

**Modeling of the mechanism of endo/exo isomerization of
dicyclopentadiene hydrogenation products in the presence of AlCl_3**

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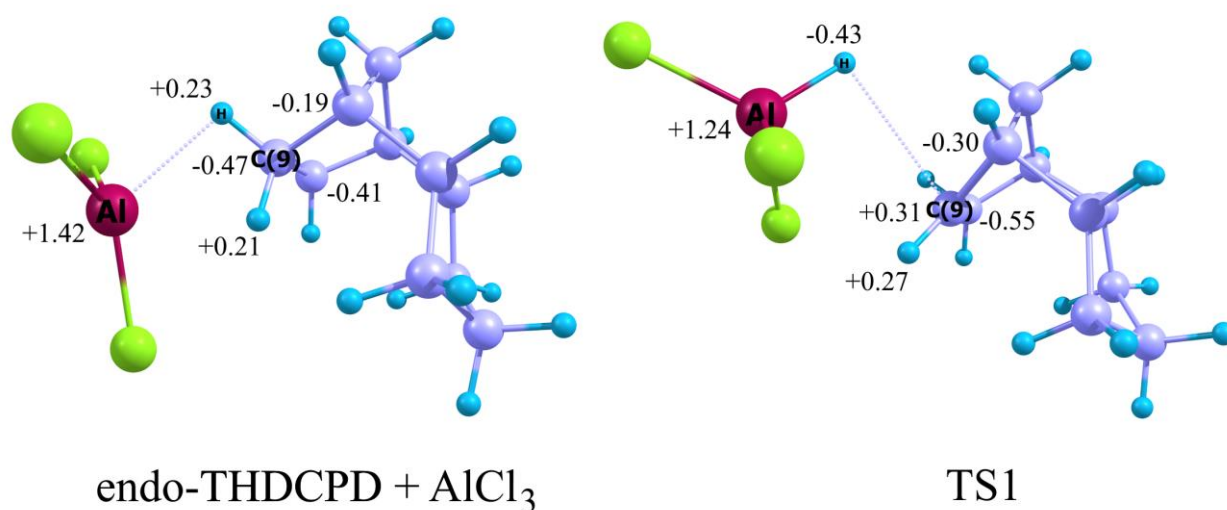


Fig. S1. NBO charges on atoms involved in C(9)-H bond cleavage and surrounding atoms in the pre-reaction complex and TS1 of endo/exo-isomerization of THDCPD

Table S1. NBO charges on atoms involved in C(9)-H bond cleavage in the pre-reaction complex and TS1 of endo/exo-isomerization of THDCPD

Component	C(9)	H
endo-THDCPD + AlCl ₃	-0.47 e	+0.23 e
TS1	+0.31 e	-0.43 e
$\Delta\delta$	+0.78 e	-0.66 e

Table S2. Energies, enthalpies and Gibbs energies (kcal mol⁻¹) of components of endo/exo isomerization of THDCPD relative to isolated reactants (endo-THDCPD and AlCl₃)

Component	Gas phase			$\Delta G_{\text{solv},298}$	
	ΔE	ΔH_{298}	ΔG_{298}	CCl ₄	CH ₂ Cl ₂
endo-THDCPD + AlCl ₃	0	0	0	0	0
TS1	59.1	55.8	65.5	54.5	47.1
Int1	33.4	32.2	41.9	38.8	37.6
TS2	57.3	54.6	63.8	52.4	44.7
Int2	29.5	28.2	37.5	34.2	33.0
TS3	54.7	51.5	61.0	50.2	42.8
exo-THDCPD + AlCl ₃	-4.0	-4.0	-3.9	-3.9	-3.9

Table S3. Comparison of DFT-PBE0 and DLPNO-CCSD(T) total energies of components of endo/exo-THDCPD isomerization mechanism relative to isolated reactants (endo-THDCPD and AlCl₃)

Component	ΔE , kcal mol ⁻¹	
	PBE0/cc-pVTZ	DLPNO-CCSD(T)/cc-pVTZ//PBE0/cc-pVTZ
endo-THDCPD + AlCl ₃	0	0
TS1	59.13	59.27
Int1	33.37	31.71
TS2	57.34	56.17
Int2	29.52	28.00
TS3	54.72	54.81
exo-THDCPD + AlCl ₃	-3.98	-3.93