.972	0.756	3.658
PR-16	-6.997	0.726	3.633
PR-17	-7.116	0.885	3.514

Ⅴ. Condensed Fukui indices for radical attack

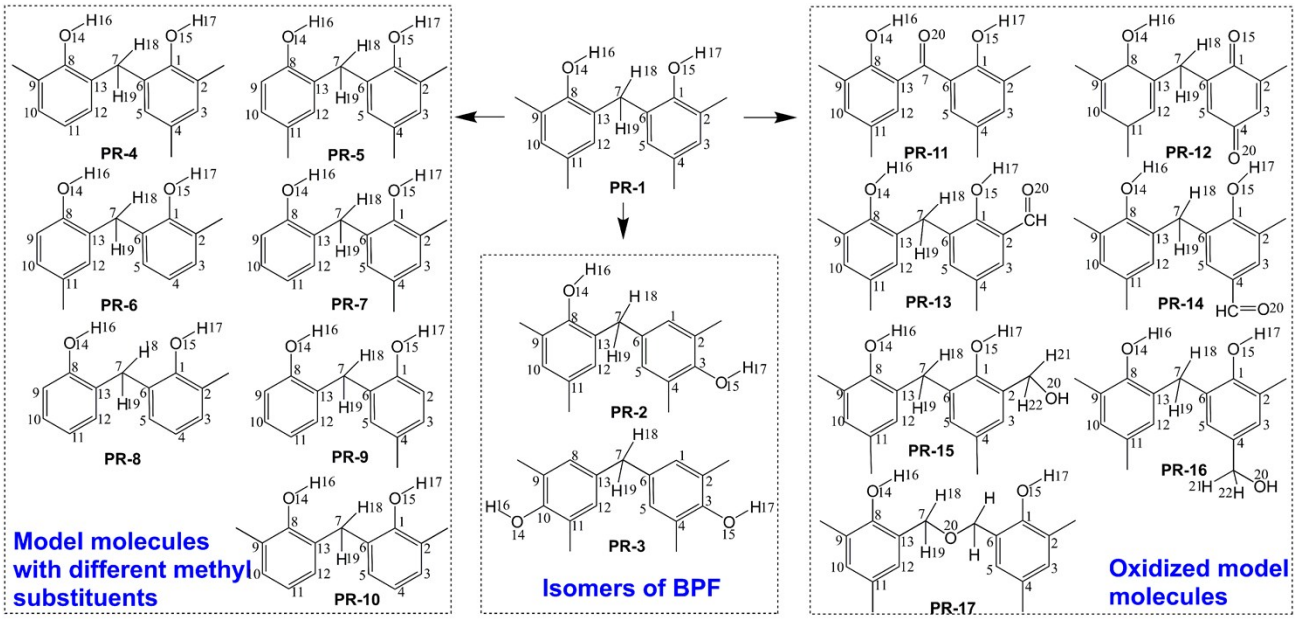


Fig. S3 Simplified models for cured PR

Table S4 Condensed Fukui indices for radical attack of main atoms in the simplified models of cured PR. Part I. The isomerized models and the models with different methyl substituents

	PR-1	PR-2	PR-3	PR-4	PR-5	PR-6	PR-7	PR-8	PR-9	PR-10
C1	0.047	0.042	0.029	0.031	0.035	0.036	0.034	0.033	0.030	0.031
C2	0.019	0.039	0.034	0.024	0.032	0.036	0.029	0.031	0.032	0.035
C3	0.044	0.049	0.039	0.046	0.058	0.049	0.057	0.048	0.051	0.045
C4	0.040	0.042	0.037	0.052	0.052	0.058	0.057	0.056	0.060	0.055
C5	0.033	0.031	0.045	0.043	0.042	0.049	0.047	0.056	0.045	0.049
C6	0.027	0.035	0.041	0.049	0.050	0.038	0.049	0.040	0.032	0.036
C7	0.009	0.013	0.012	0.013	0.013	0.014	0.013	0.014	0.014	0.014
C8	0.043	0.041	0.030	0.026	0.013	0.028	0.013	0.032	0.014	0.029
C9	0.048	0.042	0.046	0.038	0.027	0.041	0.029	0.046	0.037	0.041
C10	0.027	0.038	0.039	0.046	0.031	0.033	0.034	0.038	0.049	0.033
C11	0.048	0.032	0.036	0.024	0.044	0.030	0.050	0.036	0.038	0.040
C12	0.040	0.031	0.038	0.053	0.015	0.047	0.018	0.053	0.038	0.057
C13	0.032	0.037	0.038	0.043	0.049	0.052	0.056	0.056	0.052	0.048
O14	0.043	0.046	0.044	0.027	0.034	0.050	0.031	0.049	0.043	0.044
O15	0.035	0.033	0.043	0.054	0.044	0.042	0.049	0.047	0.053	0.047
H16	0.022	0.020	0.019	0.017	0.022	0.016	0.022	0.014	0.019	0.020
H17	0.021	0.019	0.019	0.022	0.022	0.020	0.024	0.021	0.017	0.015
H18	0.016	0.022	0.021	0.027	0.024	0.020	0.024	0.020	0.021	0.029
H19	0.017	0.017	0.022	0.015	0.018	0.027	0.019	0.028	0.028	0.019

Table S5 Condensed Fukui indices for radical attack of main atoms in the simplified models of cured PR. Part II. The oxidized models

	PR-11	PR-12	PR-13	PR-14	PR-15	PR-16	PR-17
C1	0.022	0.026	0.015	0.012	0.028	0.030	0.032
C2	0.036	0.045	0.030	0.024	0.030	0.028	0.033
C3	0.033	0.031	0.031	0.030	0.045	0.042	0.043
C4	0.046	0.039	0.030	0.030	0.041	0.046	0.042
C5	0.041	0.047	0.042	0.036	0.041	0.039	0.038
C6	0.026	0.042	0.025	0.024	0.045	0.040	0.038
C7	0.053	0.010	0.009	0.008	0.011	0.011	0.010
C8	0.022	0.021	0.027	0.030	0.022	0.027	0.043
C9	0.033	0.031	0.028	0.037	0.029	0.033	0.033
C10	0.036	0.043	0.053	0.044	0.046	0.033	0.032
C11	0.026	0.015	0.023	0.045	0.015	0.025	0.038
C12	0.041	0.051	0.041	0.045	0.047	0.039	0.038
C13	0.046	0.036	0.043	0.040	0.037	0.042	0.042
O14	0.040	0.074	0.034	0.026	0.033	0.031	0.036
O15	0.040	0.051	0.046	0.047	0.043	0.037	0.036
H16	0.021	0.023	0.018	0.016	0.018	0.017	0.018
H17	0.021	-	0.022	0.021	0.021	0.018	0.018
H18	-	0.021	0.016	0.015	0.019	0.021	0.016
H19	-	0.013	0.017	0.015	0.017	0.017	0.019
O20	0.075	0.092	-	0.084	0.022	0.023	0.015

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