Electronic Supplementary Material (ESI) for RSC Advances.


# Elucidation of hydrogen bonding formation by computational,FT-IR Spectroscopic and theoretical study between benzylalcohol with isomeric cresols

**Supplementary Information**

**Table S1:**

Standard deviation σ ($V^E$) and values of constants ($a_0$, $a_1$, $a_2$; $b_0$, $b_1$, $b_2$) for Redlich-Kister, Eq. (2) and Hwang et al., Eq. (3) for benzylalcohol (1) with *o,m,p*-cresols(2)

| Temperature | Redlich-Kister | | | | Hawang | | | |
|---|---|---|---|---|---|---|---|---|
| | $a_0$ | $a_1$ | $a_2$ | $\sigma(V^E)$ | $b_0$ | $b_1$ | $b_2$ | $\sigma(V^E)$ |
| | $cm^{-3}.mol^{-1}$ | | | | $cm^{-3}.mol^{-1}$ | | | |
| | Benzylalcohol(1) + *o*-cresol (2) | | | | | | | |
| 303.15K | -0.195 | 0.003 | 0.053 | 0.001 | -0.212 | 0.074 | 0.067 | 0.001 |
| 308.15K | -0.215 | 0.003 | 0.046 | 0.001 | -0.229 | 0.065 | 0.058 | 0.001 |
| 313.15K | -0.234 | -0.005 | 0.035 | 0.001 | -0.245 | 0.041 | 0.050 | 0.001 |
| 318.15K | -0.268 | -0.008 | 0.032 | 0.001 | -0.278 | 0.033 | 0.050 | 0.001 |
| 323.15K | -0.325 | -0.003 | 0.044 | 0.001 | -0.339 | 0.056 | 0.061 | 0.001 |
| | Benzylalcohol(1)+ *m*-cresol (2) | | | | | | | |
| 303.15K | -0.085 | -0.008 | -0.015 | 0.001 | -0.080 | -0.030 | -0.010 | 0.001 |
| 308.15K | -0.089 | -0.004 | -0.048 | 0.001 | -0.073 | -0.069 | -0.059 | 0.001 |
| 313.15K | -0.094 | -0.004 | -0.063 | 0.001 | -0.073 | -0.089 | -0.079 | 0.001 |
| 318.15K | -0.106 | -0.005 | -0.066 | 0.001 | -0.084 | -0.094 | -0.082 | 0.001 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 323.15K | -0.113 | -0.001 | -0.083 | 0.001 | -0.085 | -0.112 | -0.109 | 0.001 |
| | | | | Benzylalcohol (1)+ *p*-cresol (2) | | | | |
| 303.15K | -0.009 | -0.090 | 0.014 | 0.001 | -0.013 | -0.088 | 0.126 | 0.001 |
| 308.15K | -0.003 | -0.096 | 0.041 | 0.001 | -0.017 | -0.060 | 0.170 | 0.001 |
| 313.15K | -0.0003 | -0.096 | 0.053 | 0.001 | -0.018 | -0.043 | 0.186 | 0.001 |
| 318.15K | 0.010 | -0.099 | 0.063 | 0.001 | -0.011 | -0.034 | 0.202 | 0.001 |
| 323.15K | 0.023 | -0.109 | 0.076 | 0.001 | -0.002 | -0.029 | 0.231 | 0.001 |

**Table S2:**

Standard deviation σ ($\kappa_s^E$) and values of constants ($a_0$, $a_1$, $a_2$; $b_0$, $b_1$, $b_2$) for Redlich–Kister and Hwang et al. for excess isentropic compressibility data.

| Temp. | Function | Redlich-Kister | | | | Hawang | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $a_0$ | $a_1$ | $a_2$ | σ ($\kappa_s^E$) | $b_o$ | $b_1$ | $b_2$ | σ ($\kappa_s^E$) |
| | | TPa$^{-1}$ | | | | TPa$^{-1}$ | | | |
| Benzylalcohol(1)+ *o*-cresol (2) | | | | | | | | | |
| 303.15K | $\kappa_s^E$ | 1.150 | 0.052 | 0.119 | 0.004 | 1.110 | 0.221 | 0.097 | 0.004 |
| 313.15K | $\kappa_s^E$ | 1.040 | 0.030 | 0.011 | 0.003 | 1.036 | 0.050 | -0.021 | 0.003 |
| Benzylalcohol(1)+ *m*-cresol (2) | | | | | | | | | |
| 303.15K | $\kappa_s^E$ | -2.248 | 0.035 | 0.035 | 0.002 | -2.260 | 0.088 | 0.005 | 0.002 |
| 313.15K | $\kappa_s^E$ | -2.590 | 0.020 | -0.199 | 0.004 | -2.524 | -0.242 | -0.289 | 0.004 |
| Benzylalcohol(1)+ *p*-cresol (2) | | | | | | | | | |
| 303.15K | $\kappa_s^E$ | -4.056 | -0.322 | -0.007 | 0.004 | -4.054 | -0.393 | 0.374 | 0.004 |
| 313.15K | $\kappa_s^E$ | -4.676 | -0.413 | 0.048 | 0.002 | -4.692 | -0.428 | 0.556 | 0.003 |

