Digitale chemie:
een duurzame oplossing
voor chemische uitdagingen

C³ **masterclass**

Centrum
JongerenCommunicatie
Chemie

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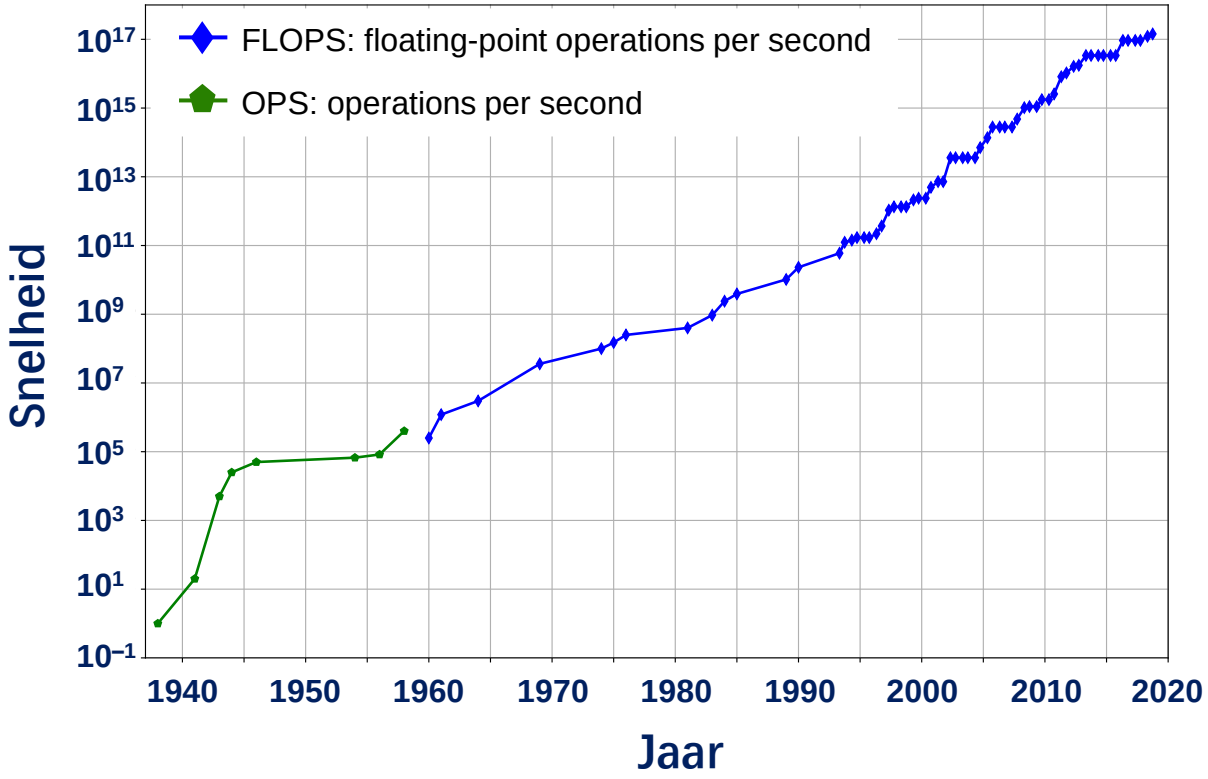
Universiteit Leiden
UNIVERSITAT DE BARCELONA

@THansenChem

De experimentele wetenschap scheikunde

De digitale eeuw

Computerkracht over de laatste eeuw



Bron: TOP500 Supercomputer database

Wat is computationele chemie?

- De tak van de chemie die computersimulaties gebruikt om chemische problemen op te lossen.
- Hierbij gebruikt men mathematische algoritmen, statistiek en grote databanken om chemie te modelleren.

Theoretische chemie

- Een wiskundige beschrijving van chemie.
- Tijdsonafhankelijke Schrödingervergelijking.

$$\hat{H}\psi = E\psi$$

Theoretische chemie

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$$\hat{H}\psi = E\psi$$

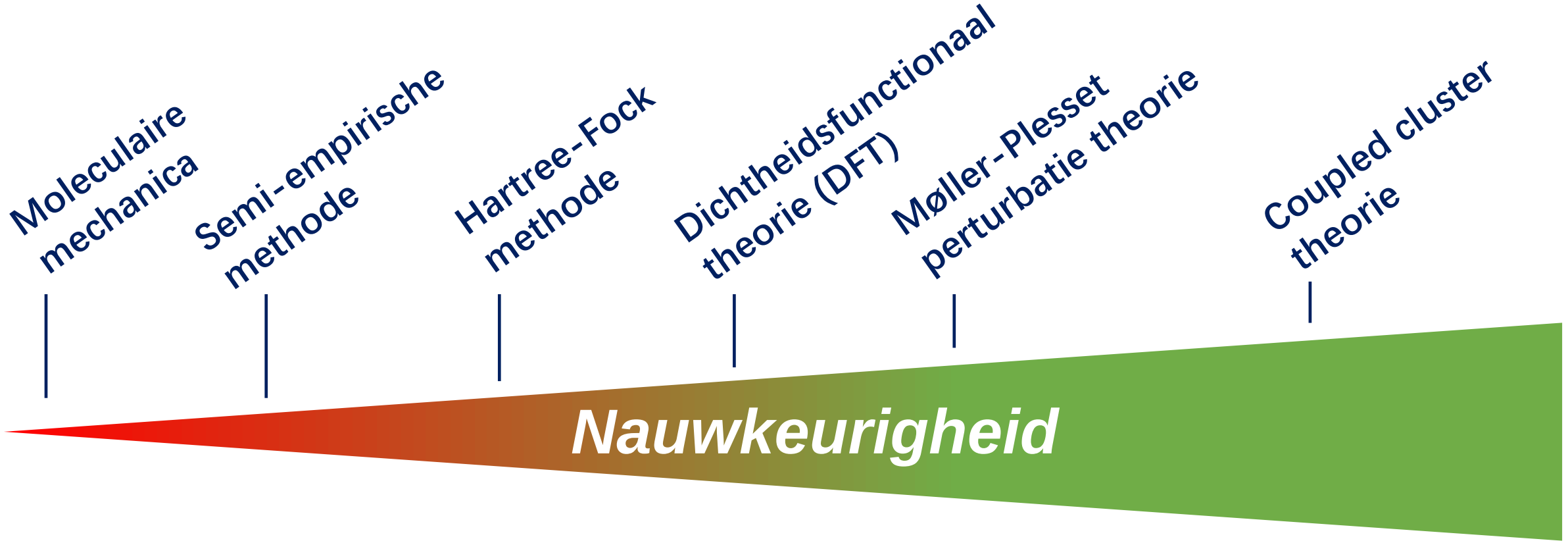
$\hat{H}$ = kinetische energie (KE) + potentiele energie (PE)

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2}\sum_{\alpha}\frac{1}{m_\alpha}\nabla_\alpha^2}_{\text{KE nucleus}} \underbrace{-\frac{\hbar^2}{2m_e}\sum_{i}\nabla_i^2}_{\text{KE electrons}} + \underbrace{\sum_{\alpha}\sum_{\alpha>\beta}\frac{Z_\alpha Z_\beta e'^2}{r_{\alpha\beta}} - \sum_{\alpha}\sum_{i}\frac{Z_\alpha e'^2}{r_{i\alpha}}}_{\text{PE nucleus–electrons}} + \underbrace{\sum_{j}\sum_{i>j}\frac{e'^2}{r_{ij}}}_{\text{PE electrons–electrons}}$$

Computationele methodes

Theoretische en computationele chemie gebruikt een veelvoud van benaderingen:

- **Moleculaire mechanica**
- **Golffunctietheorie (*ab initio*)**
  - Semi-empirische methode
  - Hartree-Fock methode
  - Møller-Plesset perturbatie theorie
  - Coupled cluster theorie
- **Dichtheidsfunctionaaltheorie (DFT)**


Moleculaire mechanica
Semi-empirische methode
Hartree-Fock methode
Dichtheidsfunctionaal theorie (DFT)
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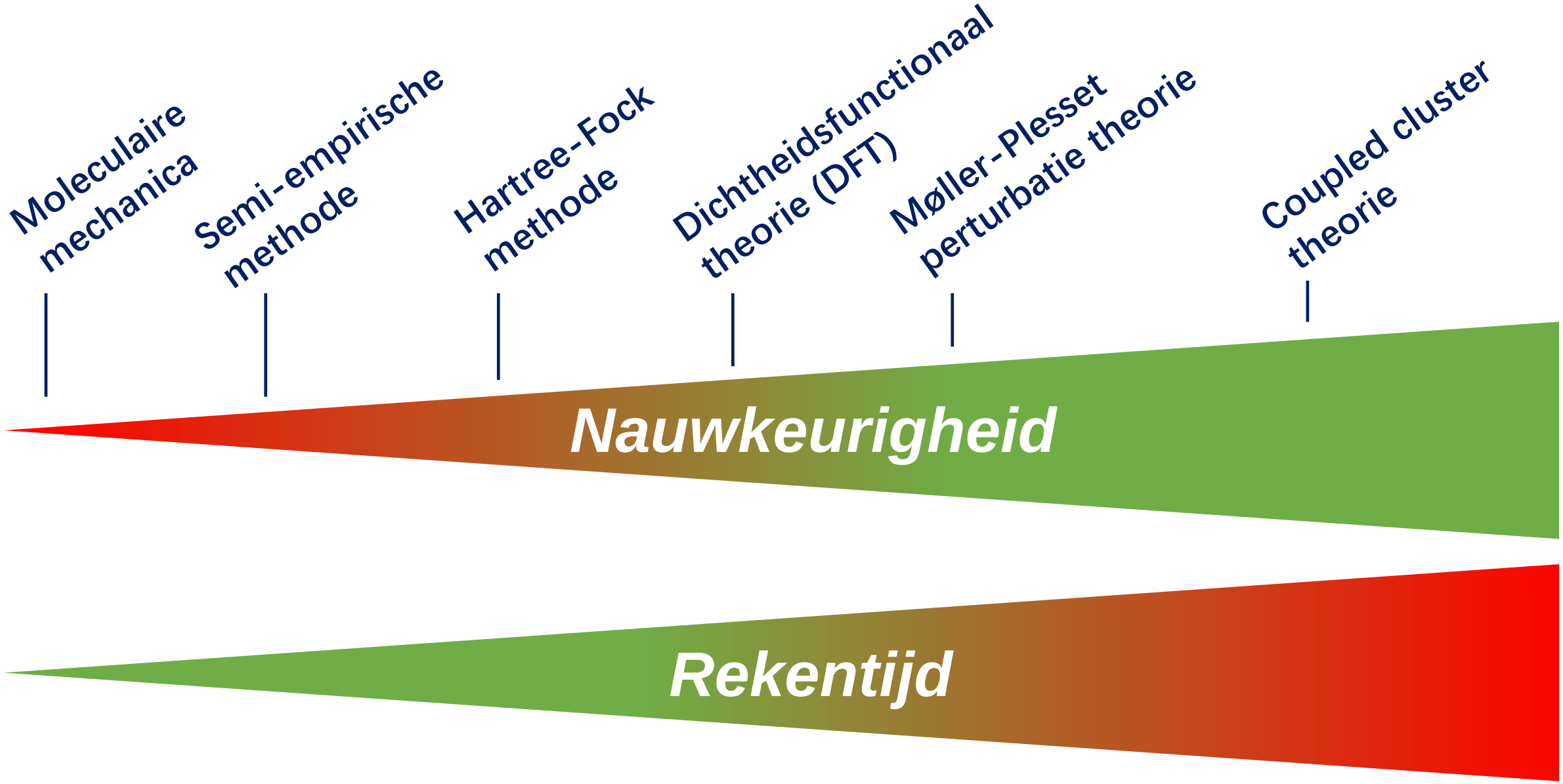
Coupled cluster theorie
Nauwkeurigheid


Moleculaire mechanica
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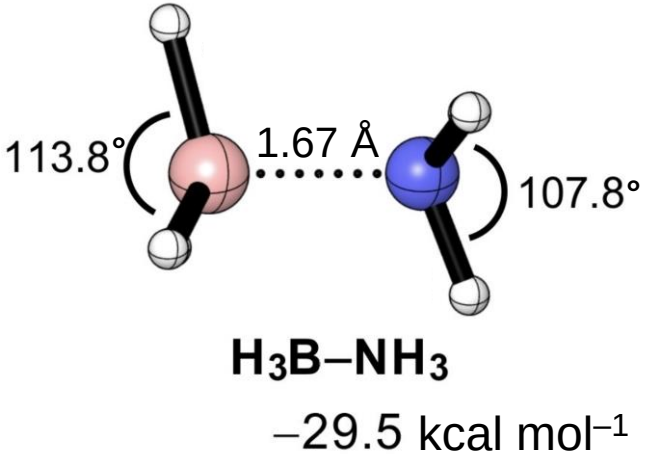
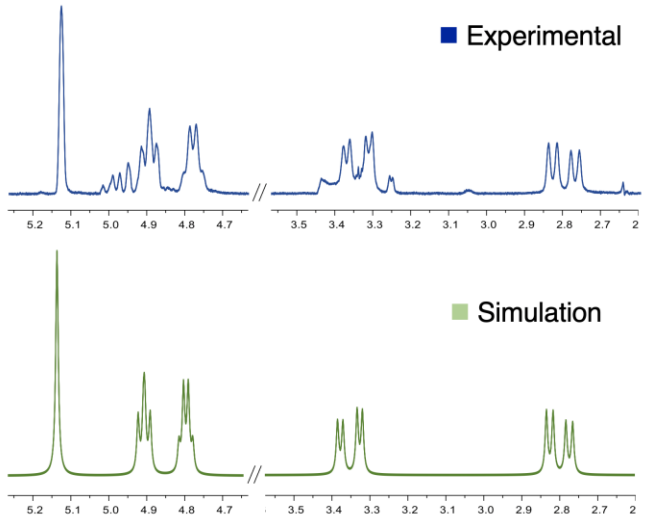
Hartree-Fock methode
Dichtheidsfunctionaal theorie (DFT)
Møller-Plesset perturbatie theorie
Coupled cluster theorie
Nauwkeurigheid
Rekentijd

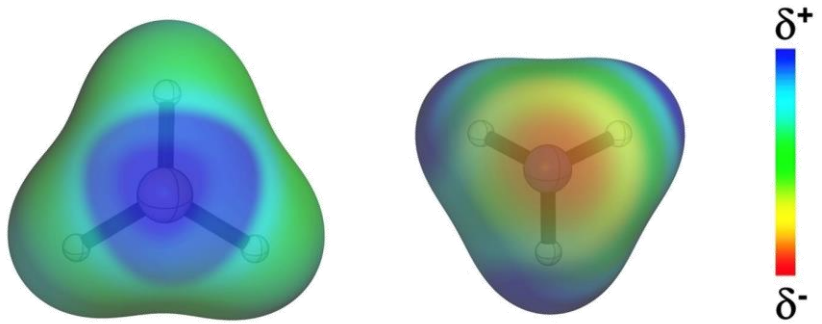
Wat kun je berekenen met computationele chemie?

