

# A Combined Experimental and Density Functional Theory Study of Metformin Oxy-Cracking for Pharmaceutical Wastewater Treatment

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## Supplementary Information

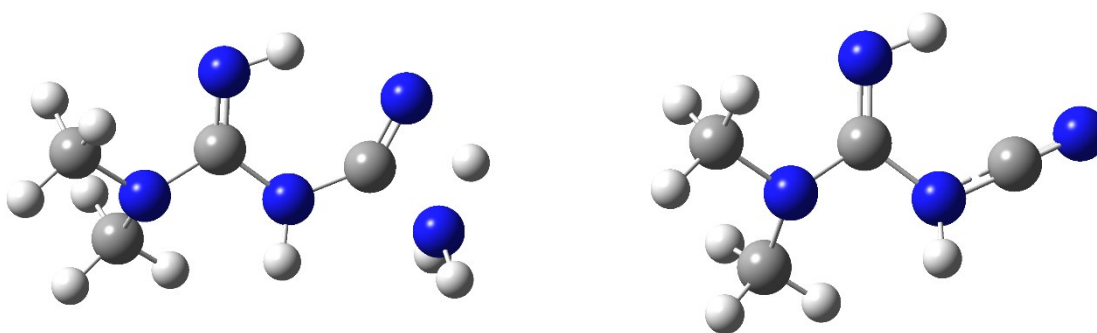
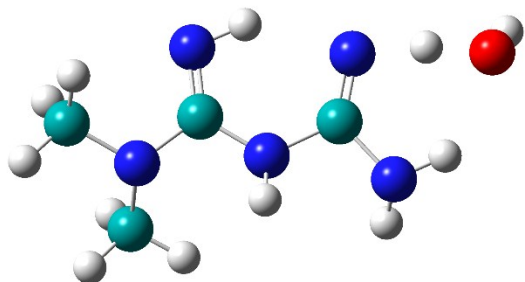
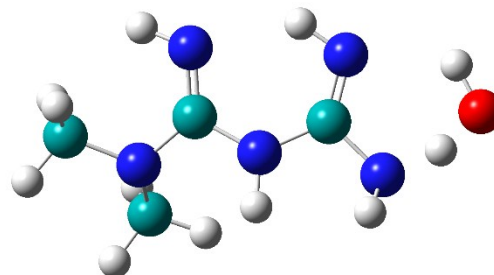


Figure S1: Optimized structures for a) the transition state for the 1,3-H shift in metformin leading to the formation of ammonia, and b) the product of this shift. Both obtained at B3LYP/6-31+G(d,p) level of theory. C atom, grey; N atom, blue.

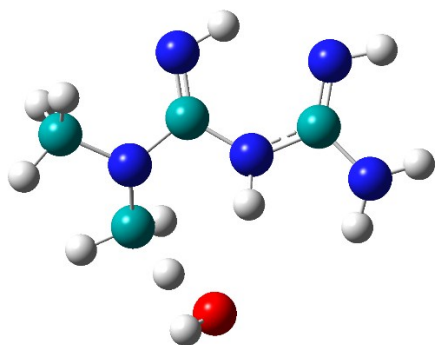
TS1



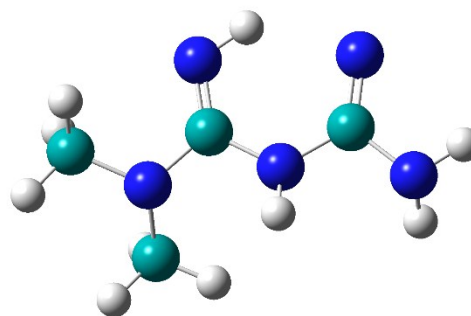
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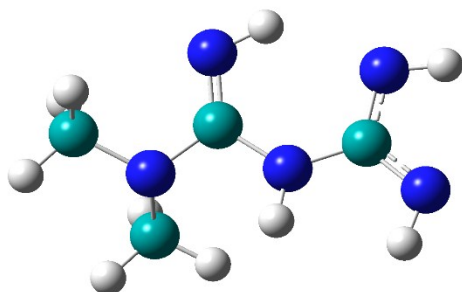
TS3