**Table S3:**

Distances ($A^0$) and angles ($^0$) of the hydrogen bonds for all hydrogen bond associations at the B3LYP/6-311++G (d, p).

| Complexes | X-H….Y | R(X-H) | ΔR (X-H) | R(H…..Y) | ΔR(H…Y) | R(X…Y) | ∠XHY |
|---|---|---|---|---|---|---|---|
| I | O2-H16…O1 | 0.9732 | 0.0115 | 1.8812 | 0.8388 | 2.8392 | 167.535 |
| II | O2-H16…O1 | 0.9707 | 0.0080 | 1.9322 | 0.7878 | 2.8854 | 166.676 |
| III | O2-H16…O1 | 0.9704 | 0.0081 | 1.9161 | 0.8040 | 2.8820 | 173.273 |
| IV | O2-H16…O1 | 0.9706 | 0.0078 | 1.9163 | 0.8037 | 2.8837 | 174.334 |
| V | O1-H8…O2 | 0.9687 | 0.0070 | 2.0369 | 0.6831 | 2.9537 | 157.164 |
| Va | O2-H13…O1 | 0.9751 | 0.0125 | 1.8434 | 0.8766 | 2.8150 | 174.002 |
| VI | O2-H13…O1 | 0.9687 | 0.0070 | 2.0363 | 0.6838 | 2.9496 | 156.413 |
| VIa | O2-H13…O1 | 0.9751 | 0.0129 | 1.8453 | 0.8748 | 2.8149 | 172.504 |
| VII | O1-H8…O2 | 0.9689 | 0.0072 | 1.9686 | 0.7514 | 2.9263 | 169.337 |
| VIIa | O2-H13…O1 | 0.9748 | 0.0121 | 1.8596 | 0.8604 | 2.8223 | 168.798 |

**Table S4**:

Topological Properties (in a. u.) of the BCPs of intermolecular H-bonds in Benzyl alcohol and cresol complexes obtained from the B3LYP/6-311++ G (d, p) level calculations

| Complexes | X-H….Y | ρ | $\nabla^2\rho$ | H(r) | $\lvert V(r)\rvert / G(r)$ |
|---|---|---|---|---|---|
| I | O2-H16…O1 | 0.028676 | 0.103512 | 0.001596 | 0.93427 |
| II | O2-H16…O1 | 0.024337 | 0.091802 | 0.002273 | 0.89008 |
| III | O2-H16…O1 | 0.024804 | 0.093081 | 0.002283 | 0.88672 |
| IV | O2-H16…O1 | 0.025173 | 0.095618 | 0.002287 | 0.89421 |
| V | O1-H8…O2 | 0.021904 | 0.082080 | 0.001517 | 0.92017 |
| Va | O2-H13…O1 | 0.031167 | 0.109377 | 0.000018 | 0.99921 |
| VI | O2-H13…O1 | 0.022112 | 0.083770 | 0.001680 | 0.91159 |
| Via | O2-H13…O1 | 0.030992 | 0.105946 | 0.001011 | 0.96161 |
| VII | O1-H8…O2 | 0.022417 | 0.086099 | 0.002519 | 0.86746 |
| VIIa | O2-H13…O1 | 0.030107 | 0.091774 | 0.001139 | 0.95507 |

**Table S5:**

Interaction energy corrected with BSSE (ΔE. kJ. $mol^{-1}$) for all dimers at the B3LYP/6-311++G(d, p) level.

| Complexes | X-H….Y | $\Delta E$ | BSSE | $\Delta E^{cp}$ |
|---|---|---|---|---|
| I | O2-H16…O1 | -24.3720 | 0.73 | -23.6420 |
| II | O2-H16…O1 | -20.3062 | 0.76 | -19.5462 |
| III | O2-H16…O1 | -20.7755 | 0.81 | -19.9655 |
| IV | O2-H16…O1 | -17.5275 | 0.80 | -16.7275 |
| V | O1-H8…O2 | -25.2681 | 0.86 | -24.4081 |
| Va | O2-H13…O1 | -34.6280 | 0.91 | -33.7180 |
| VI | O2-H13…O1 | -24.8573 | 0.83 | -24.0273 |
| Via | O2-H13…O1 | -33.6073 | 0.93 | -32.6773 |
| VII | O1-H8…O2 | -20.5784 | 0.79 | -19.7884 |
| VIIa | O2-H13…O1 | -26.6809 | 0.94 | -25.7409 |

**Table S6:**

Second-perturbation energies (E (2) / kJ · $mol^{-1}$) of hydrogen bonds for all hydrogen bond associations obtained by NBO analysis at the B3LYP/6-311++G (d, p) level.

| Complexes | Donor NBO(i) | Acceptor NBO(j) | E(2) |
|---|---|---|---|
| I | LP(1) O1 | BD*(1)O2-H16 | 1.95 |
| II | LP(1) O1 | BD*(1)O2-H16 | 1.14 |
| III | LP(1) O1 | BD*(1)O2-H16 | 1.75 |
| IV | LP(1) O1 | BD*(1)O2-H16 | 1.52 |
| V | LP(1) O2 | BD*(1)O1-H8 | 0.60 |
| Va | LP(1) O1 | BD*(1)O2-H13 | 2.58 |
| VI | LP(1) O1 | BD*(1)O2-H13 | 0.46 |
| Via | LP(1) O1 | BD*(1)O2-H13 | 2.66 |
| VII | LP(1) O2 | BD*(1)O1-H8 | 0.34 |
| VIIa | LP(1) O1 | BD*(1)O2-H13 | 2.44 |

