SUPPLEMENTARY DATA

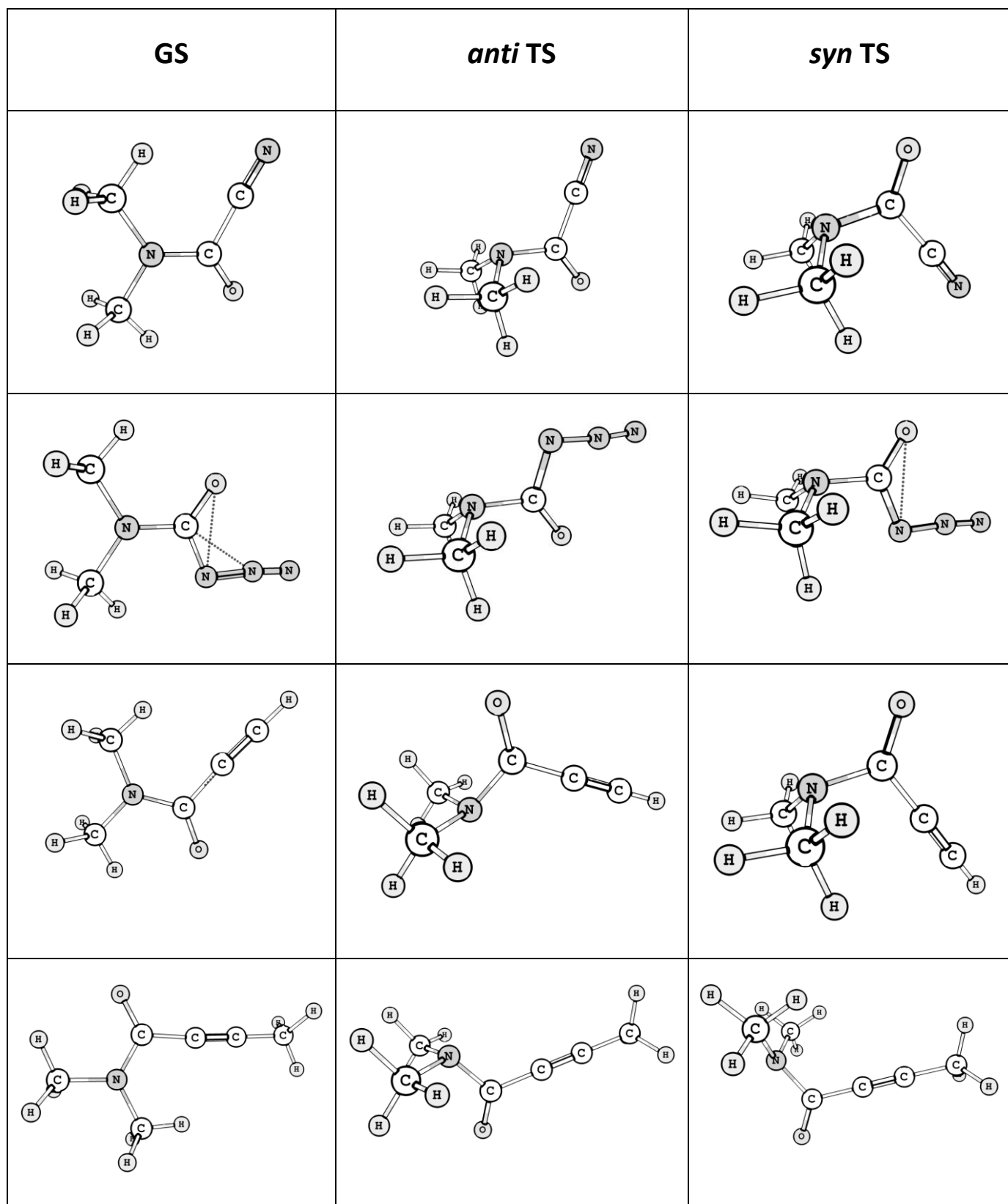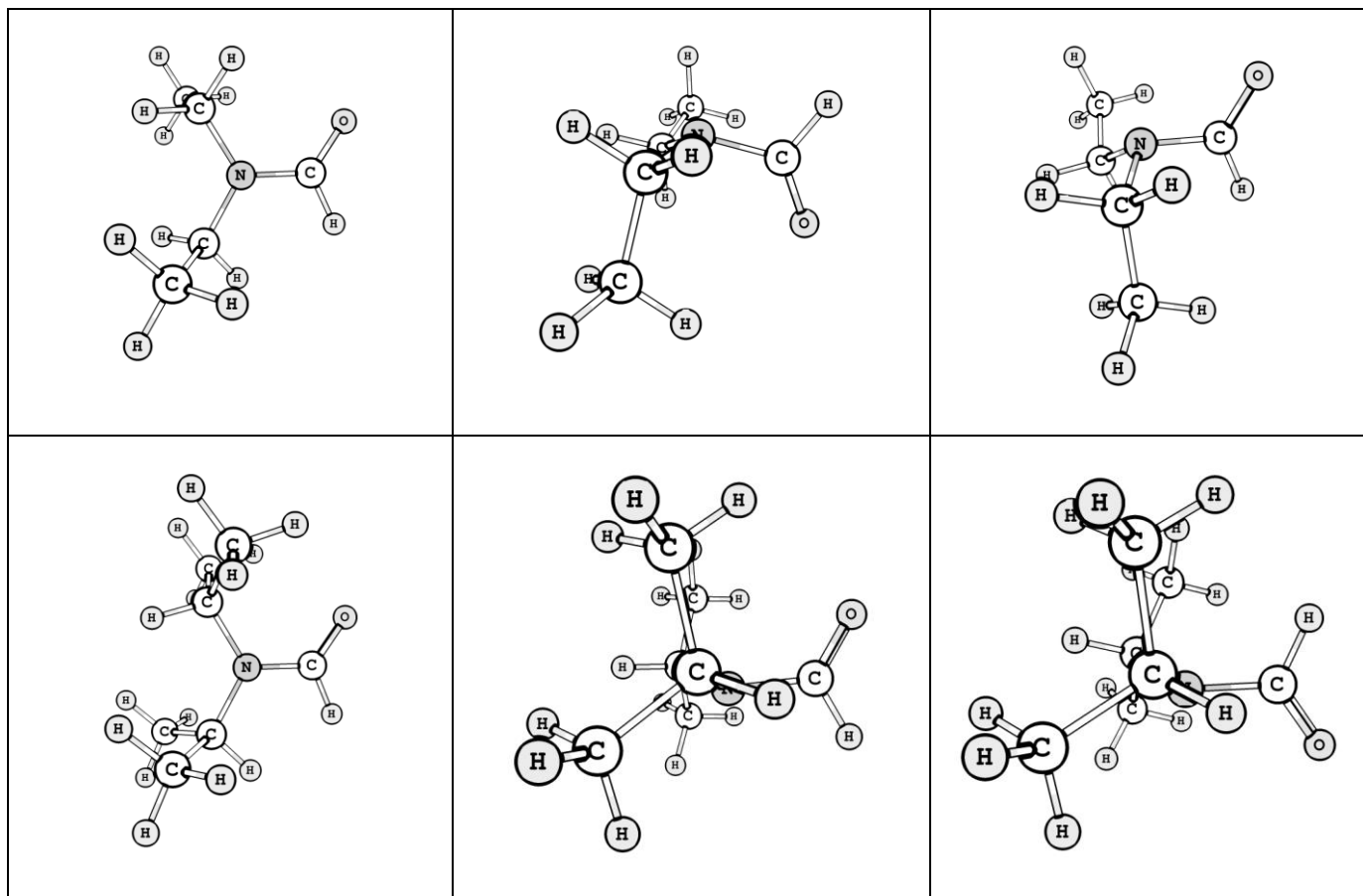## *Ab Initio* SCF study of the barrier to internal rotation in simple amides