Radical 1



Radical 2



Radical 3

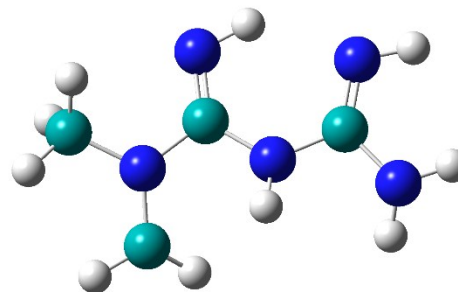
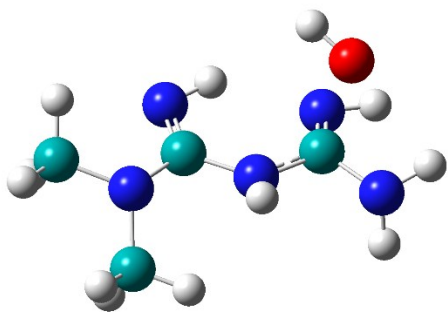
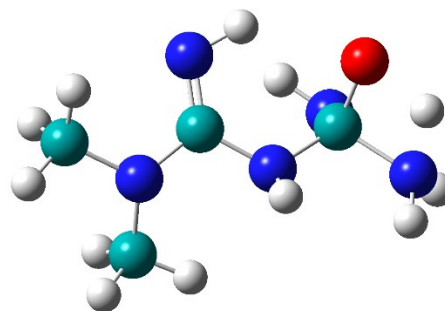


Figure S2: Optimized structures for the transition states and free radicals involved in reaction mechanism A, hydrogen abstraction by OH radical in metformin, obtained at B3LYP/6-31+G(d,p) level of theory. C atom, grey; N atom, blue; O atom, red.

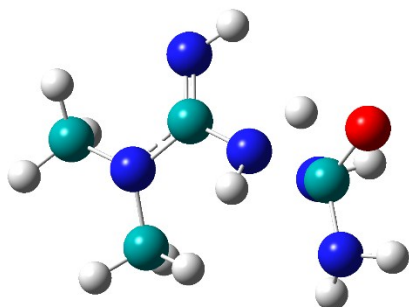
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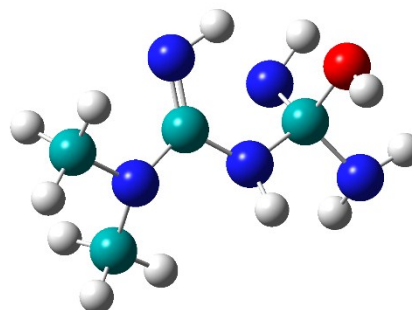
TS5



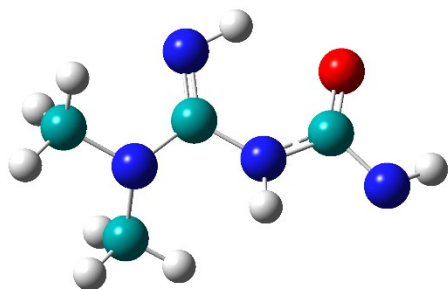
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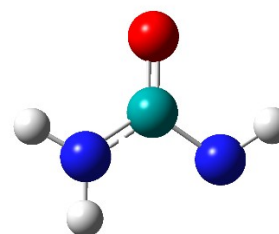
Radical 4