Eigenschappen van atomen, moleculen of systemen.

- Structuur
- Energie
- Ladingsverdeling
- Vibrationele frequenties
- Spectroscopische eigenschappen
- Reactiviteit



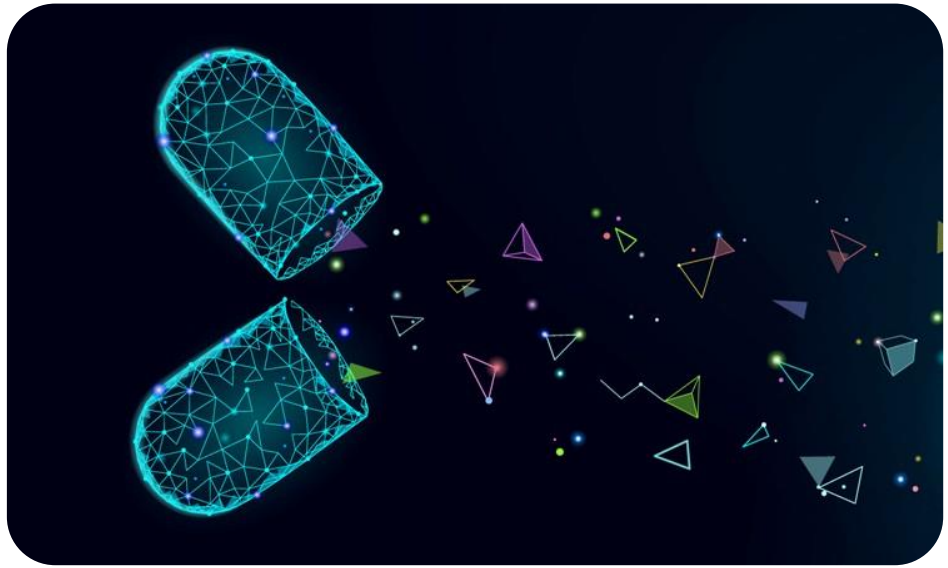




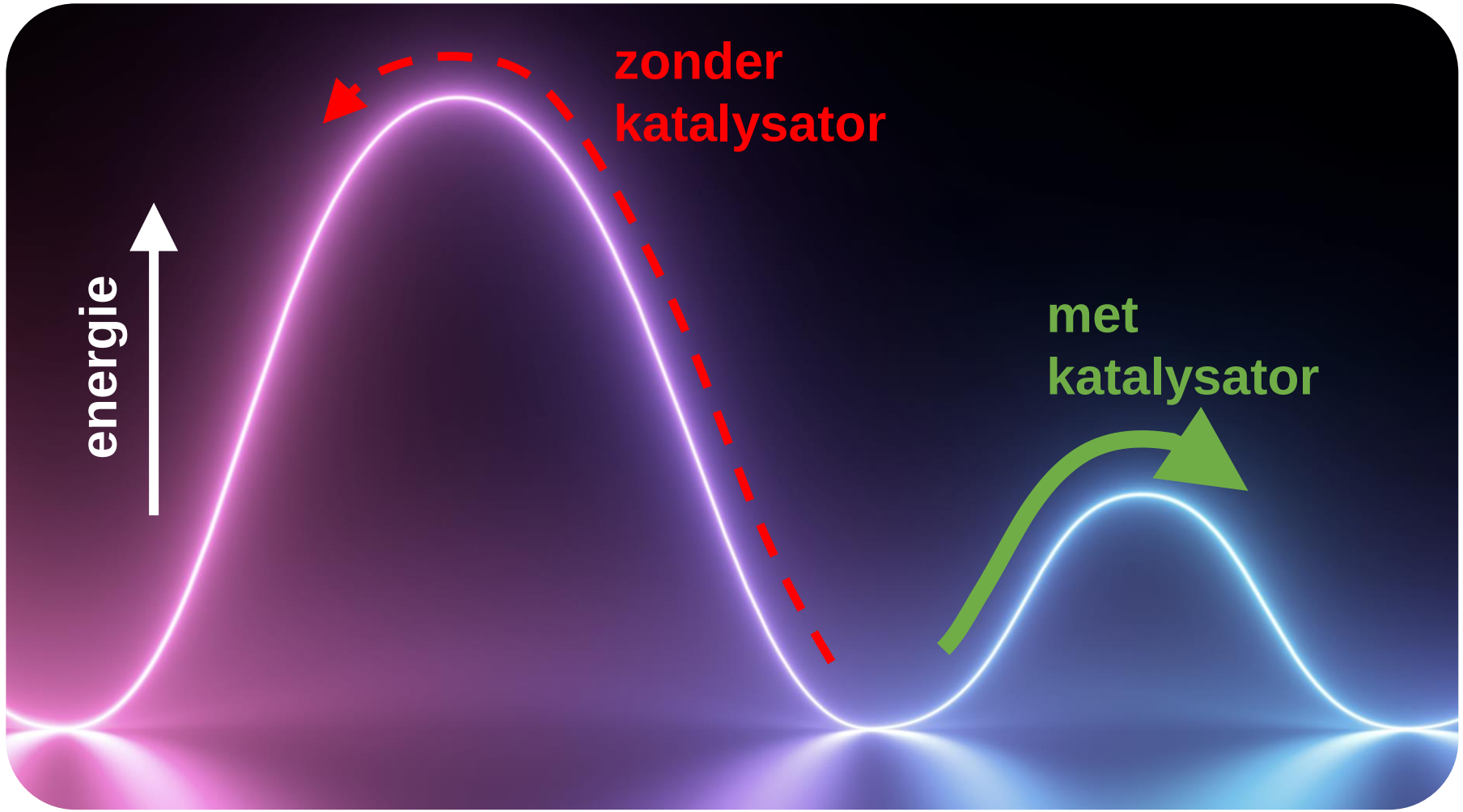
Wat zijn de praktische toepassingen van computationele chemie?

Duurzame oplossing

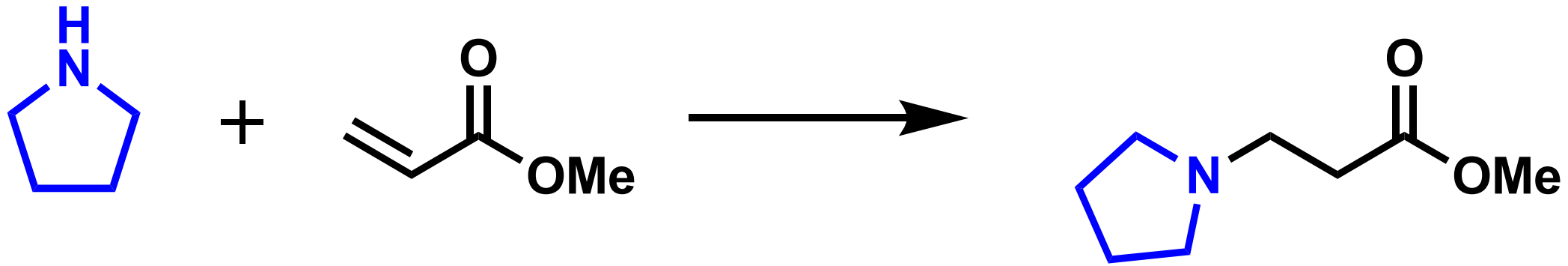
- Nieuwe medicijnen ontwikkelen.
- Optimaliseren van energie opslag.
- Betere katalysatoren maken.
- Chemische reacties beter begrijpen en sturen.



Katalysator



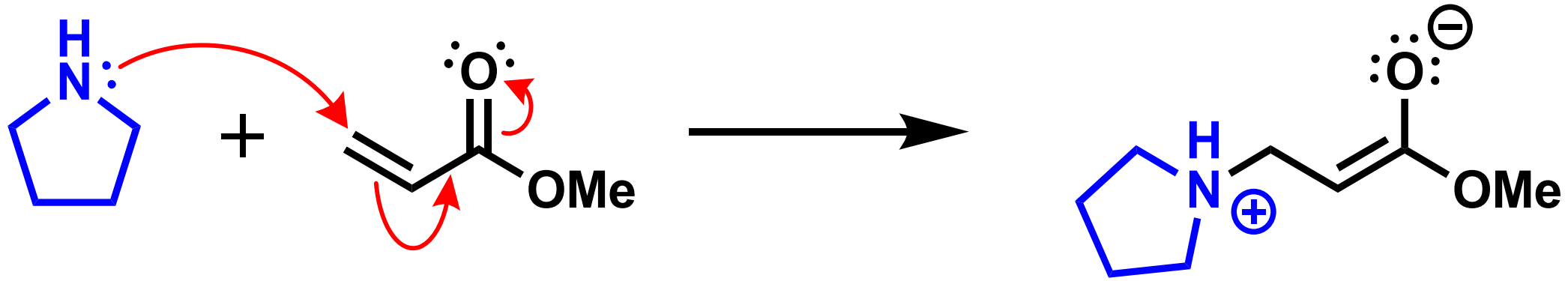
Michael additie reactie



pyrrolidine methyl acrylaat product

Synth. Commun. **2010**, *40*, 2830

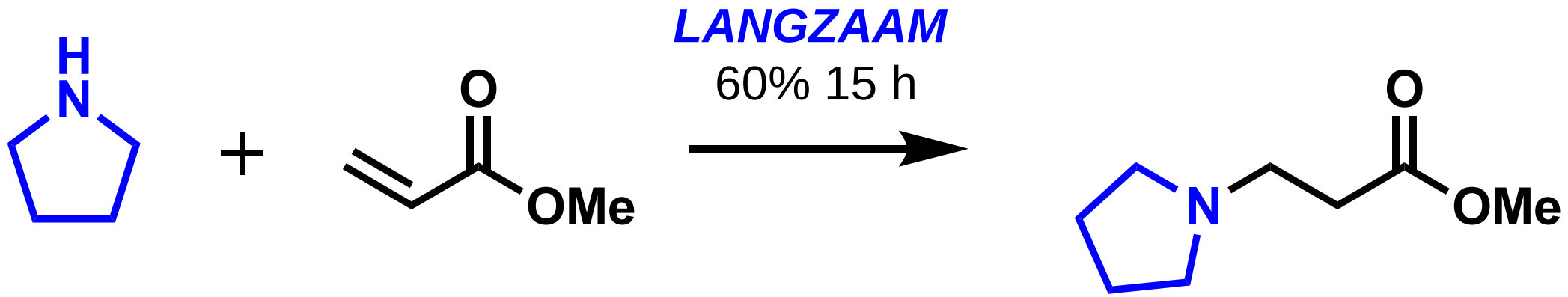
Michael additie reactie



nucleofiel electrofiel zwitterionisch intermediair

Synth. Commun. **2010**, *40*, 2830

Michael additie reactie



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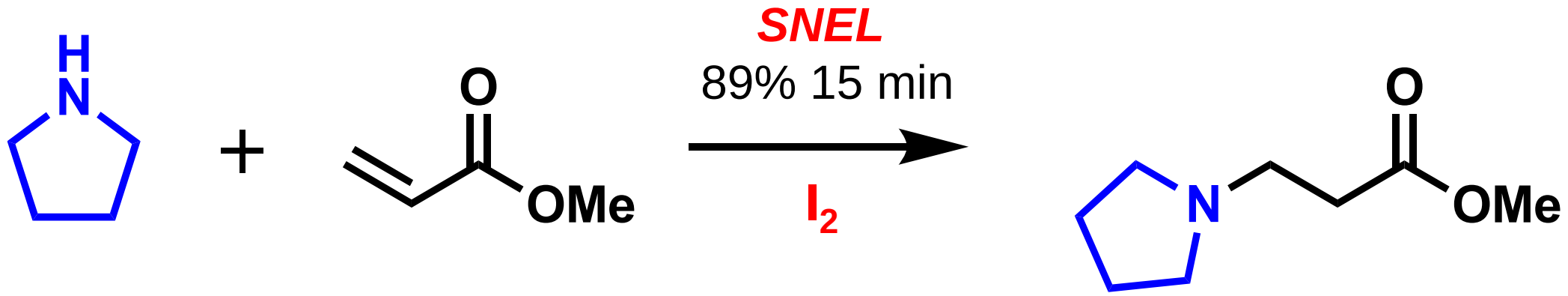
Synth. Commun. **2010**, *40*, 2830