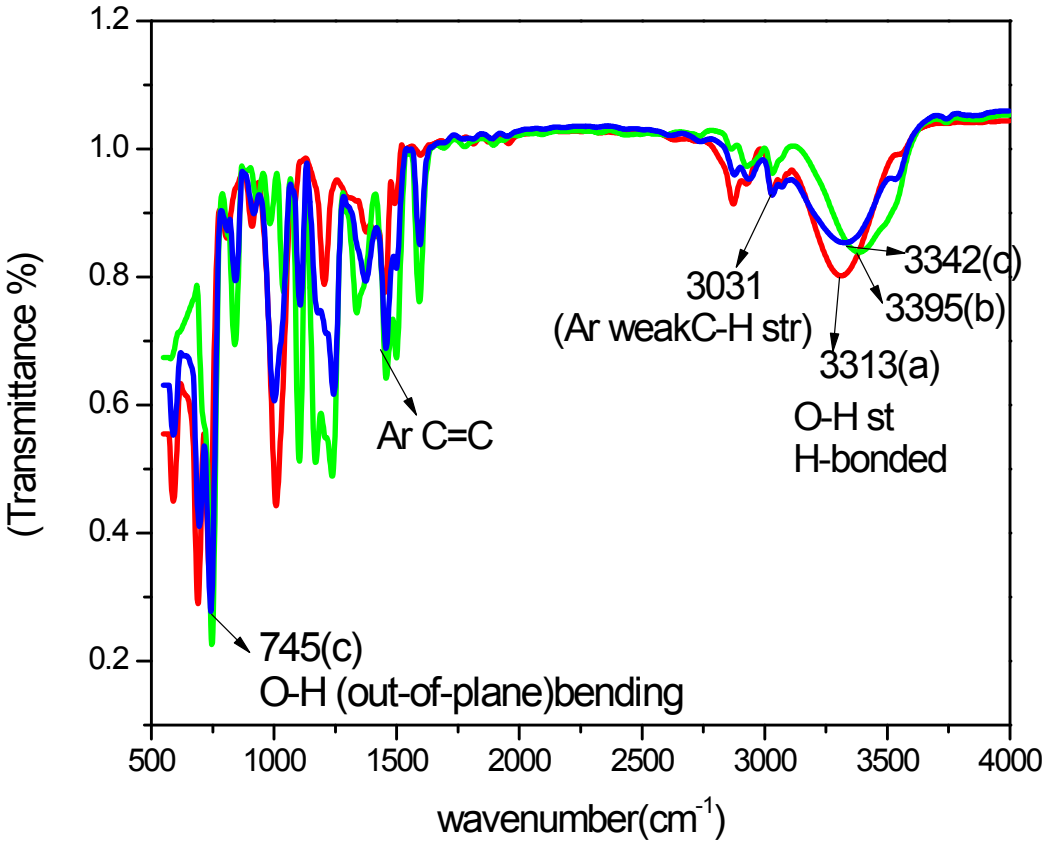



**Figure S1:** Normalized FT-IR spectra of (benzylalcohol + *o*-cresol) binary mixture over the range (4000–500 $cm^{-1}$). Peak a: Benzylalcohol; Peak b: *o*-cresol; Peak c: Benzylalcohol with *o*-cresol.

