Influence of hydroxyl functional group on the structure and stability of xanthone: a computational approach

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Appendix A

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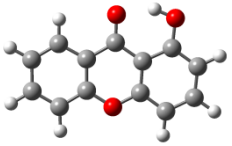
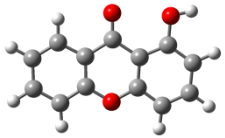
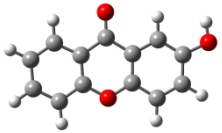
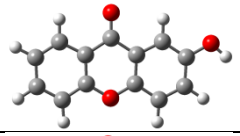
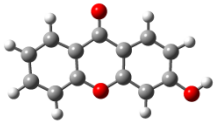
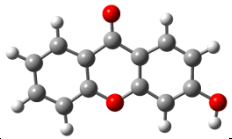
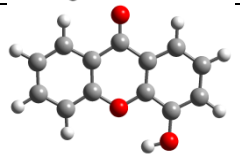
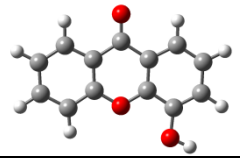
Acronims used throughout this supplementary data:
1OHXT for 1-hydroxyxanthone
2OHXT for 2-hydroxyxanthone
3OHXT for 3-hydroxyxanthone
4OHXT for 4-hydroxyxanthone

Standard thermodynamic property:
The standard state of a pure gas refers to its standard state is that of an ideal gas at p of 0.1 MPa (or, which is equivalent, that of a real gas at p = 0).
Standard states will be denoted by a superscript "o".

Table A1. Absolute standard enthalpies, $H^{\circ}_{298.15\,K}$, and entropies, $S^{\circ}_{298.15\,K}$, obtained by G3(MP2)//B3LYP composite method for 1-hydroxyxanthone (1OHXT), 2-hydroxyxanthone (2OHXT), 3-hydroxyxanthone (3OHXT), and 4-hydroxyxanthone (4OHXT), conformers, and the corresponding derived gas-phase standard molar enthalpies, $\Delta_f H^{\circ}_m(g)$, entropies, $\Delta_f S^{\circ}_m(g)$, and Gibbs energy of formation, $\Delta_f G^{\circ}_m(g)$, at T = 298.15 K, and the conformational composition, χ_i. 1 a. u. (Hartree) corresponds to 2625.50 kJ·mol^{-1}.

Specie	Conformation[a]	$H^{\circ}_{298.15K}$ [b] / a.u.	$\Delta_f H^{\circ}_m(g)$ [c] / kJ·mol^{-1}	$S^{\circ}_{298.15K}$ [d] / J·K^{-1}·mol^{-1}	$\Delta_f S^{\circ}_m(g)$ [e] / J·K^{-1}·mol^{-1}	$\Delta_f G^{\circ}_m(g)$ [f] / kJ·mol^{-1}	χ_i [g]
1OHXT		–724.833530	–301.5 ± 2.9	429.22	–475.8	–159.6	1.000
		–724.814707	–252.1 ± 2.9	439.20	–465.9	–113.2	0
2OHXT		–724.821536	–270.0 ± 2.9	438.09	–467.0	–130.8	0.834
		–724.819853	–265.6 ± 2.9	439.40	–465.7	–126.8	0.166
3OHXT		–724.823791	–276.0 ± 2.9	438.08	–467.0	–136.8	0.558
		–724.823601	–275.5 ± 2.9	437.83	–467.20	–136.2	0.442
4OHXT		–724.821967	–271.2 ± 2.9	437.59	–467.7	–131.8	0.991
		–724.817464	–259.3 ± 2.9	438.49	–466.6	–120.2	0.009

[a]Spheres color code: grey, C; red, O; white, H.