Gekatalyseerde Michael additie reactie



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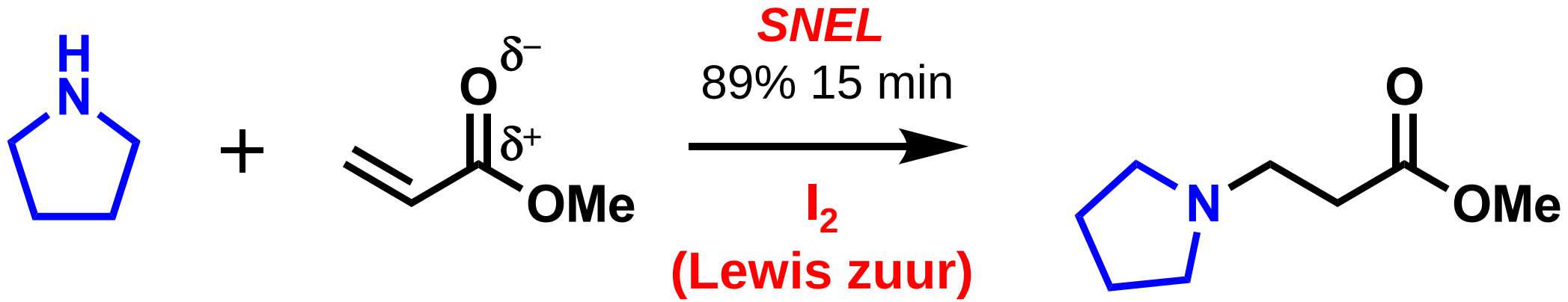

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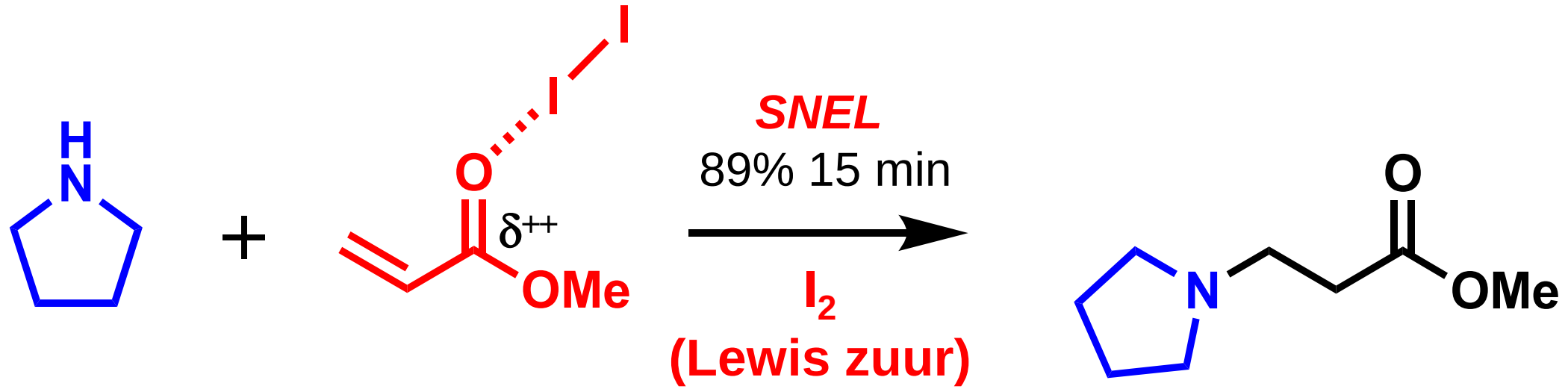
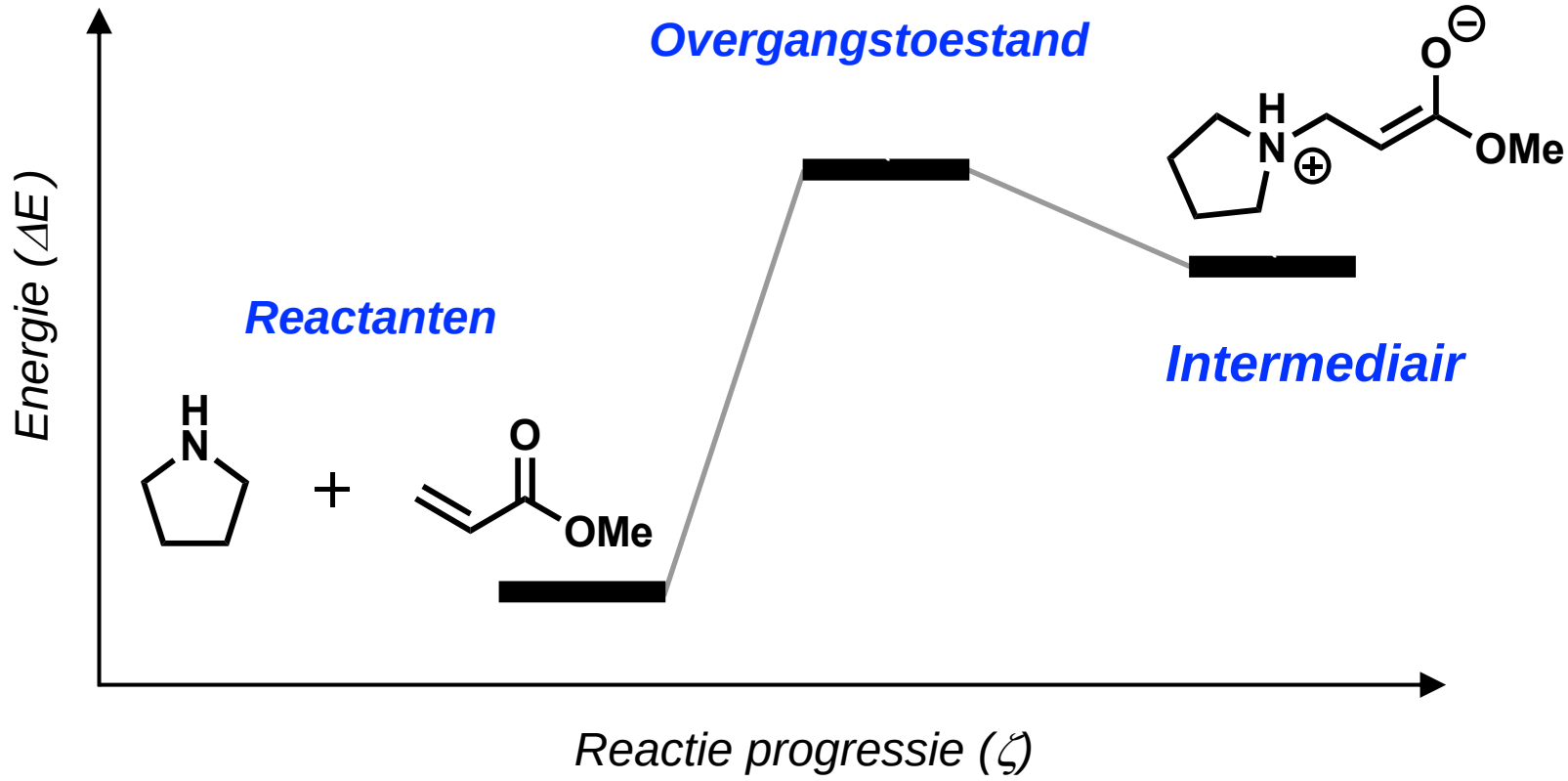


pyrrolidine methyl acrylaat zwitterionisch intermediair

Synth. Commun. **2010**, *40*, 2830

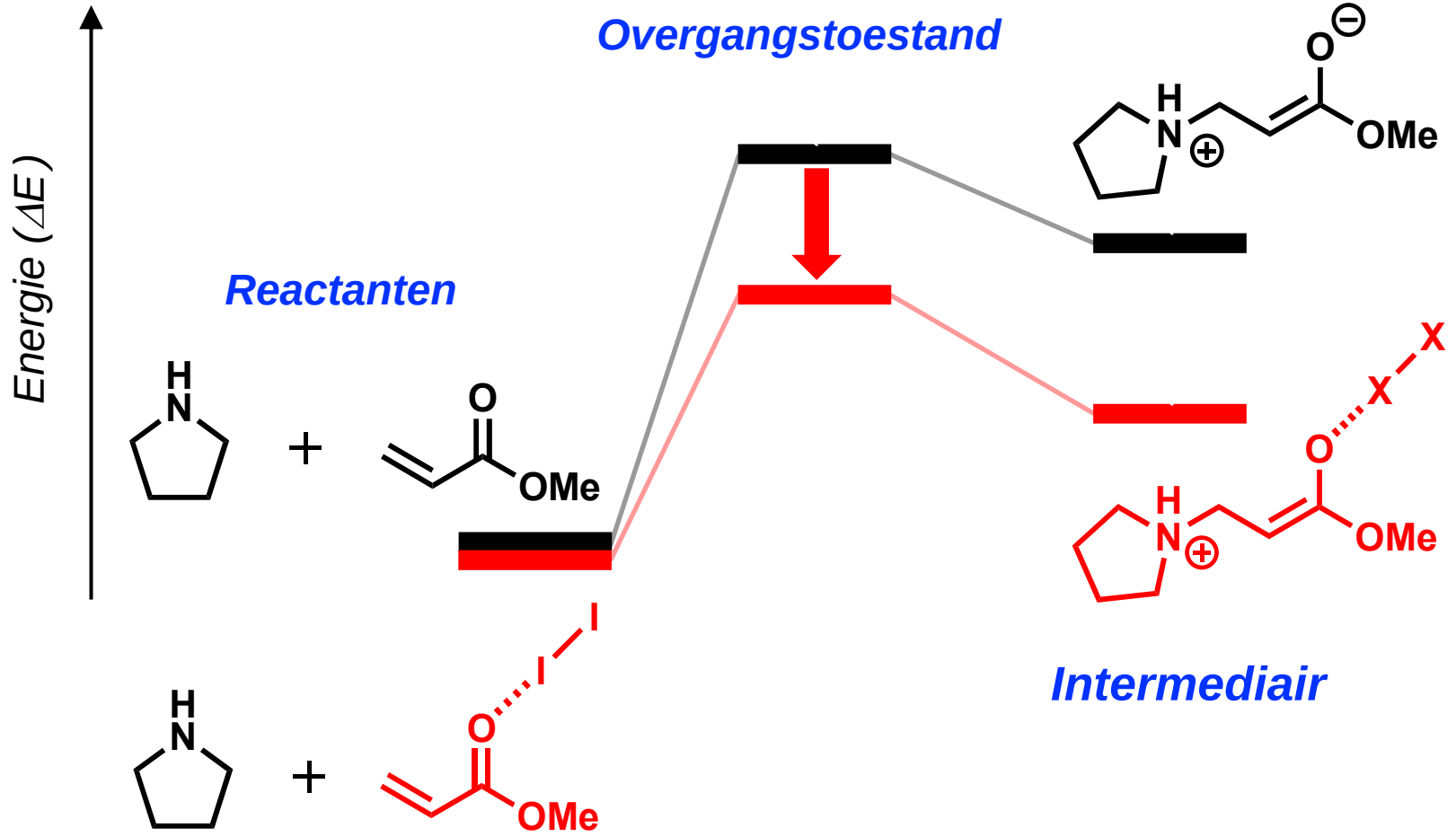
Berekend reactieprofiel



ACS Catal. **2016**, *6*, 3203

B2PLYP-D3/aug-cc-pVTZ/IEFPCM//M06-2X-D3/6-311+G(d,p)/IEFPCM, aug-cc-pVTZ-PP for I_2