Radical 5



Radical 6



Dimethylguanidin

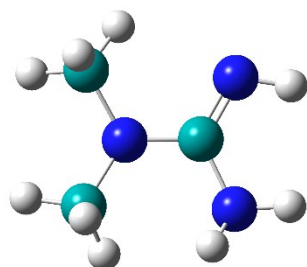
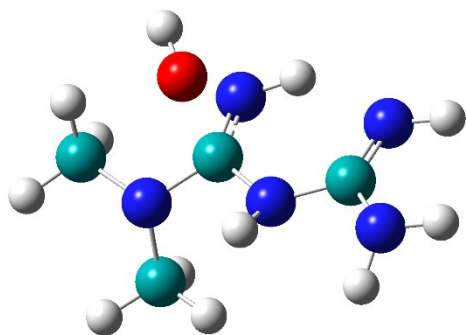
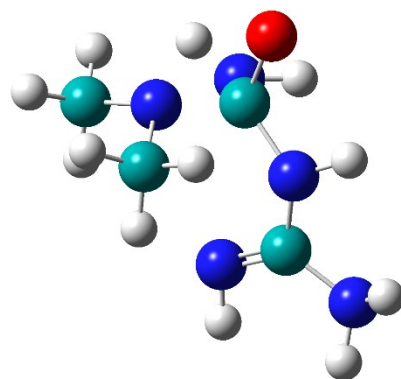


Figure S3: Optimized structures for the transition states and free radicals involved in reaction mechanism B initiated by OH radical attack on C1 in metformin, obtained at B3LYP/6-31+G(d,p) level of theory. C atom, grey; N atom, blue; O atom, red.

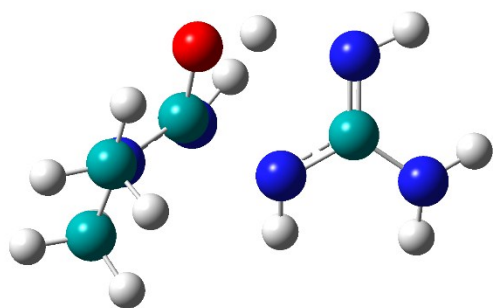
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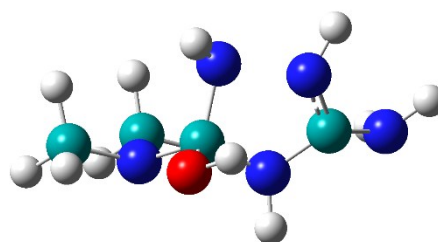
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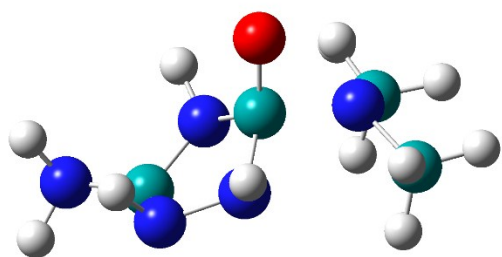
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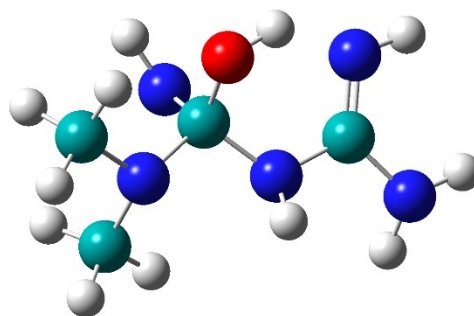
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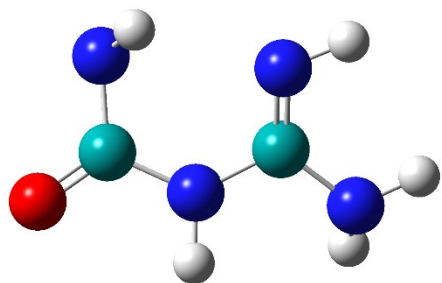
TS11



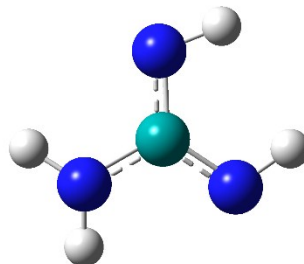
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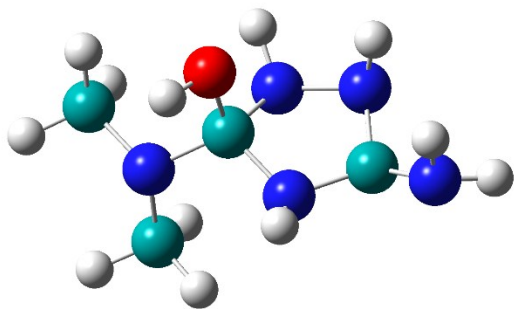
Radical 8