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GS	*anti* TS	*syn* TS

Figure 1S. Ground state (GS) and two transition states (TS) structures of the studied amides: (R'=CH$_3$, R = CN, N$_3$, C≡C-H, C≡C-CH$_3$; R'=H, R = C$_2$H$_5$, CH(CH$_3$)$_2$)

Table 1S. Calculated energies for the studied amides R-C(O)NR'$_2$ in Hartrees

R	R'	State	ZPE[b]	HF/6-31G*	MP2(fc)/6-31+G*//6-31G*	HF/6-311++G**	MP2(fc)/6-311++G**//6-311++G**	PCM/6-311++G**
CH$_3$C≡C	CH$_3$	GS	84.20	-361.705110	-362.822927	-361.800779	-363.035250	-7.2 [c]
CH$_3$C≡C	CH$_3$	*anti* TS	83.98	-361.680512 [a]	-362.796311 [a]	-361.776673 [a]	-363.009445 [a]	-5.6 [c]
CH$_3$C≡C	CH$_3$	*syn* TS	83.92	-361.678469	-362.795327	-361.774802	-363.009209	-6.6 [c]
HC≡C	CH$_3$	GS	67.31	-322.657584	-323.645785	-322.744732	-323.828466	-6.9 [c]
HC≡C	CH$_3$	*anti* TS	67.05	-322.632508 [a]	-323.618149 [a]	-322.720096 [a]	-323.801902 [a]	-5.3 [c]
HC≡C	CH$_3$	*syn* TS	66.98	-322.630536	-323.617324	-322.718336	-323.801782	-6.1 [c]
N≡C	CH$_3$	GS	60.93	-338.712595	-339.732431	-338.802302	-339.915725	-7.2 [c]
N≡C	CH$_3$	*anti* TS	60.60	-338.685550 [a]	-339.701189	-338.775457 [a]	-339.885634	-5.4 [c]
N≡C	CH$_3$	*syn* TS	60.48	-338.684050	-339.701347 [a]	-338.774331	-339.886375 [a]	-6.0 [c]
N$_3$	CH$_3$	GS	63.94	-409.694259	-410.926097	-409.803606	-411.140548	-3.4 [d]
N$_3$	CH$_3$	*anti* TS	63.70	-409.669832 [a]	-410.901043 [a]	-409.779826 [a]	-411.116520 [a]	-3.9 [d]
N$_3$	CH$_3$	*syn* TS	63.67	-409.667923	-410.900286	-409.778106	-411.116026	-4.0 [d]
H	C$_2$H$_5$	GS	107.70	-325.064127	-326.070618	-325.152833	-326.287625	-7.3 [e]
H	C$_2$H$_5$	*anti* TS	106.95	-325.031517 [a]	-326.035407 [a]	-325.120101 [a]	-326.253552 [a]	-4.4 [e]
H	C$_2$H$_5$	*syn* TS	106.73	-325.029234	-326.033911	-325.118689	-326.252694	-6.4 [e]
H	i-C$_3$H$_7$	GS	129.54	-403.131352	-404.411288	-403.238596	-404.688025	-3.7 [f]
H	i-C$_3$H$_7$	*anti* TS	128.60	-403.096938 [a]	-404.373029 [a]	-403.204072 [a]	-404.650673 [a]	-2.3 [f]
H	i-C$_3$H$_7$	*syn* TS	128.51	-403.095152	-404.371845	-403.203395	-404.650225	-3.3 [f]
CH$_3$C≡C	H	GS	50.16	-283.649266	-284.500681	-283.732702	-284.658790	
CH$_3$C≡C	H	*anti* TS	50.04	-283.624609 [a]	-284.475042 [a]	-283.707864 [a]	-284.634549 [a]	
CH$_3$C≡C	H	*syn* TS	50.03	-283.621808	-284.472365	-283.705592	-284.632523	
HC≡C	H	GS	33.31	-244.601362	-245.323182	-244.676136	-245.451906	
HC≡C	H	*anti* TS	33.09	-244.576376 [a]	-245.296724 [a]	-244.651003 [a]	-245.426980 [a]	
HC≡C	H	*syn* TS	33.06	-244.573643	-245.294253	-244.648782	-245.425100	
N≡C	H	GS	26.98	-260.654219	-261.407503	-260.730905	-261.536917	
N≡C	H	*anti* TS	26.60	-260.628429 [a]	-261.379307 [a]	-260.705090 [a]	-261.510356 [a]	
N≡C	H	*syn* TS	26.52	-260.625624	-261.376991	-260.702800	-261.508455	
N$_3$	H	GS	29.92	-331.638605	-332.604377	-331.735570	-332.764778	
N$_3$	H	*anti* TS	29.80	-331.613499 [a]	-332.579125 [a]	-331.710547 [a]	-332.741088 [a]	
N$_3$	H	*syn* TS	29.76	-331.612009	-332.577935	-331.709426	-332.740094	