Berekend gekatalyseerd reactieprofiel



ACS Catal. **2016**, *6*, 3203

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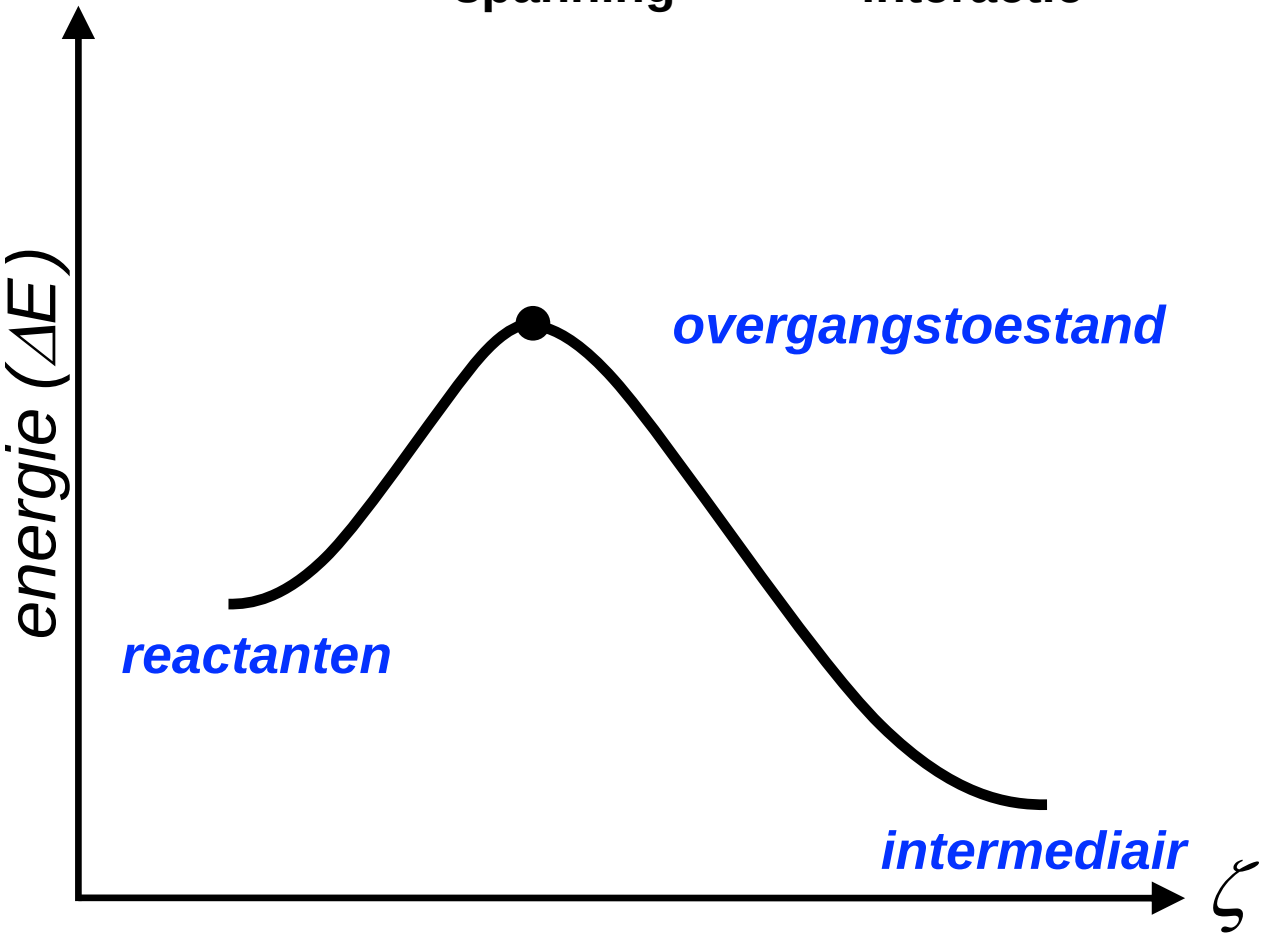
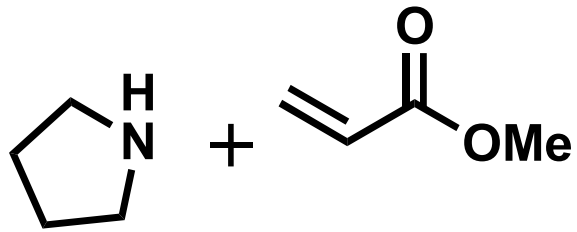
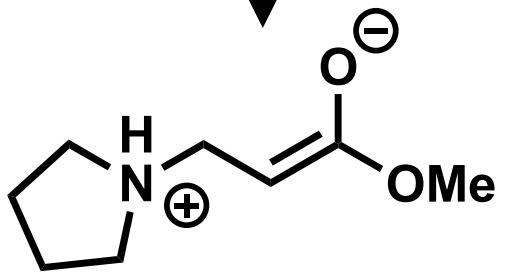
Activeringsspanningsmodel

$$\Delta E = \Delta E_{\text{spanning}} + \Delta E_{\text{interactie}}$$





reactanten



intermediair

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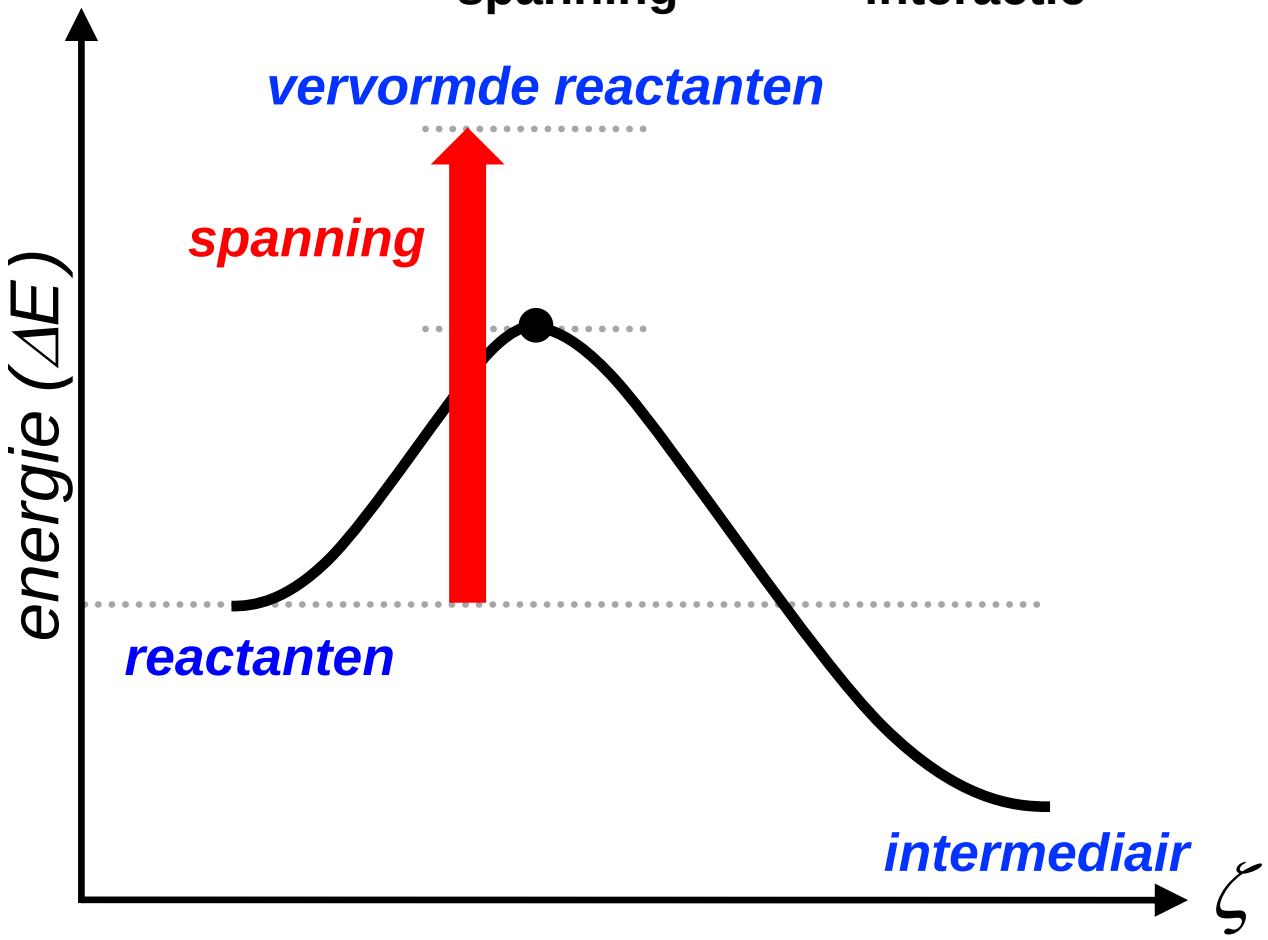

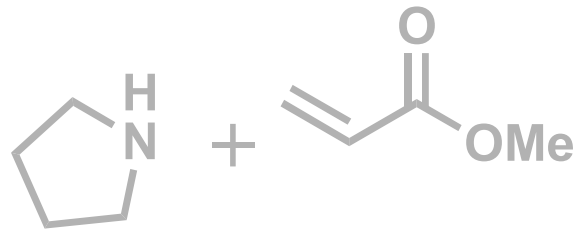

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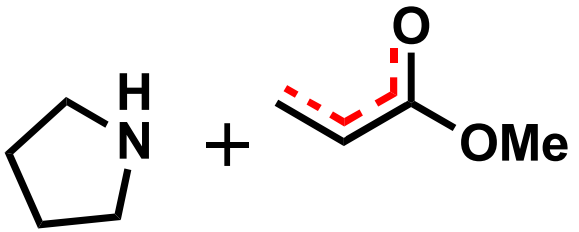
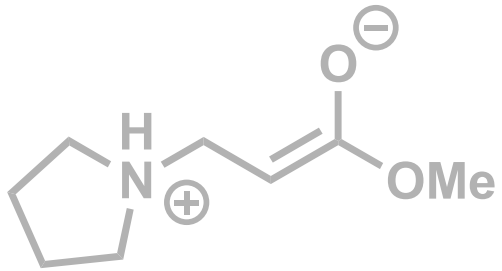


vervomde reactanten



intermediair

Angew. Chem. Int. Ed. **2017**, *56*, 10070–10086

Activeringsspanningsmodel

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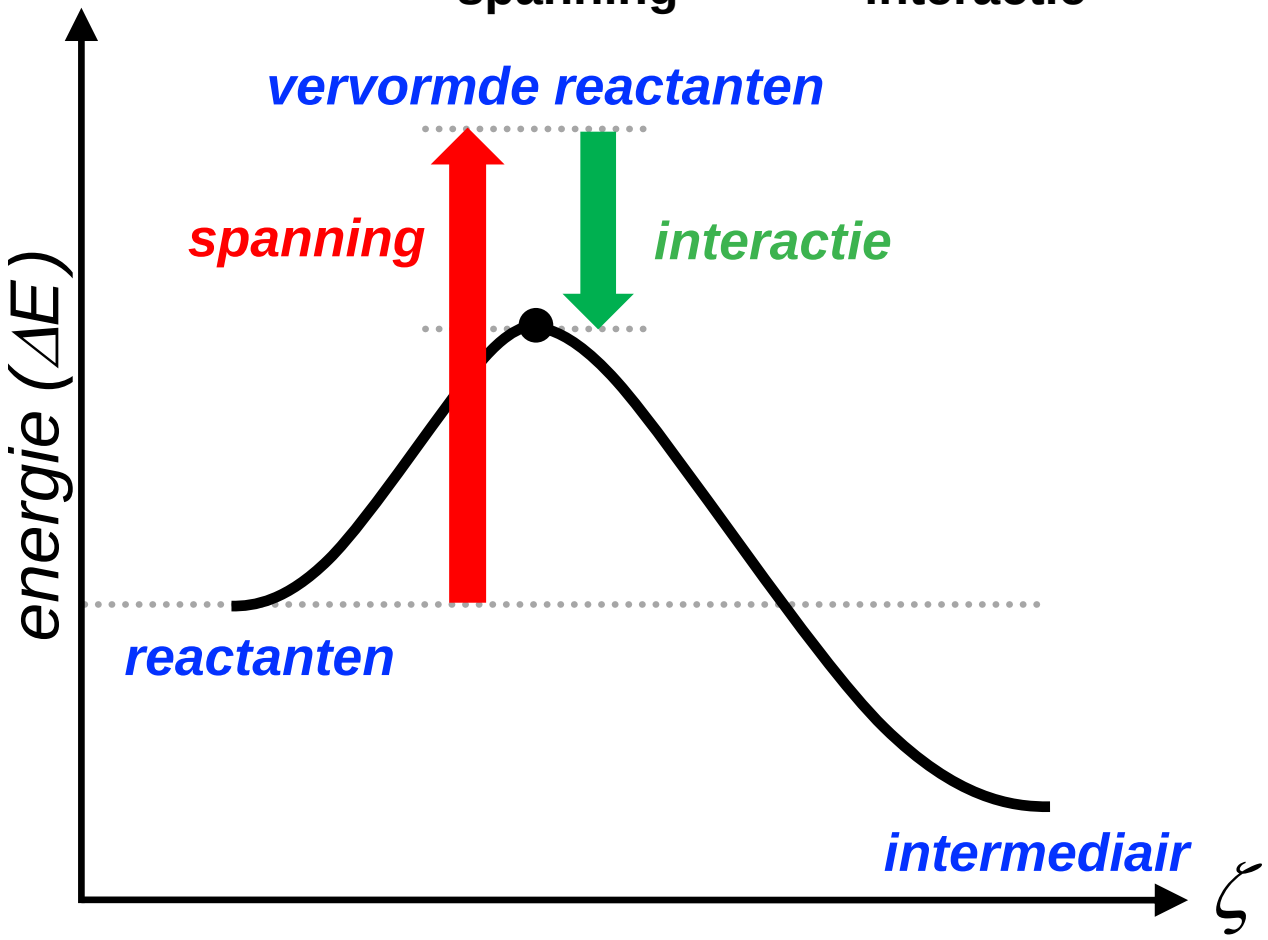
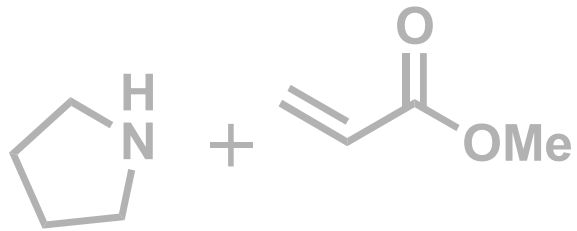
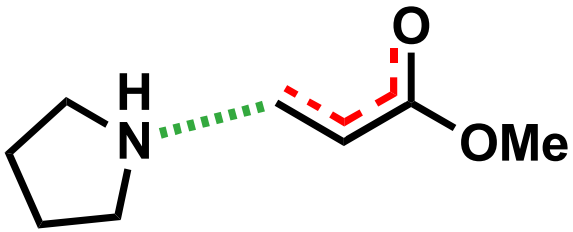
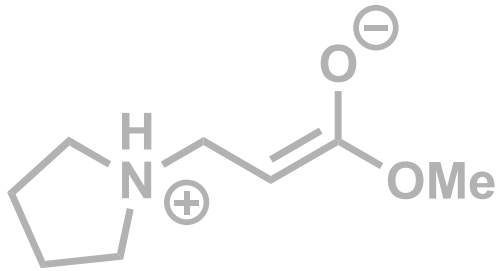