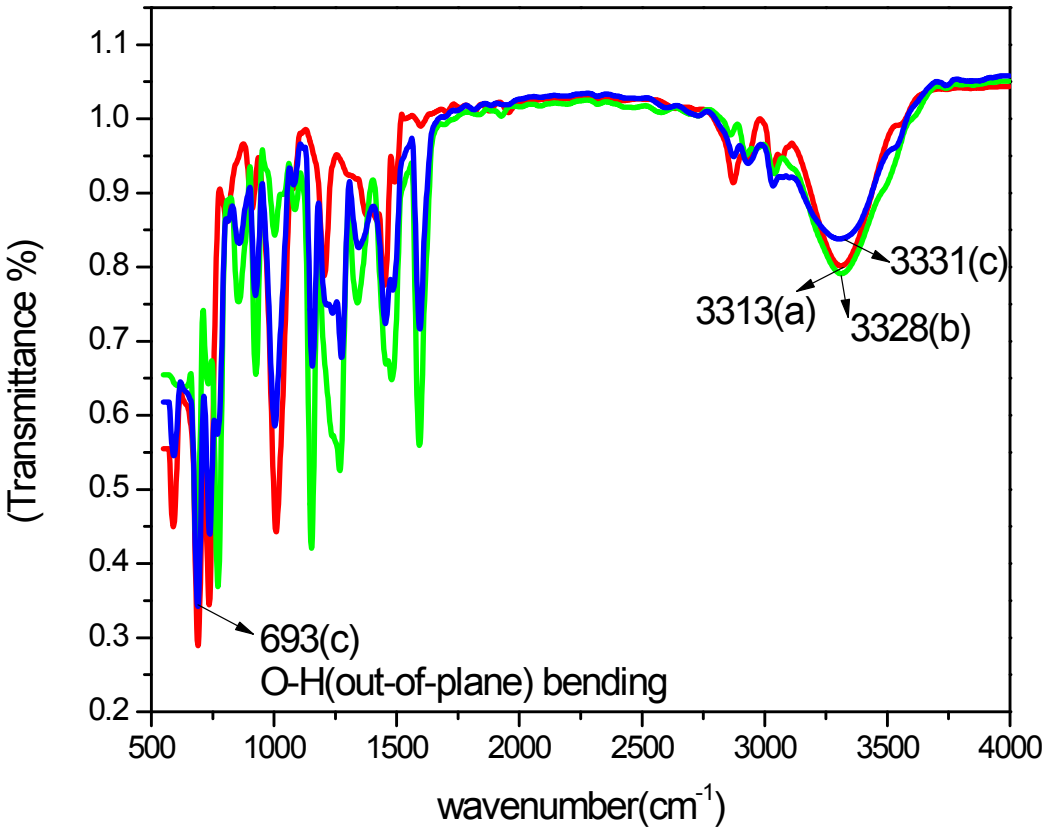



**Figure S2:** Normalized FT-IR spectra of (Benzylalcohol + *m*-cresol) binary mixture over the range (4000–500 $cm^{-1}$). Peak a: Benzylalcohol; Peak b: *m*-cresol; Peak c: Benzylalcohol with *m*-cresol.

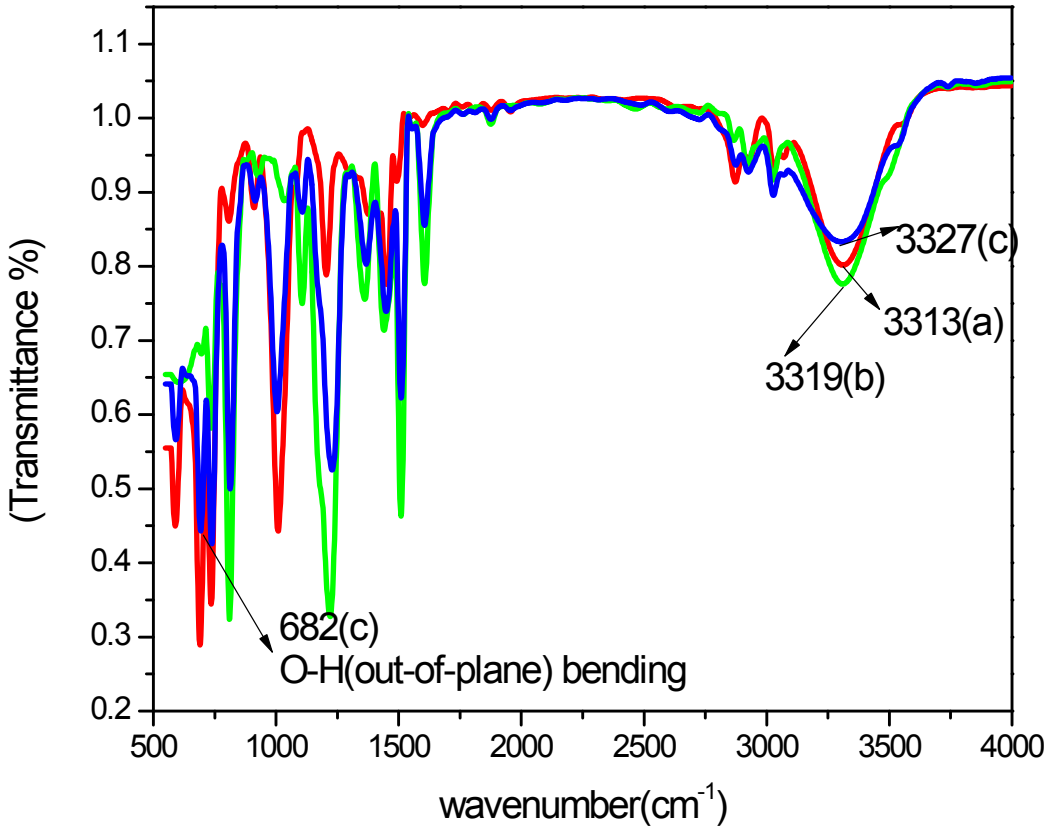
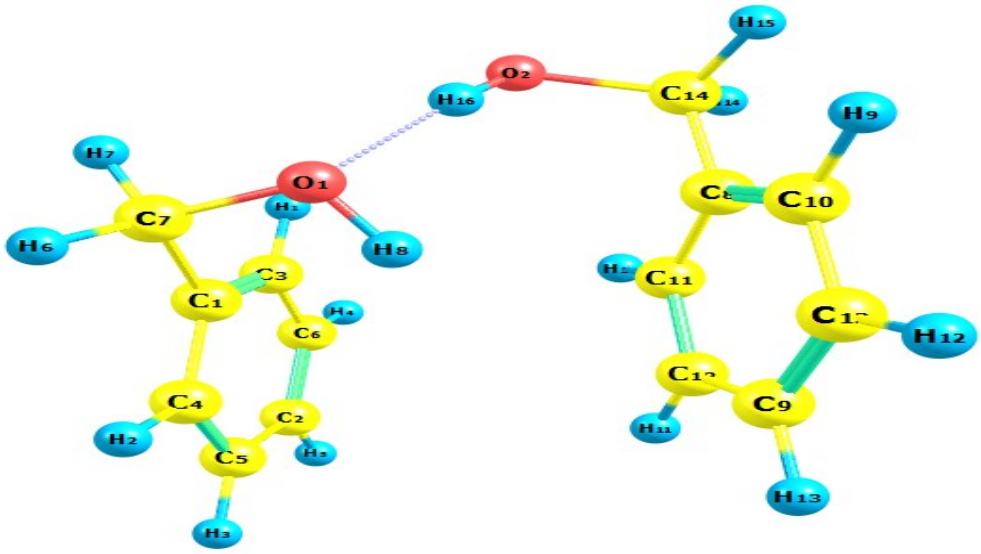