[b]Obtained from G3(MP2)//B3LYP method [1]

[c]Estimated from 19 working reactions presented on Table 1 of manuscript;

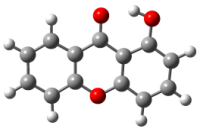
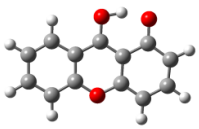
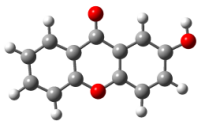
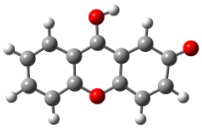
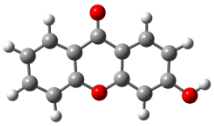
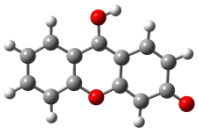
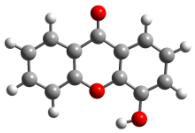
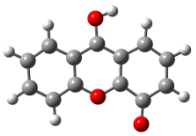
[d]Obtained from B3LYP/6-31G(*d*) method for a frequency factor scale of 1.0029 [2];

[e]Calculated from $\Delta_f S^\circ_m(g) = S^\circ_{298.15K}$ (conformer i) $- \sum S^\circ_{298.15K}$ (elements), considering the standard absolute entropy elements values, at 298.15 K, $S^\circ_{298.15K}(H_2, g)$ = 130.680 J·K^{-1}·mol^{-1}, $S^\circ_{298.15K}$(C, graphite) = 5.740 J·K^{-1}·mol^{-1} and $S^\circ_{298.15K}(O_2, g)$ = 205.147 J·K^{-1}·mol^{-1} taken from ref. [3];

[f]Calculated from $\Delta_f G^\circ_m(g) = \Delta_f H^\circ_m(g) - T\Delta_f S^\circ_m(g)$;

[g] Calculated from $\chi_i = e^{-[\Delta_f G^\circ_m(g)/RT]} / \sum_i^n e^{-[\Delta_f G^\circ_m(g)/RT]}$.

Table A2. Gas-phase absolute standard Gibbs energies, $G^{\circ}_{298.15K}$, obtained by G3(MP2)//B3LYP composite method for keto and enol forms of monohydroxyxanthones isomers, and the theoretically predicted gas-phase standard molar Gibbs energies, $\Delta_r G^{\circ}_m(g)$, for the keto-enol equilibrium, at T = 298.15 K, with the corresponding fractions (x) of the two tautomers. 1 a. u. (Hartree) corresponds to 2625.50 kJ·mol^{-1}.[a]

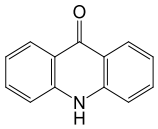
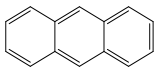
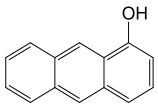
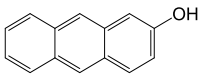
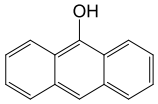
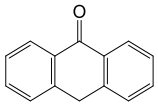
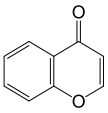
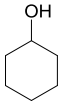
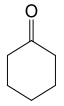
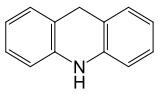
	1OHXT		2OHXT	
	keto form	**enol form**	**keto form**	**enol form**
				
$G^{\circ}_{298.15K}$ /a. u.	–724.883106	–724.866965	–724.872146	–724.816688
$\Delta_r G^{\circ}_m(g)$ [b]/kJ·mol^{-1}	–42.4		–145.6	
fraction[c]	x_{keto} = 1.0	x_{enol} = 0	x_{keto} = 1.0	x_{enol} = 0
	3OHXT		**4OHXT**	
	keto form	**enol form**	**keto form**	**enol form**
				
$G^{\circ}_{298.15K}$ /a. u.	–724.874401	–724.845105	–724.872519	–724.814434
$\Delta_r G^{\circ}_m(g)$ [b] / kJ·mol^{-1}	–76.9		–152.5	
fraction[c]	x_{keto} = 1.0	x_{enol} = 0	x_{keto} = 1.0	x_{enol} = 0

[a] Most stable conformation; Spheres color code: grey, C; red, O; and white, H.

[b] Calculated from $\Delta_r G^{\circ}_m(g) = G^{\circ}_{298.15\,K}(\text{keto}) - G^{\circ}_{298.15\,K}(\text{enol})$;

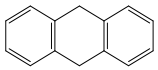
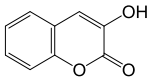
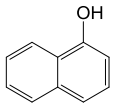
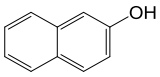
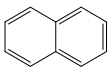
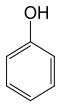
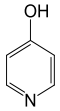
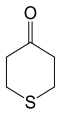
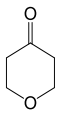
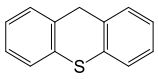
[c] Calculated according: $x_{keto} = \frac{e^{-[\Delta_f G^{\circ}_m(g)/RT]}}{1+ e^{-[\Delta_f G^{\circ}_m(g)/RT]}}$ and $x_{enol} = 1 - x_{keto}$.