reactanten



vervomde reactanten



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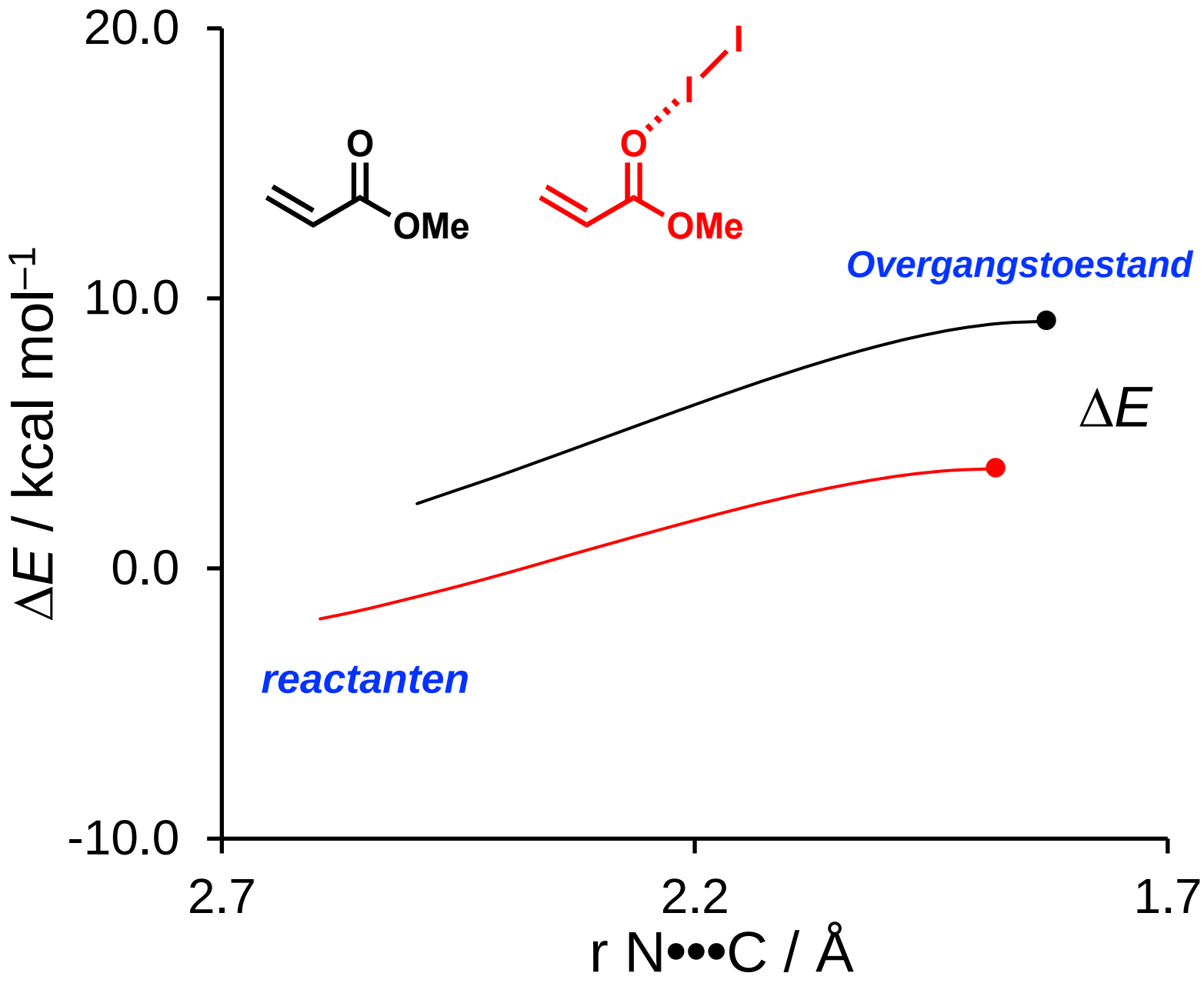
Angew. Chem. Int. Ed. **2017**, *56*, 10070–10086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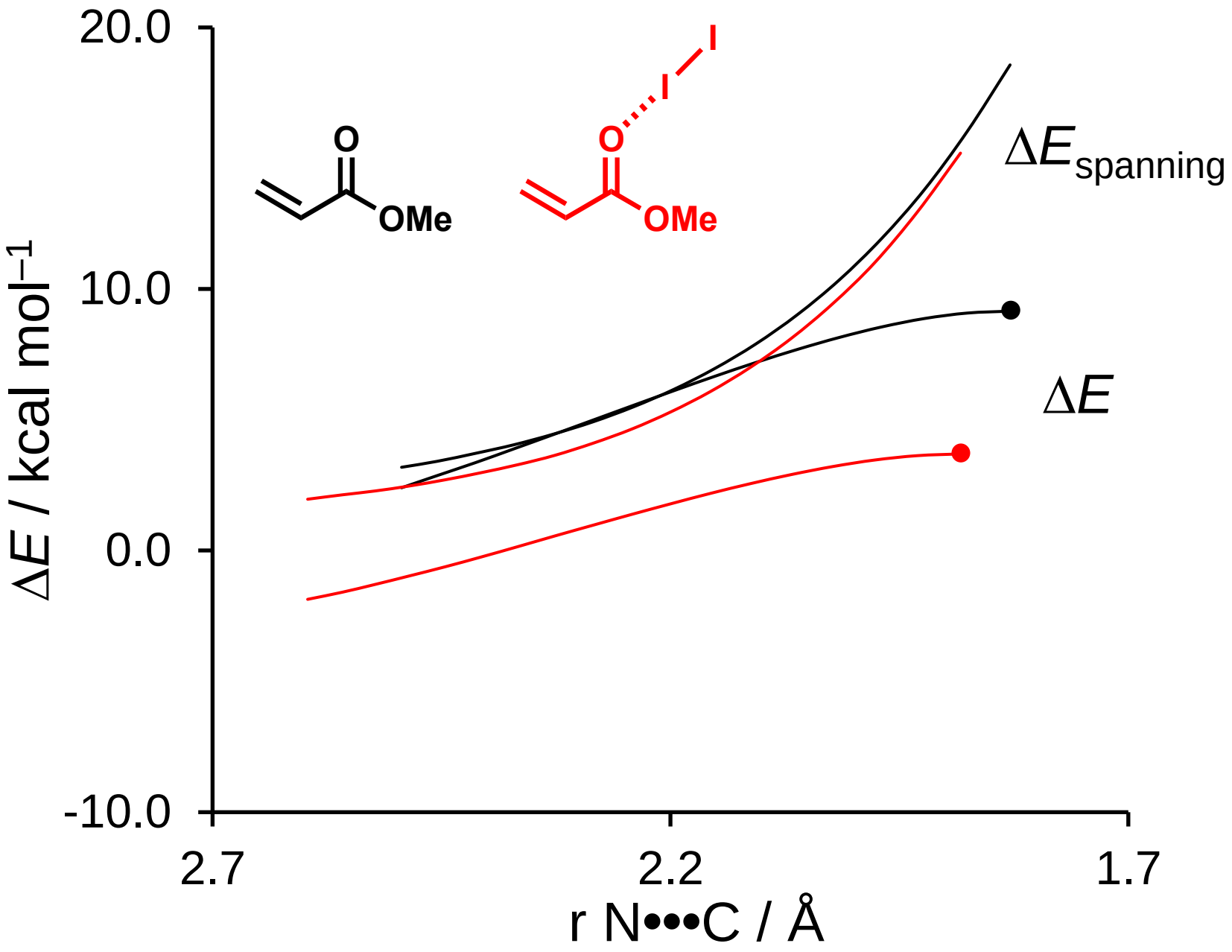

Angew. Chem. Int. Ed. **2019**, *58*, 8922–8926

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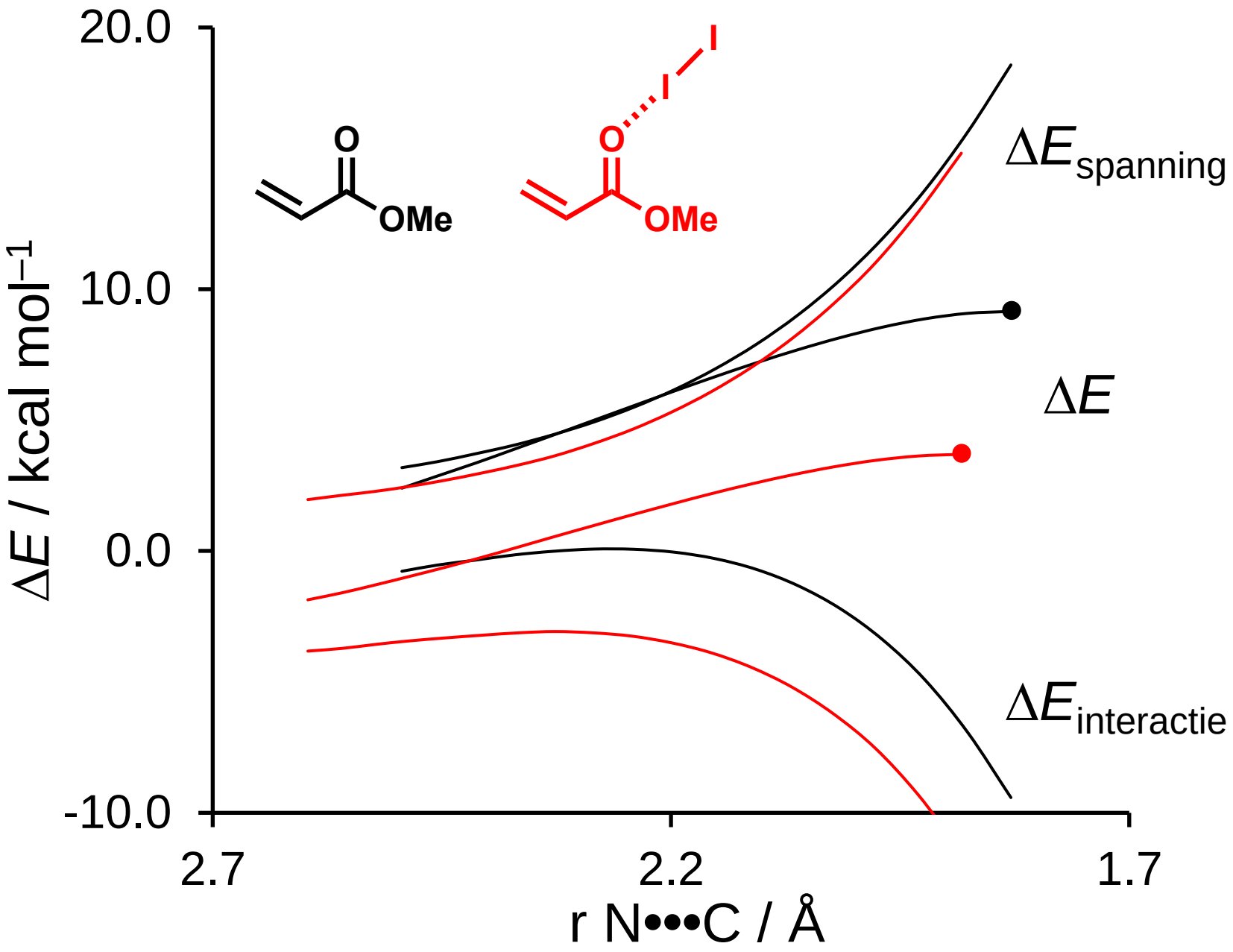
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10.0
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ΔE / kcal mol–1
2.7
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1.7
r N•••C / Å
O
OMe
I
I
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ΔEspanning
ΔE
ΔEinteractie

Energie-decompositie analyse (EDA)

$$\Delta E = \Delta E_{\text{spanning}} + \Delta \boldsymbol{E}_{\textbf{interactie}}$$

$$\Delta \boldsymbol{E}_{\textbf{interactie}} = \Delta \boldsymbol{V}_{\textbf{electrostatische interacties}} + \Delta \boldsymbol{E}_{\textbf{sterische repulsie}} + \Delta \boldsymbol{E}_{\textbf{orbitaal interacties}}$$

