

Supplementary Materials

Density Functional Theory-based Calculation Shed New Light on The Bizarre Addition of Cysteine Thiol to Dopaquinone.

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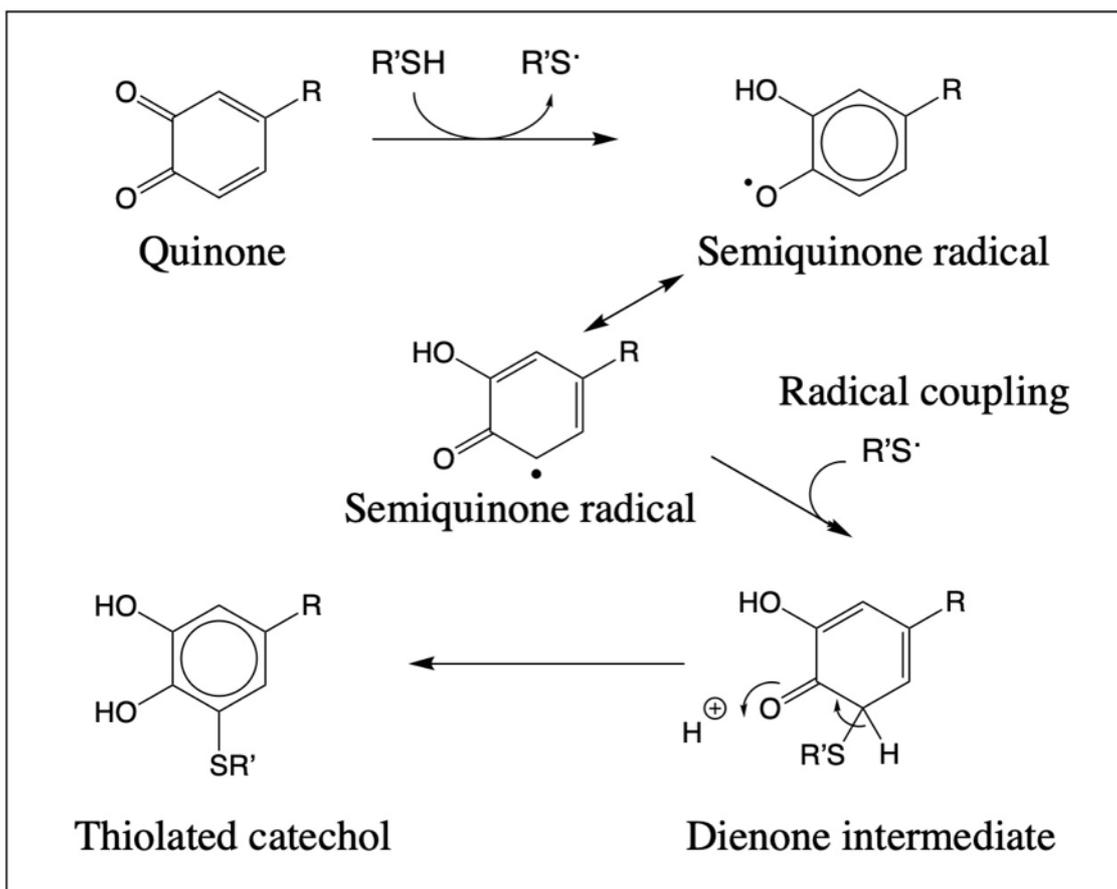
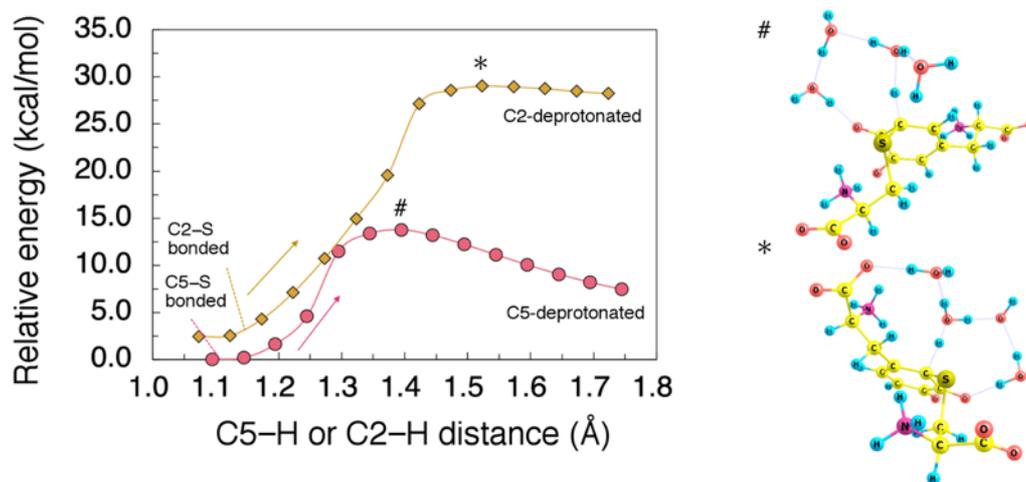


Figure S1. Alternate mechanism to account for the abnormal addition of thiols to quinone. Thiols being strong reductants, could reduce the *o*-quinone by one electron transfer to semiquinone radical. Further coupling of the semiquinone to the thiny radical allows only Michael 1,6-addition and not the 1,4-addition observed with other typical nucleophiles.



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17 **Figure S2.** (Left) Minimum energy path for proton dissociation from C5 before $\text{-NH}_3\text{-}$
 18 to-O3 proton rearrangement, and from C2 before $\text{-NH}_3\text{-}$ to-O4 proton rearrangement. H_2O
 19 tetramer was used as an acceptor for dissociating proton. Energies were referenced to the
 20 total energy of the initial state structure for C5-deprotonation. All geometrical parameters
 21 except for the C5-H or C2-H distance were allowed to relax. (Right) Transition state
 22 structure for C5- (#) and C2- (*) deprotonation.

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24 **Table S1.** Comparison of binding energies at C5 and C3-C4 using different exchange
 25 correlation functionals

Exchange correlation functional	Binding energy (kcal/mol)	
	C5	C3-C4
B3LYP	5.8	10.9
mPW1PW91	12.7	16.8
M06-2X	20.3	25.4
CAM-B3LYP	10.1	15.9

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