Table A3. G3(MP2)//B3LYP enthalpies, $H^{\circ}_{298.15K}$, with corresponding conformer composition (χi), and experimental gas-phase standard (p° = 0.1 MPa) molar enthalpies of formation, $\Delta_f H^{\circ}_m(g)$, at T = 298.15 K, for monohydroxyxanthone isomers and for the auxiliary species. 1 a. u. (Hartree) corresponds to 2625.50 kJ·mol^{-1}.

Compound	Molecular structure	$H^{\circ}_{298.15K}$ / a. u. (χi)[a]	$\Delta_f H^{\circ}_m(g)$ / kJ·mol^{-1}
acridin-9(10*H*)-one		–629.817480	50.0 ± 5.0 [4]
anthracene		–538.606511	230.9 ± 2.2 [5]
1-anthrol		–613.758408 (**0.847**) –613.756318 (**0.153**)	50.3 ± 5.3 [6]
2-anthrol		–613.758495 (**0.721**) –613.757394 (**0.279**)	50.6 ± 5.3 [6]
9-anthrol		–613.756647	56.5 ± 5.3 [6]
anthrone		–613.762341	36.1 ± 3.2 [7]
benzene		–231.835164	82.6 ± 0.7 [5]
4*H*-chromen-4-one		–496.270967	–126.1 ± 2.5 [8]
cyclohexane		–235.407852	–123.3 ± 0.8 [5]
cyclohexanol		–310.557138 (**0.717**) –310.556391 (**0.283**)	– 295.7 ± 1.2[a] [9,10]
cyclohexanone		–309.367618	–226.1 ± 2.1 [5]
9,10-dihydroacridine		–555.840773	198.7 ± 4.4 [11]

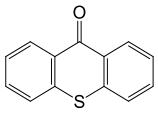
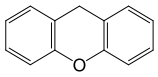
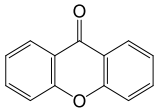
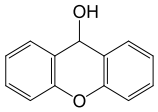
…/…

Table A3. (Continuation)

Compound	Molecular structure	$H^{\circ}_{298.15K}$ / a. u. (χ_i)[a]	$\Delta_f H^{\circ}_m$(g) / kJ·mol^{-1}
9,10-dihydroanthracene		–539.796179	159.7 ± 4.3 [5]
3-hydroxycoumarin		–571.443052	–367.7 ± 1.9 [12]
1-hydroxynaphthalene (or 1-naphthol)		–460.375351	–30.4 ± 1.6 [13]
2-hydroxynaphthalene		–460.375409	–29.9 ± 1.7 [13]
naphthalene		–385.223772	150.3 ± 1.4 [5]
phenol		–306.986472	–96.4 ± 0.9 [5]
pyridine		–247.873432	140.4 ± 0.7 [5]
pyridin-4-ol		–323.027334	–40.8 ± 5.3 [14]
tetrahydro-2*H*-thiopyran		–593.928601	–63.5 ± 1.0 [5]
tetrahydro-2*H*-pyran		–271.303681	–223.8 ± 1.0 [5]
tetrahydro-4*H*-thiopyran-4-one		–667.886742	–164.6 ± 2.0 [15]
tetrahydro-4*H*-pyran-4-one		–345.262186	–328.7 ± 2.6 [16]
thioxanthene		–898.319446	218.7 ± 4.2 [17]

…/…

Table A3. (Continuation)

Compound	Molecular structure	$H^{\circ}_{298.15K}$ / a. u. (χ_i)[a]	$\Delta_f H^{\circ}_m$(g) / kJ·mol^{-1}
thioxanthone		–972.285527	91.9 ± 2.4 [15]
xanthene		–575.697906	41.8 ± 3.5 [7]
xanthone		–649.670982	–94.0 ± 4.6 [16]
xanthydrol		–650.845504	–121.2 ± 4.6 [18]

a Calculated from the standard molar enthalpy of formation in the liquid phase given in ref. [9] and from the standard molar enthalpy of vaporization given in ref. [10], at T = 298.15 K,

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