Rev. Comput. Chem. **2000**, *15*, 1–86

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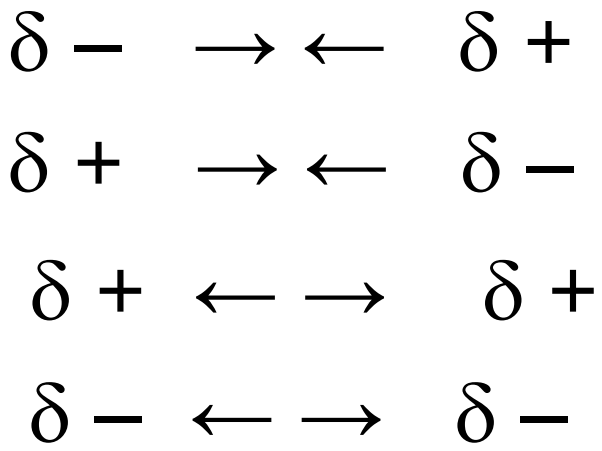
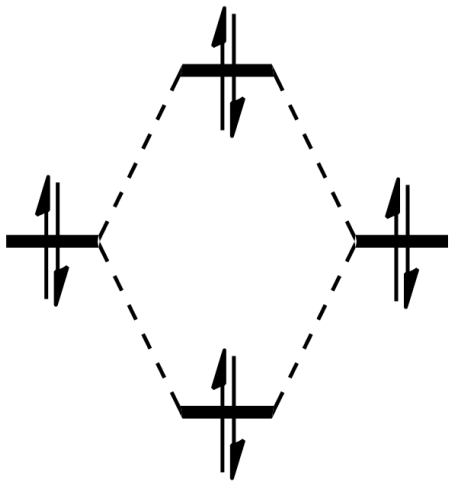
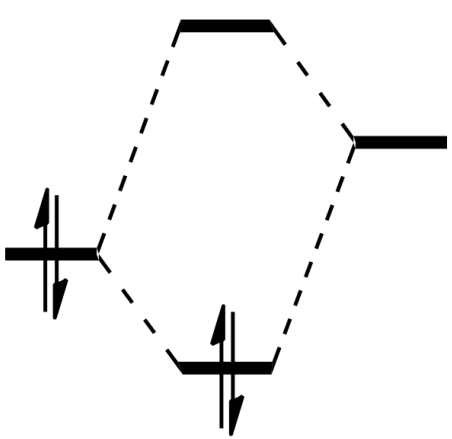
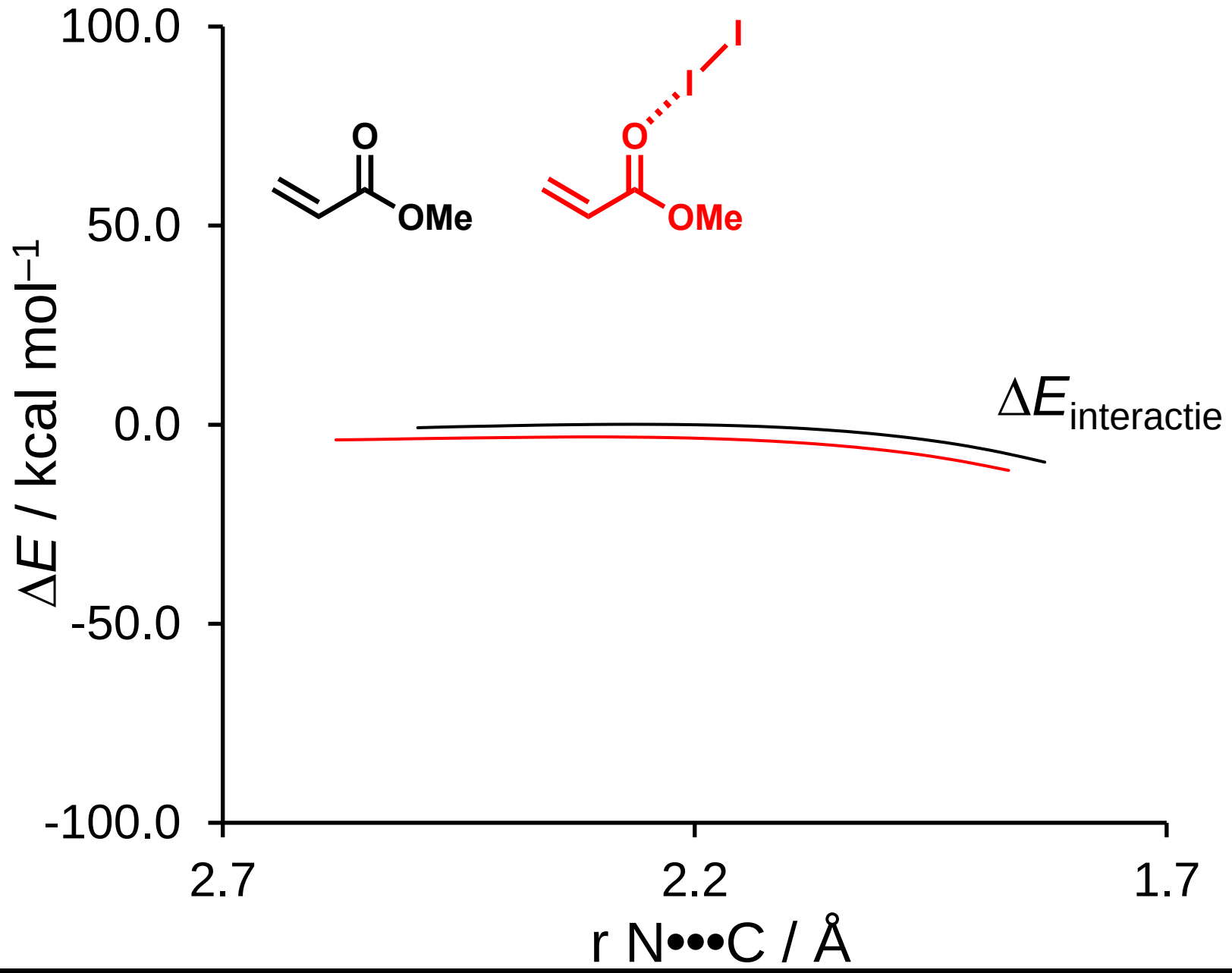






Rev. Comput. Chem. **2000**, *15*, 1–86



Angew. Chem. Int. Ed. **2019**, *58*, 8922–8926

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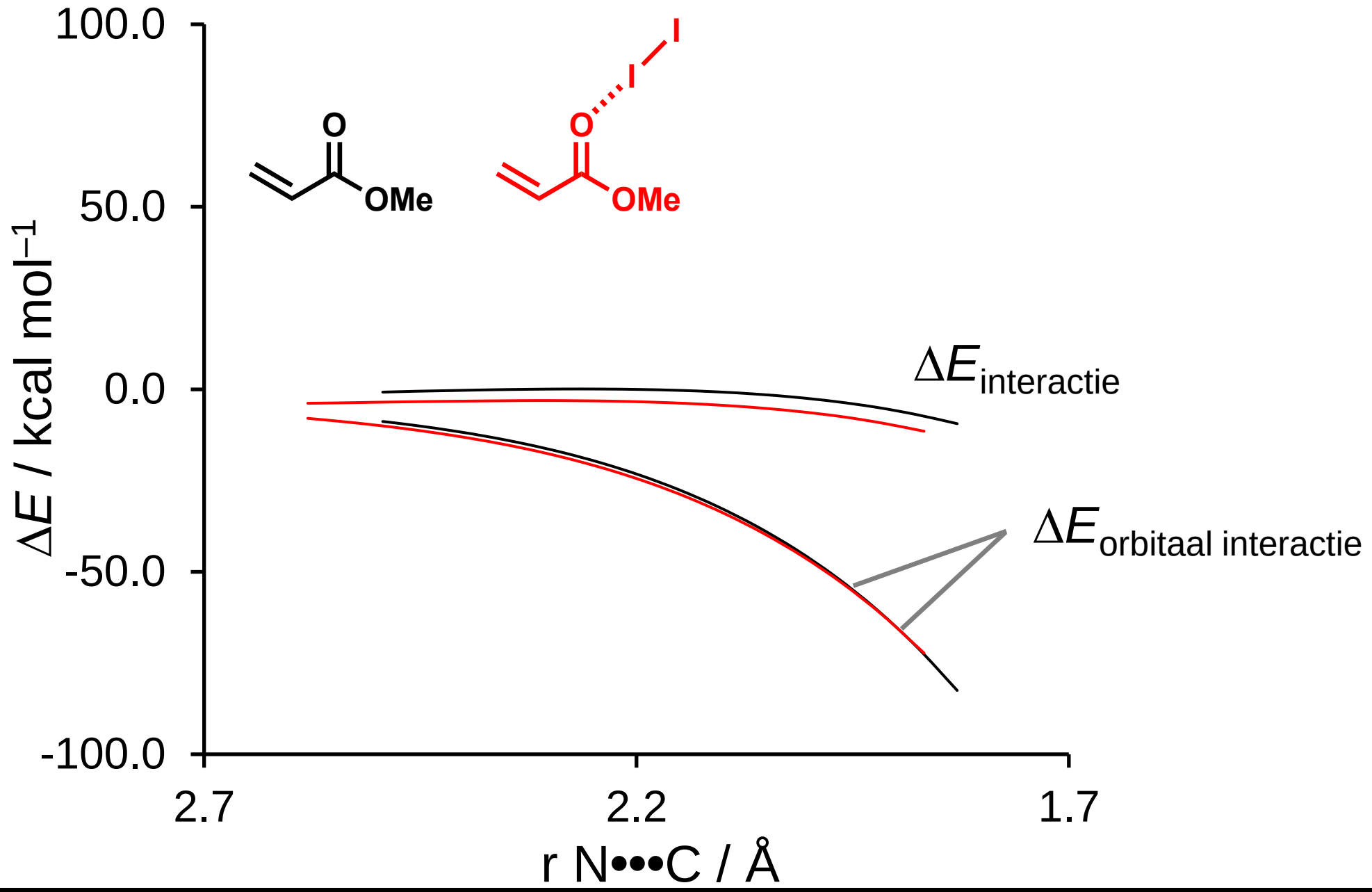

Angew. Chem. Int. Ed. **2019**, *58*, 8922–8926

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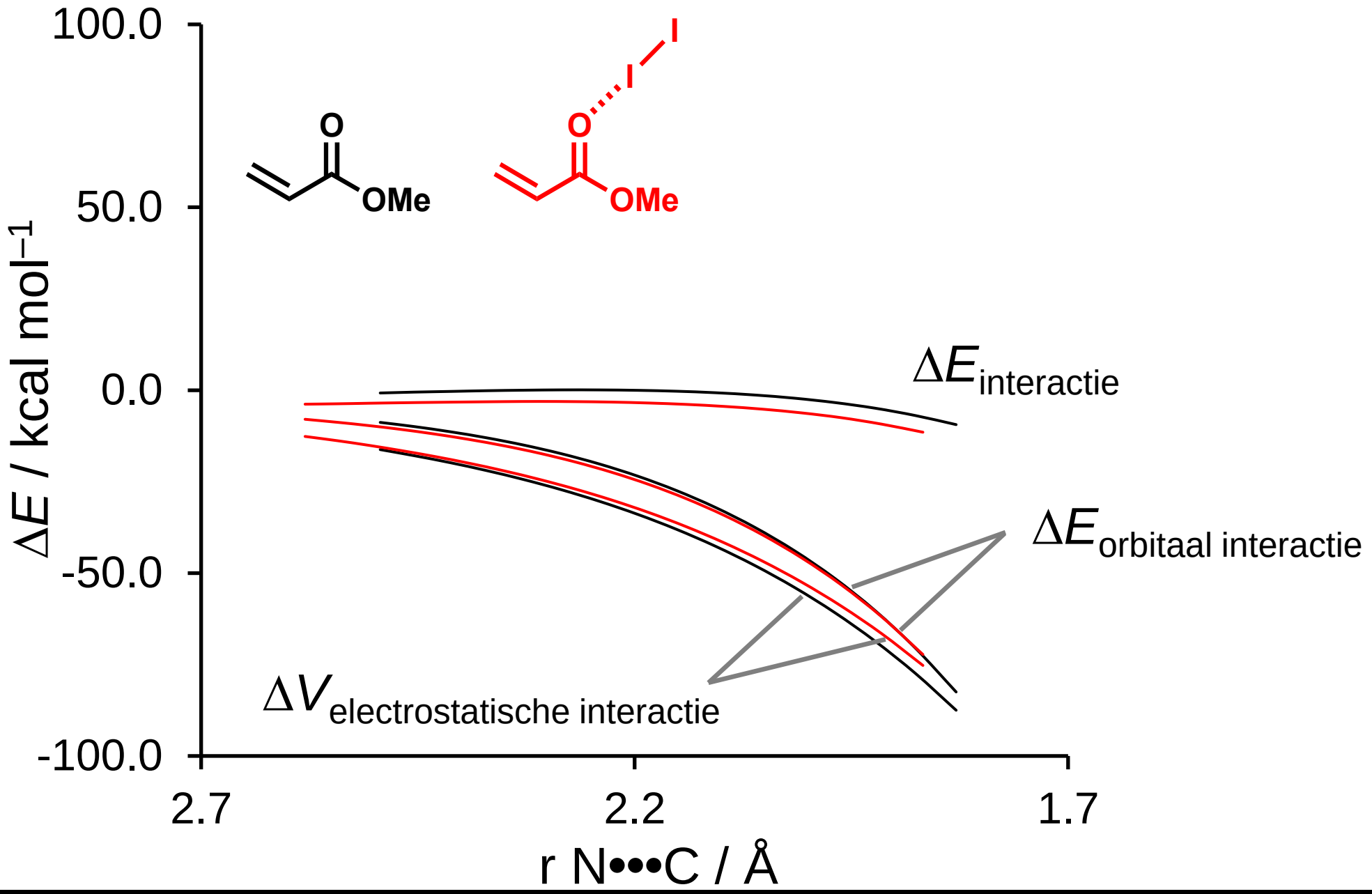