**Figure S3:** Normalized FT-IR spectra of (Benzylalcohol + *p*-cresol) binary mixture over the range (4000–500 $cm^{-1}$). Peak a: Benzylalcohol; Peak b: *p*-cresol; Peak c: Benzylalcohol with *p*-cresol.

**Figure S4:**

Geometrical optimized structures using B3LYP/6-311++G (d, p) of self-associations **I** (Benzylalcohol–Benzylalcohol), **II** (o-cresol – o-cresol), **III** (p-cresol – p-cresol), **IV** (m-cresol –m-cresol) and of cross-associations **V, Va** (Benzylalcohol + o-cresol) **VI, VIa** (Benzylalcohol + p-cresol) and **VII, VIIa** (Benzylalcohol + m-cresol).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C14
H9
H7
O1
C10
C7
H6
H8
C3
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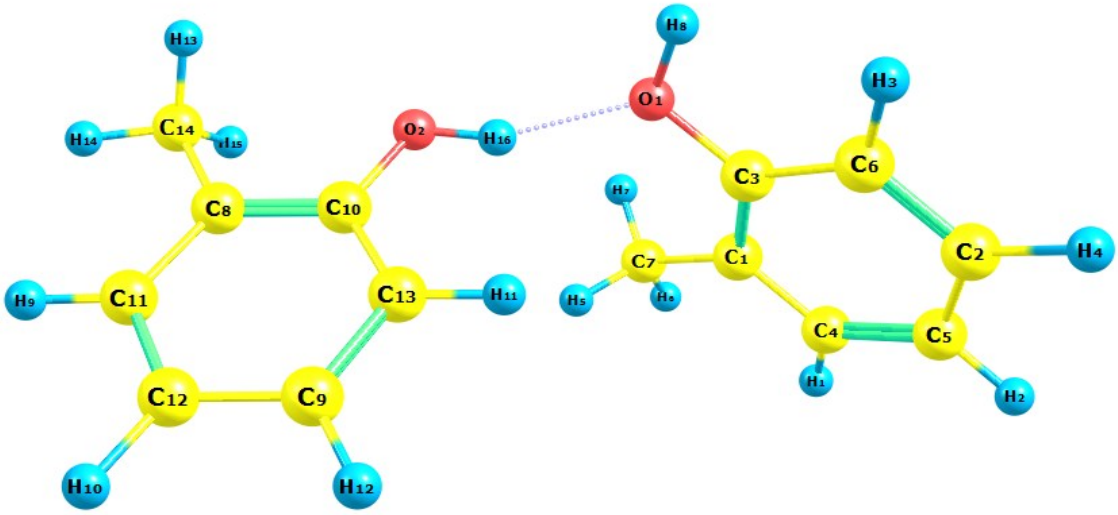
C4
C2
H2
C5
C9
H11
H13
H3

I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C1
C2
H4
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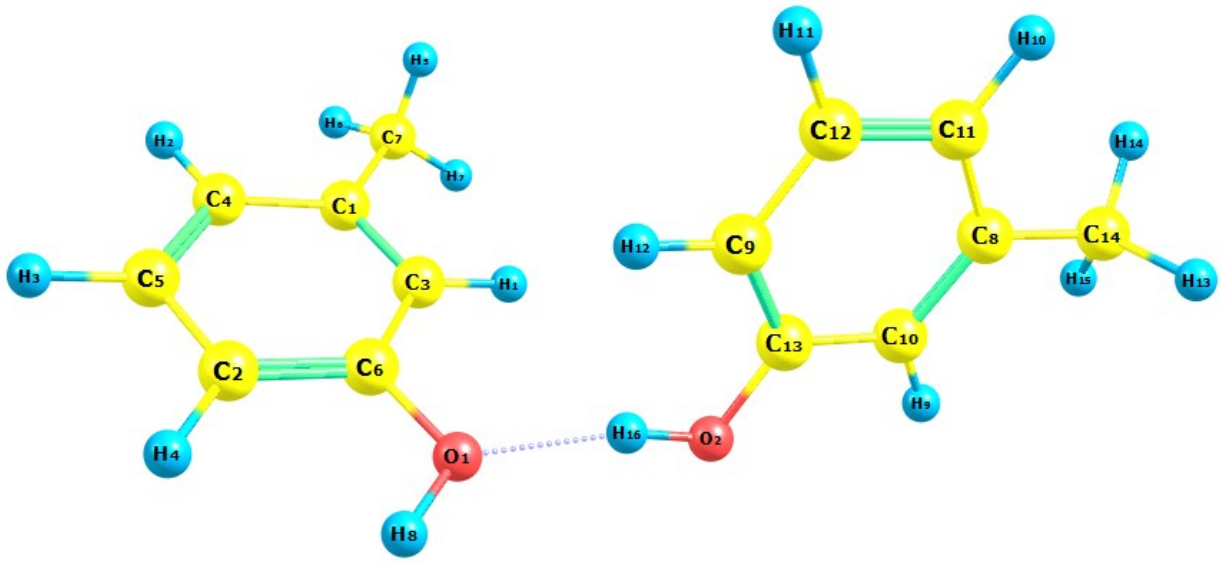
C11
C13
H11
H5
C4
C5
C12
C9
H1
H2
H10
H12