[a] more stable TS; [b] ZPE is reported in kcal/mol at the HF/6-31G* level scaled by 0.89; [c] Energy change from gas phase to TCE in kcal/mol; [d] Energy change from gas phase to CCl$_4$ in kcal/mol; [e] Energy change from gas phase to diethyl formamide in kcal/mol; [f] Energy change from gas phase to toluene in kcal/mol.

Table 2S. Origin of the difference in the rotational barriers (kcal/mol) of the studied amides $R-CON(CH_3)_2$ in the gas phase
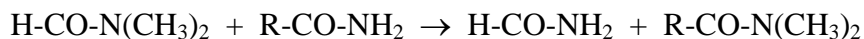
$$H-CO-N(CH_3)_2 \ + \ R-CO-NH_2 \ \rightarrow \ H-CO-NH_2 \ + \ R-CO-N(CH_3)_2$$

R	H	CN	N_3	$C\equiv CH$	$C\equiv CCH_3$
$\Delta\Delta H^o(GS)$	0	0.9(0.4)	2.6(2.5)	2.3(2.2)	2.5(2.5)
$\Delta\Delta H^o(anti\ TS)$	0	-1.2(-1.5)	-0.8(-1.0)	-0.6(-0.8)	-0.5(-0.6)
$\Delta\Delta H^o(syn\ TS)$	0	-0.2(-0.6)	1.4(1.2)	0.8(0.6)	0.9(0.8)
anti TS - GS:					
$\Delta\Delta H^{\neq}(0K)$	0	-0.4(-1.6)	-4.3(-1.6)	-2.6(-2.9)	-3.2(-3.2)
$\Delta\Delta H^o(anti\ TS)- \Delta\Delta H^o(GS)$	0	-2.1(-1.9)	-3.4(-3.5)	-2.9(-3.0)	-3.0(-3.2)
syn TS - GS:					
$\Delta\Delta H^{\neq}(0K)$	0	-0.8(-1.4)	-4.1(-1.4)	-2.3(-2.3)	-2.8(-2.5)
$\Delta\Delta H^o(syn\ TS)- \Delta\Delta H^o(GS)$	0	-1.0(-0.9)	-1.3(-1.4)	-1.5(-1.5)	-1.7(-1.7)
$\Delta\Delta G^{\neq}_{eff}(298K)$	0	-0.7(-1.9)	-3.3(-0.6)	-2.3(-2.5)	-2.3(-2.1)
$\Delta\Delta G^{\neq}_{exp}(298K)$	0	-0.4(gas)	-2.9(gas)	-1.3(liquid)	-1.3(liquid)

$\Delta\Delta H^o(GS)$, $\Delta\Delta H^o(anti\ TS)$ and $\Delta\Delta H^o(syn\ TS)$ are the energy changes (HF/6-31G* energy plus ZPE correction) for the model reaction in the ground, *anti* and *syn* transition states, respectively. $\Delta\Delta H^{\neq}(0K)$ is the difference in the calculated enthalpy of activation for the amide rotation, $\Delta\Delta G^{\neq}_{eff}(298K)$ is the change in the calculated free energy and $\Delta\Delta G^{\neq}_{exp}(298K)$ is the experimental change in free energy. The values in parenthesis correspond to the HF/6-311++G** level of theory.