Angew. Chem. Int. Ed. **2019**, *58*, 8922–8926

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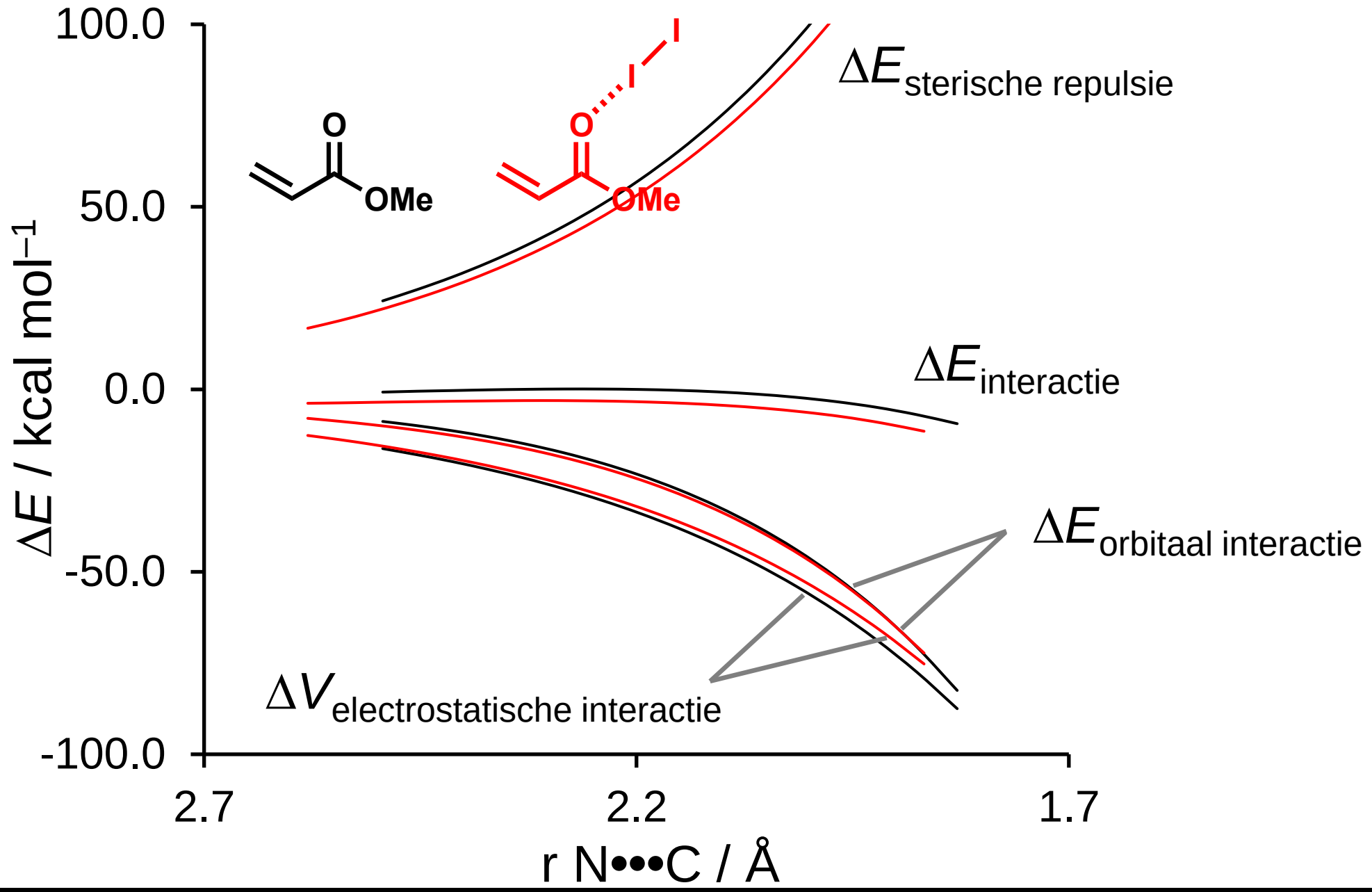
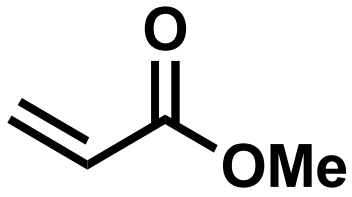
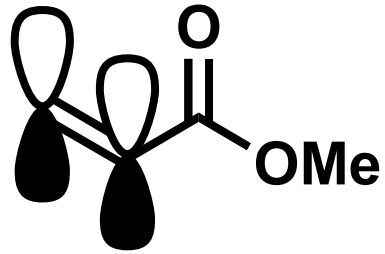


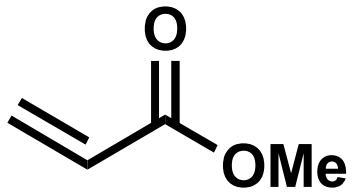
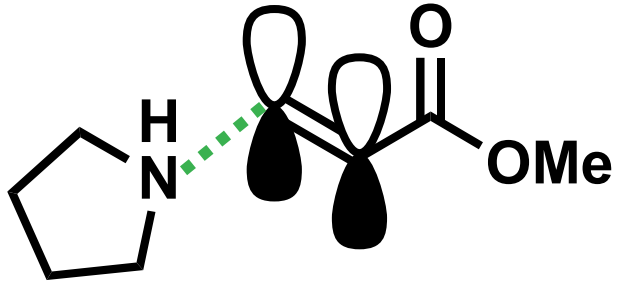
Angew. Chem. Int. Ed. **2019**, *58*, 8922–8926

ZORA-M06-2X/TZ2P//M06-2X/def2-TZVP

Sterische Pauli repulsie reductie katalyse

	structuur	schematisch orbitaal
zonder katalysator		

Sterische Pauli repulsie reductie katalyse

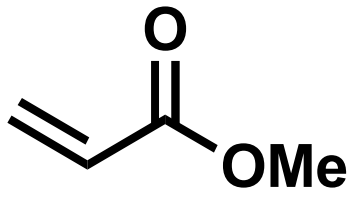
	structuur	schematisch orbitaal
zonder katalysator		

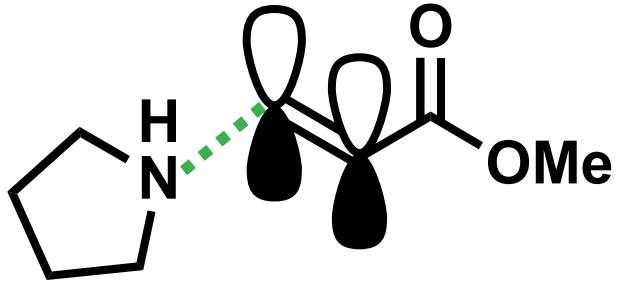
Sterische Pauli repulsie reductie katalyse

structuur

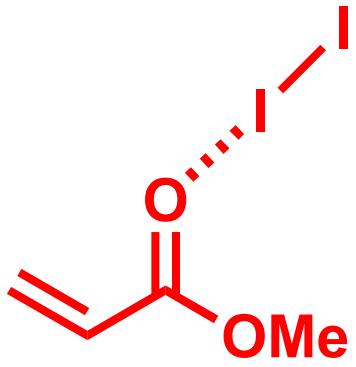
schematisch orbitaal

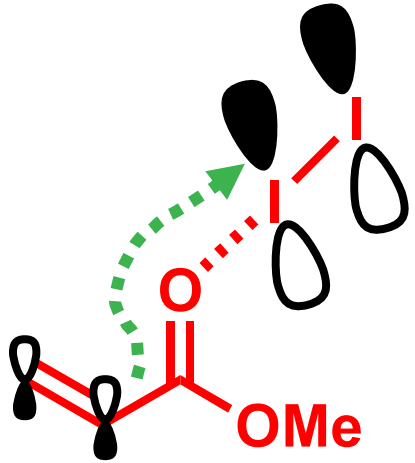
zonder katalysator



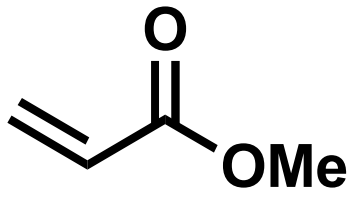
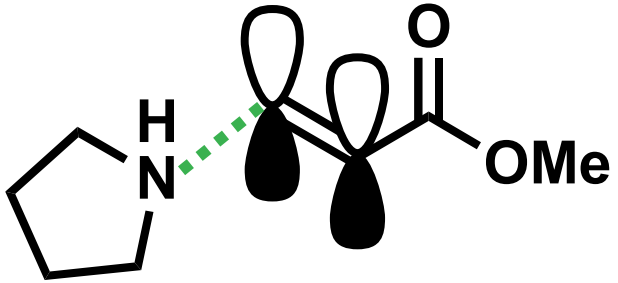
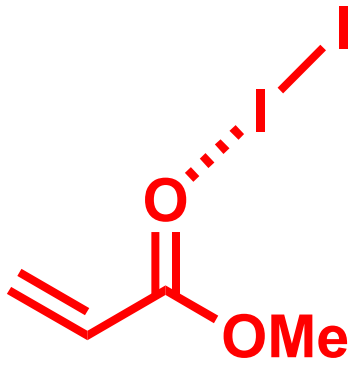
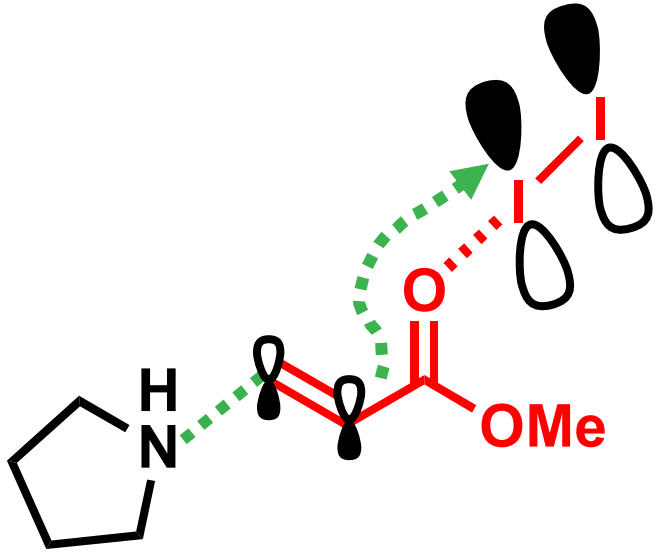


met katalysator
(I_2)

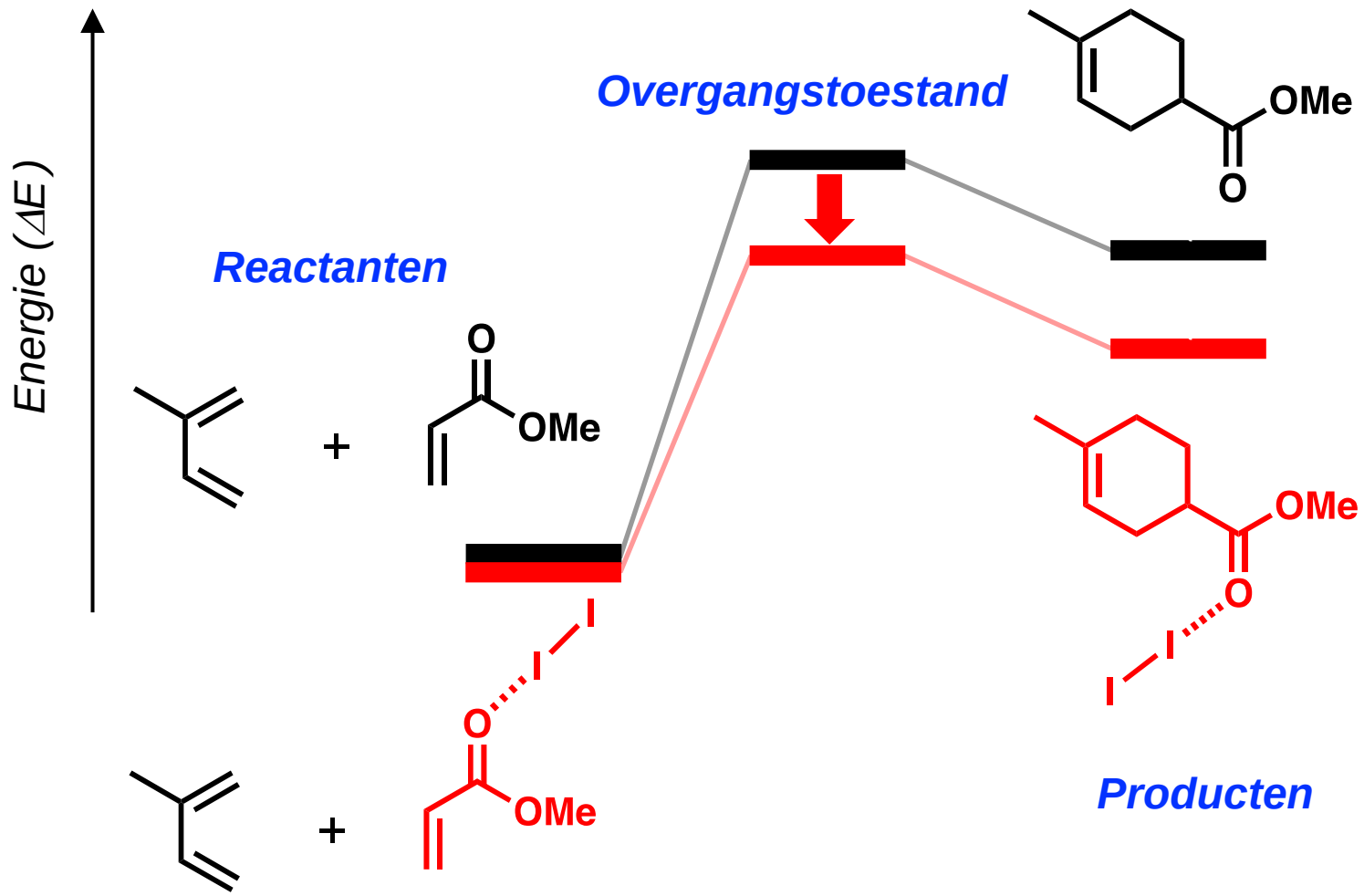




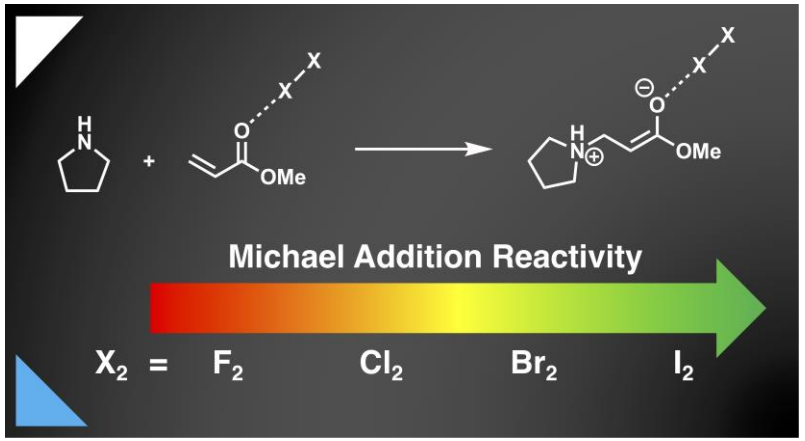
Sterische Pauli repulsie reductie katalyse