II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H7
C4
C1
H3
C5
C3
H1
C2
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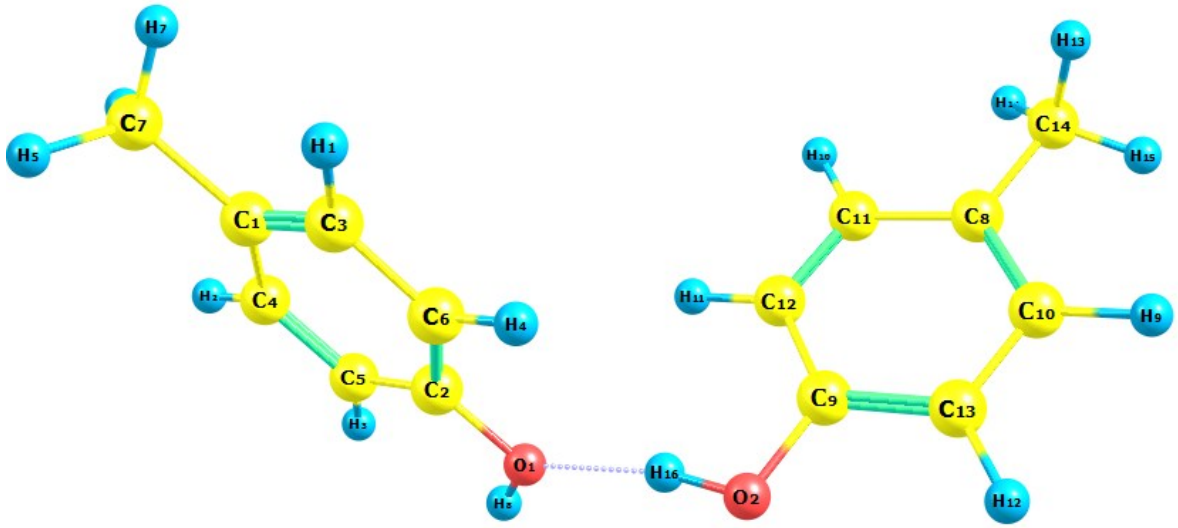
H8
H11
H10
C12
C11
H14
H12
C9
C8
C14
H15
H13
C13
C10
H9
H16
O2

III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H1
C1
C3
H2
C4
C6
H4
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C2
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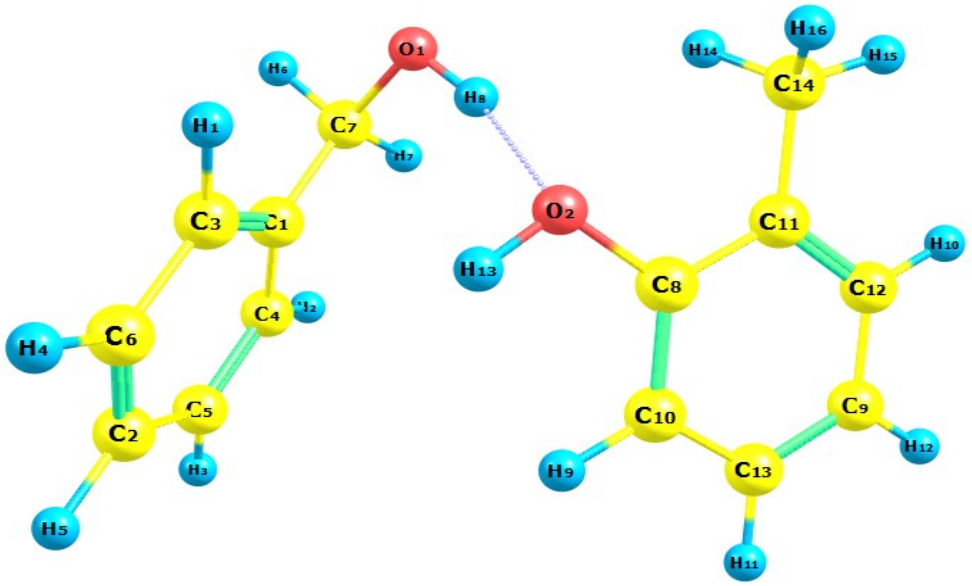
O1
H8
H13
H14
H10
H15
C11
C8
H11
C12
C10
H9
C9
C13
H16
O2
H12