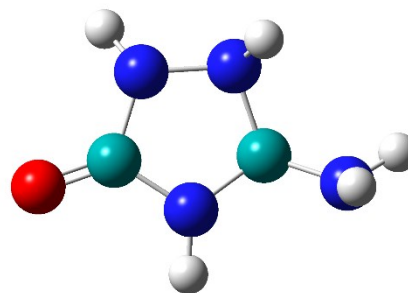
Radical 9



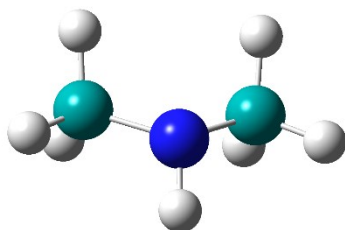
Radical 10



Radical 11



Dimethylamine



N,N-Dimethylurea

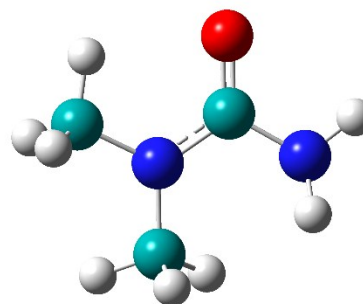
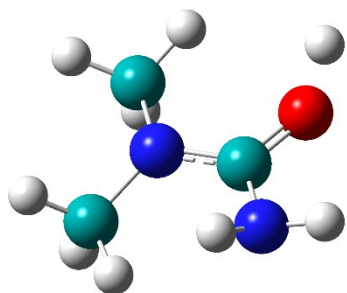
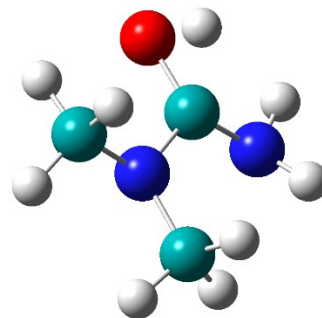


Figure S4: Optimized structures for the transition states and free radicals involved in reaction mechanism C initiated by OH radical attack on C3 in metformin, obtained at B3LYP/6-31+G(d,p) level of theory. C atom, grey; N atom, blue; O atom, red.

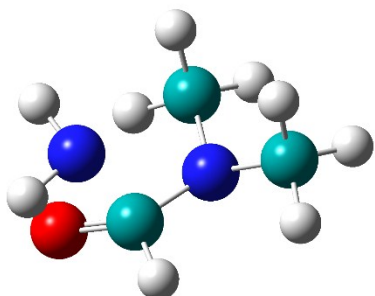
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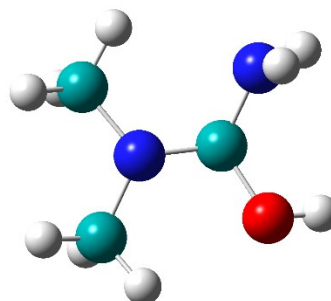
TS13



TS14



Radical 12



Dimethylformamide

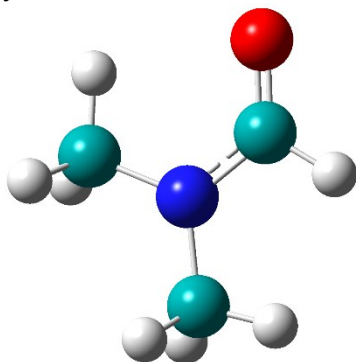


Figure S5: Optimized structures for the transition states and free radicals involved in reaction mechanism D, formation of dimethyl formamide out of dimethyl urea, obtained at B3LYP/6-31+G(d,p) level of theory. C atom, grey; N atom, blue; O atom, red.