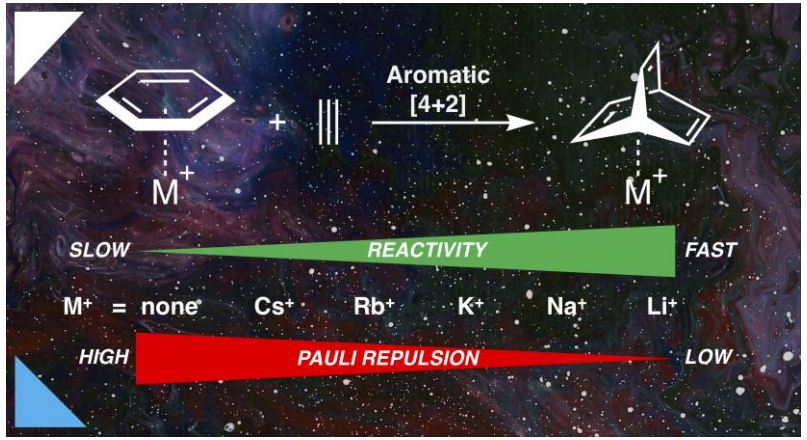
	structuur	schematisch orbitaal
zonder katalysator		
met katalysator (I_2)		

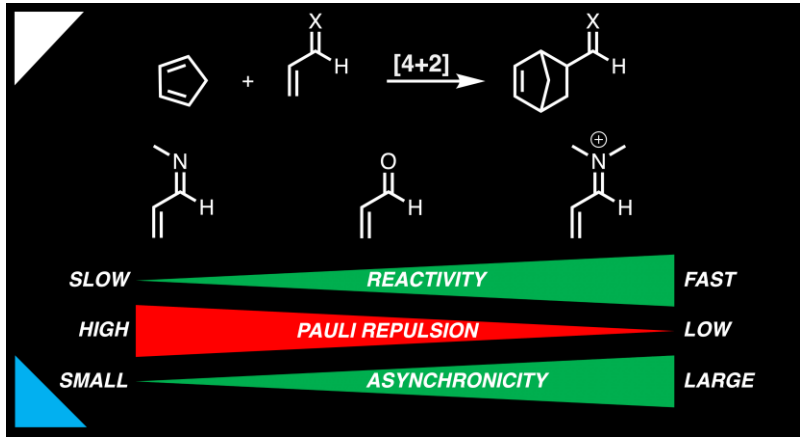
Gekatalyseerde Diels-Alder reactie

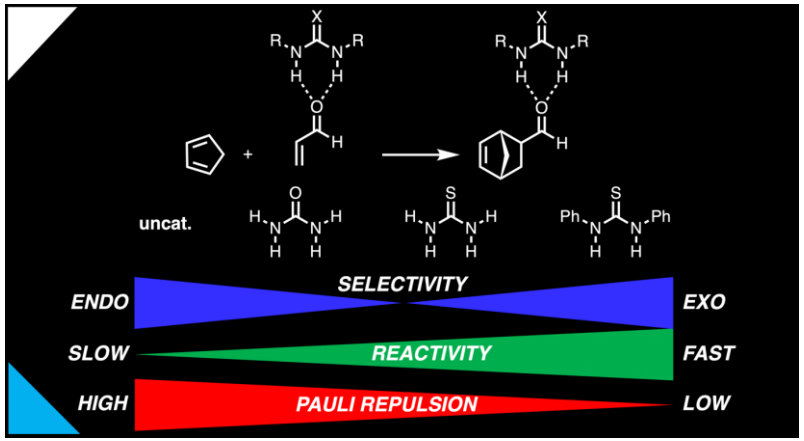


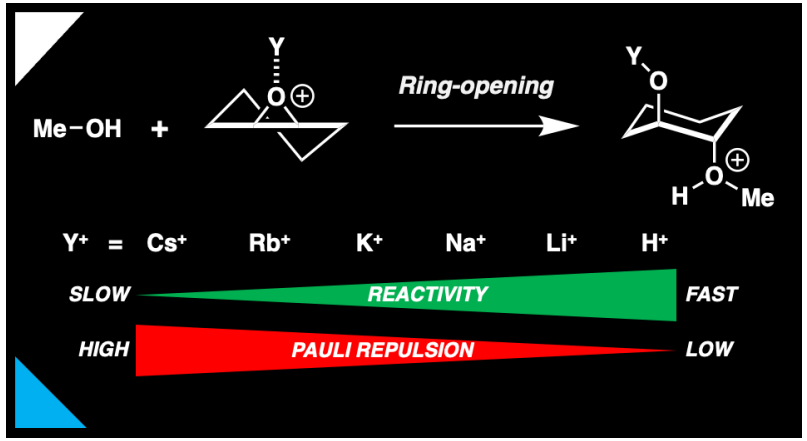
Katalyse van organische reacties is universeel

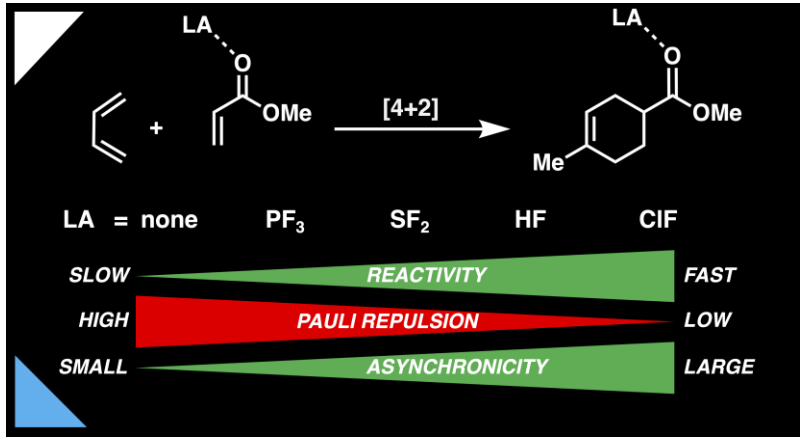












Maar hoe zouden we

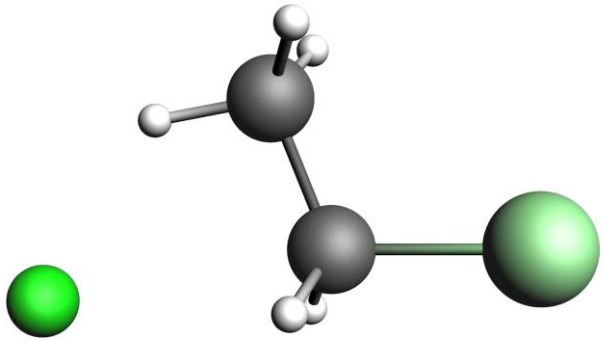
computationele chemie (modelleren)

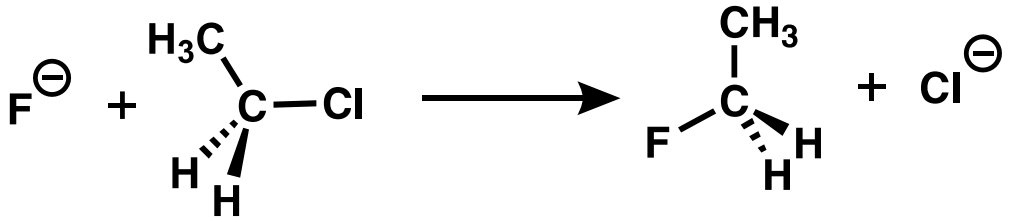
in het vo-onderwijs kunnen integreren?

Computationele chemie in het vo-onderwijs

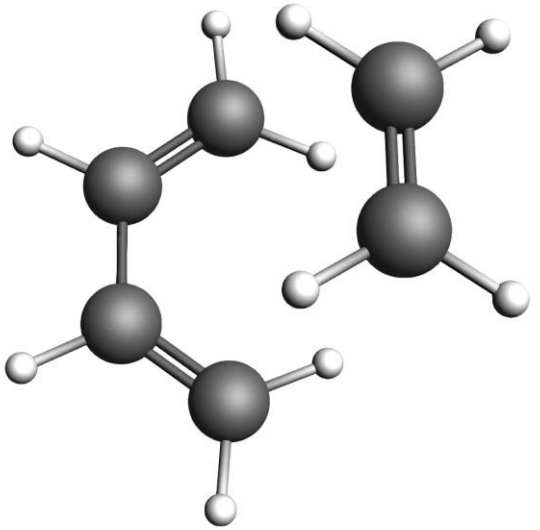
- Chemie nog meer visueel te maken!

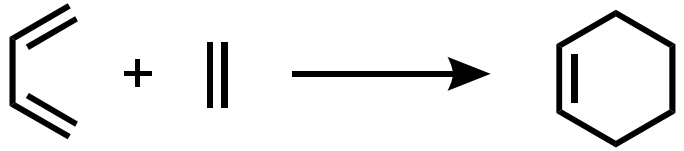
S_N2 reactie





Diels-Alder reactie

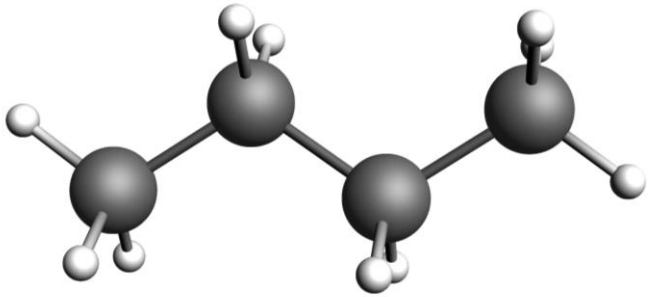


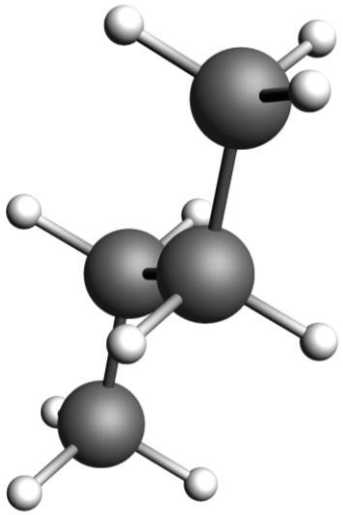


Computationele chemie in het vo-onderwijs

- Chemie nog meer visueel te maken!

Conformeren (Isomeren): Butaan C–C rotatie





Computationele chemie

admin — -zsh — 124×76

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lay_1snt+MD.png                         test15.png
2f12.cif                                    Applications                            Pictures
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2rj7.cif                                    Creative Cloud Files                    Public
lay_MD+MD-subs_without_subs.png         test3.png
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_atom_site.Cartn_x
_atom_site.Cartn_y
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_atom_site.pdbx_formal_charge
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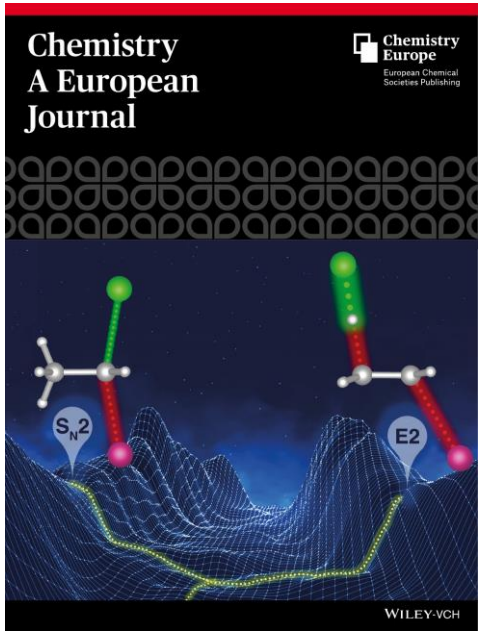
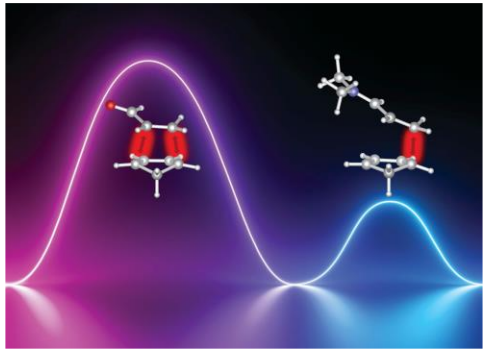
KNCV Webinar



TheoCheM

Molecular Theoretical Chemistry



Showcasing research from Professors Israel Fernández & F. Matthias Bickelhaupt's laboratories, Departamento de Química Orgánica I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Madrid (Spain) and Department of Theoretical Chemistry, Amsterdam Institute of Molecular and Life Sciences (AIMMS), Amsterdam Center for Multiscale Modeling (ACMM), Vrije Universiteit Amsterdam, Amsterdam (The Netherlands).

Origin of rate enhancement and asynchronicity in iminium catalyzed Diels–Alder reactions

In this work, we analyse the factors controlling the rate enhancement and asynchronicity of the so-called iminium-ion catalysis, For Diels–Alder reactions, it is found that the enhanced reactivity of the iminium-catalysed processes is exclusively caused by a markedly diminished Pauli repulsion between the π-systems of the reactants and not from enhanced orbital interactions. Therefore, contrary to the widely accepted *LUMO-lowering* mechanism, the *Pauli-repulsion lowering* constitutes the actual mechanism behind this mode of catalysis.

As featured in:

See T. A. Hamlin, I. Fernández, F. M. Bickelhaupt *et al.*, *Chem. Sci.*, 2020, **11**, 8105.

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