IV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C3
C1
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H15
C14
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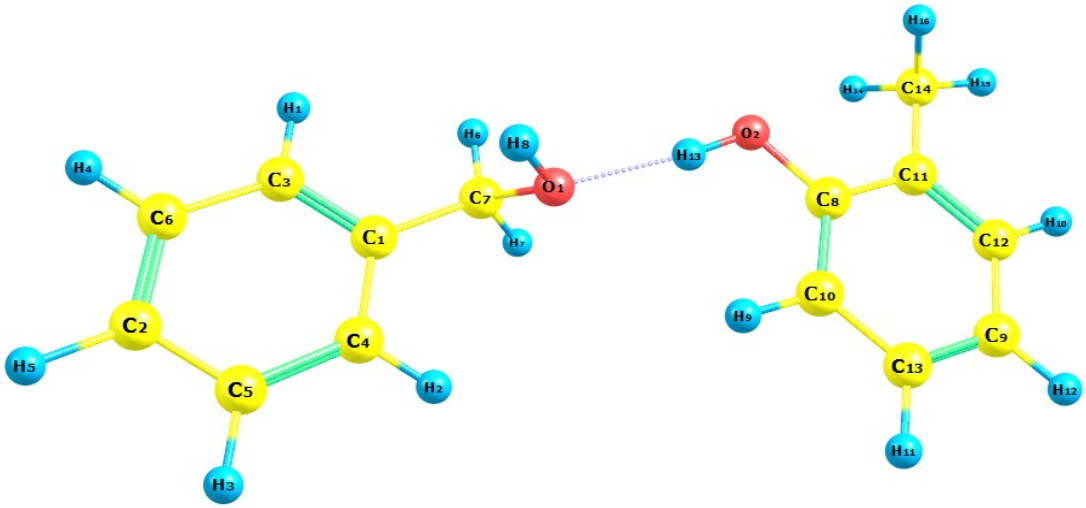
C8
C12
C4
H2
H4
C6
C10
C9
C5
C2
H9
C13
H12
H3
H5
H11

**V**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C7
C1
C12
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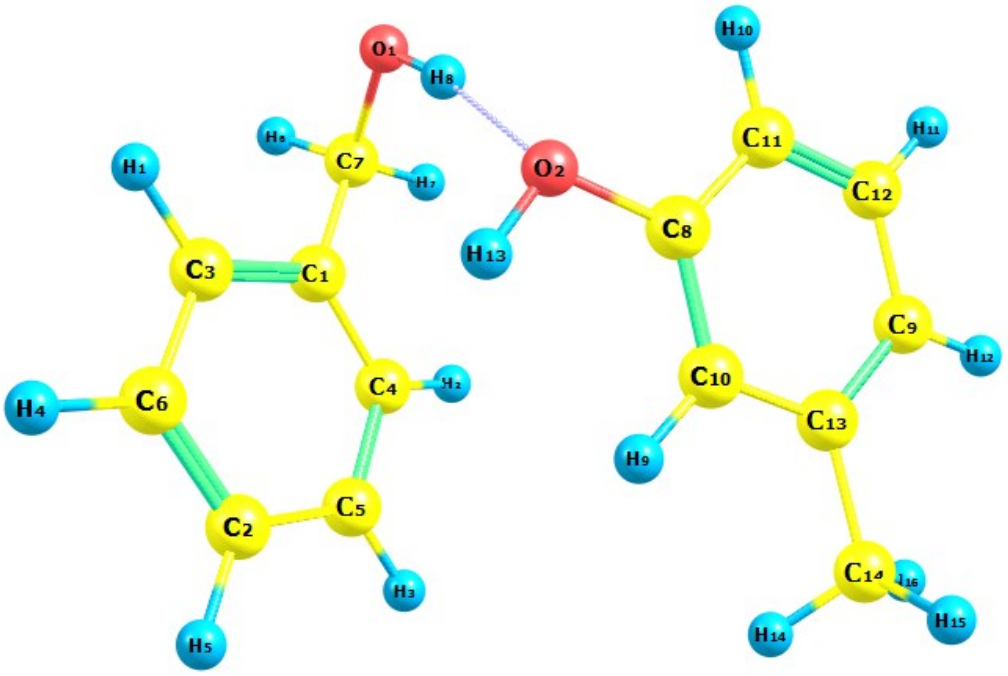
C4
C9
C5
C13
H12
H2
H3
H11

**Va**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C9
H12
C10
H4
C6
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H2
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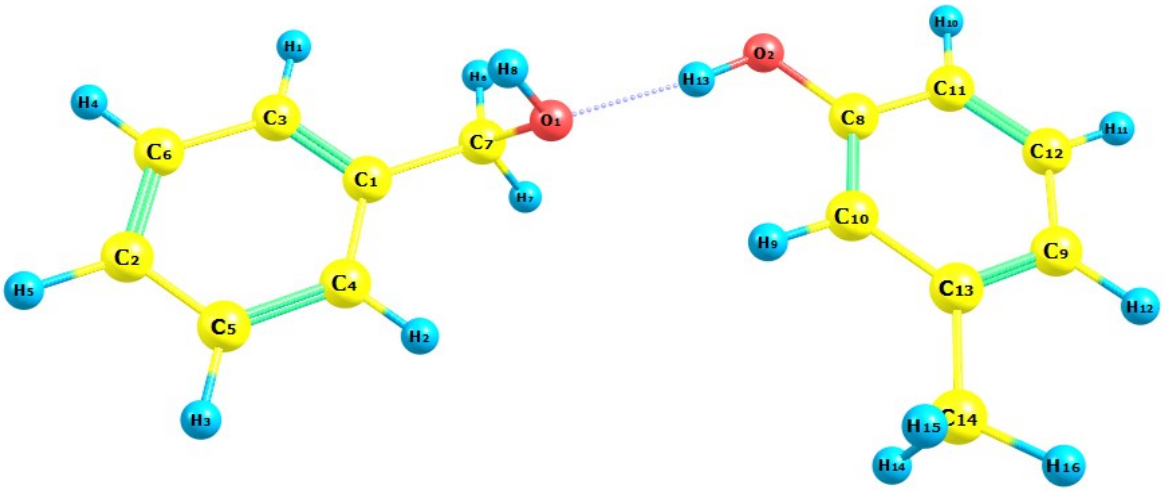
H9
C5
C2
H3
C14
H16
H5
H14
H15

**VI**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C11
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O1
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C1
H7
C10
H9
C2
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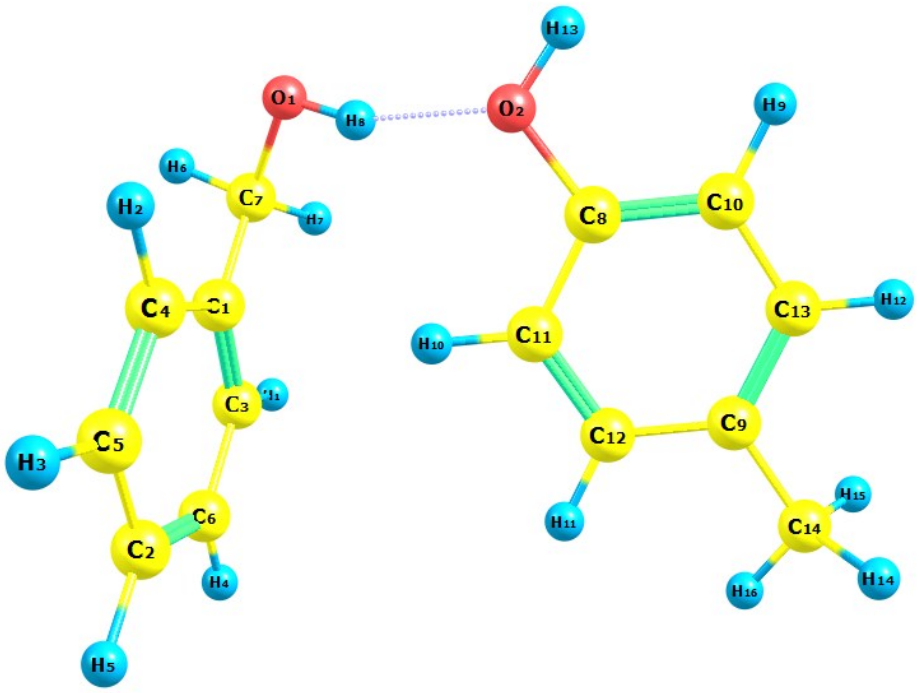
H5
H12
C5
H2
H3
H15
C14
H14
H16

**VIa**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C11
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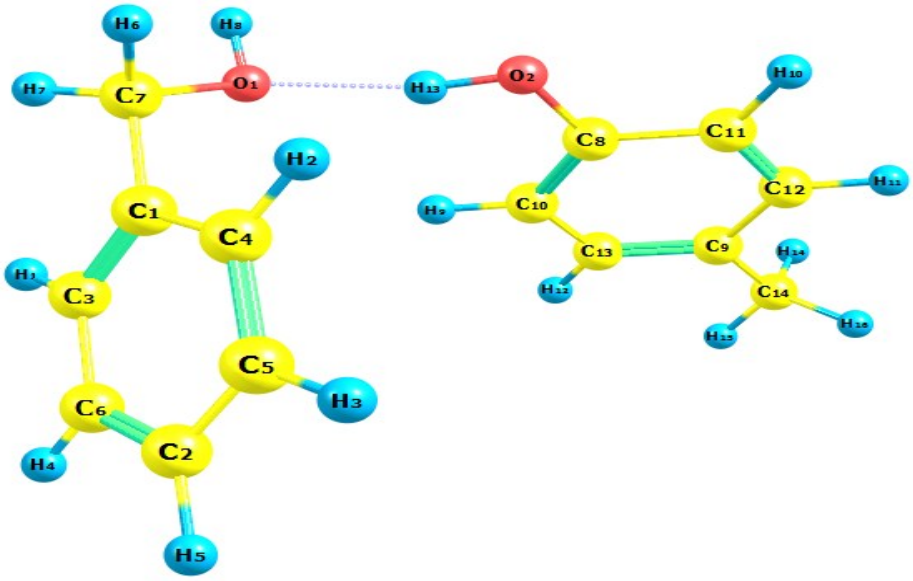
H14
H5

**VII**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C9
H14
H1
C3
H12
C14
H15
H16
C5
H3
C6
C2
H4
H5

**VIIa**