

Mechanistic Insights into the Cycloaddition of (2E,4E)-2,5-Dinitro-2,4-hexadiene with Diazomethane from Density Functional Theory

Karolina Kula, Radomir Jasiński

karolina.kula@pk.edu.pl

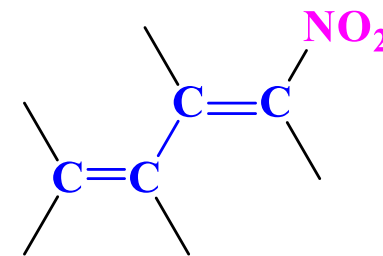


Cracow University of Technology
Faculty of Chemical Engineering
and Technology

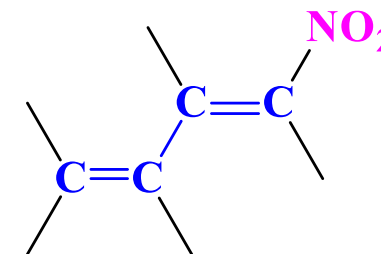


HPC Users' Conference

Zakopane, 13-15 April 2026



conjugated nitrodienes
(CND's)



conjugated nitrodienes
(**CND's**)

61 publications
(1961 → 65 years ago)

The importance of conjugated nitrodienes CND's

Contents lists available at GrowingScience

Current Chemistry Letters

homepage: www.GrowingScience.com

CHRONICLE

Article history:

Received March 25, 2023

Received in revised form

June 7, 2023

Accepted September 9, 2023

Available online

September 9, 2023

Keywords:

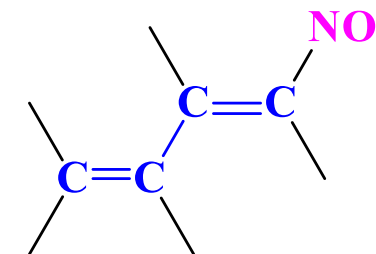
Nitrobutadiene

Synthesis

Spectral Characteristics

Chemical Transformation

Biological Activity



conjugated nitrodienes
(CND's)

Nitro-functionalized analogues of 1,3-Butadiene: An overview of characteristic, synthesis, chemical transformations and biological activity

Mikołaj Sadowski^a and Karolina Kula^{a*}

^aDepartment of Organic Chemistry and Technology, Cracow University of Technology, Warszawska 24, 31-155, Cracow, Poland

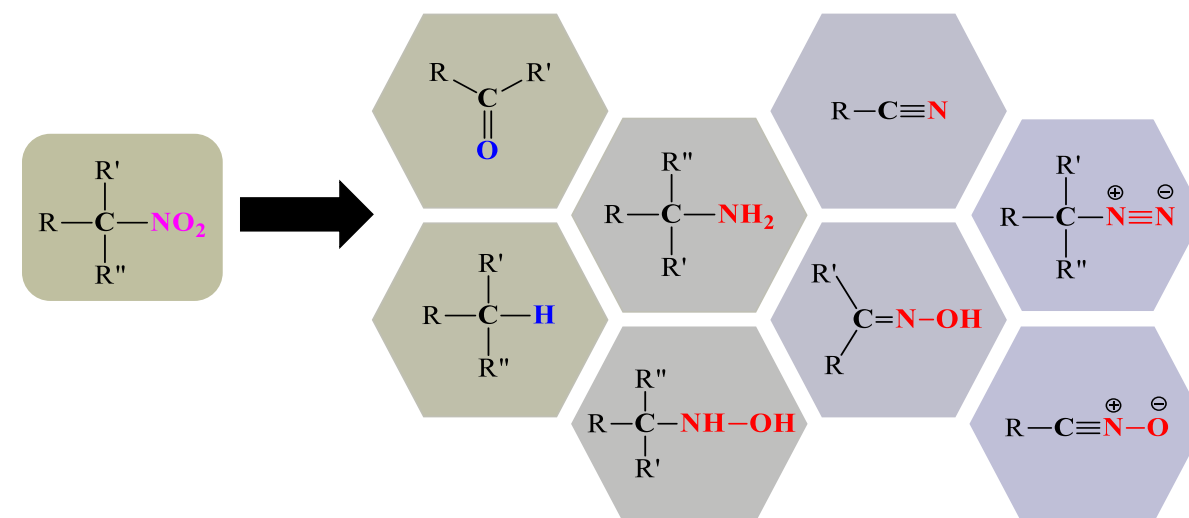
Sadowski M., Kula K.

Curr. Chem. Lett. **2023**

(DOI: 10.5267/j.ccl.2023.9.003)

61 publications

(1961 → 65 years ago)



The importance of conjugated nitrodienes CND's

Contents lists available at GrowingScience

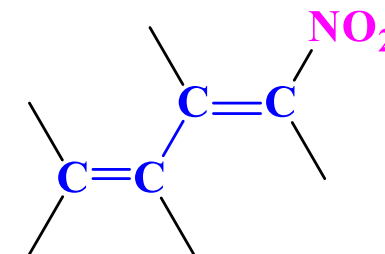
Current Chemistry Letters

homepage: www.GrowingScience.com

CHRONICLE

Article history:
 Received March 25, 2023
 Received in revised form
 June 7, 2023
 Accepted September 9, 2023
 Available online
 September 9, 2023

Keywords:
 Nitrobutadiene
 Synthesis
 Spectral Characteristics
 Chemical Transformation
 Biological Activity



conjugated nitrodienes
(CND's)

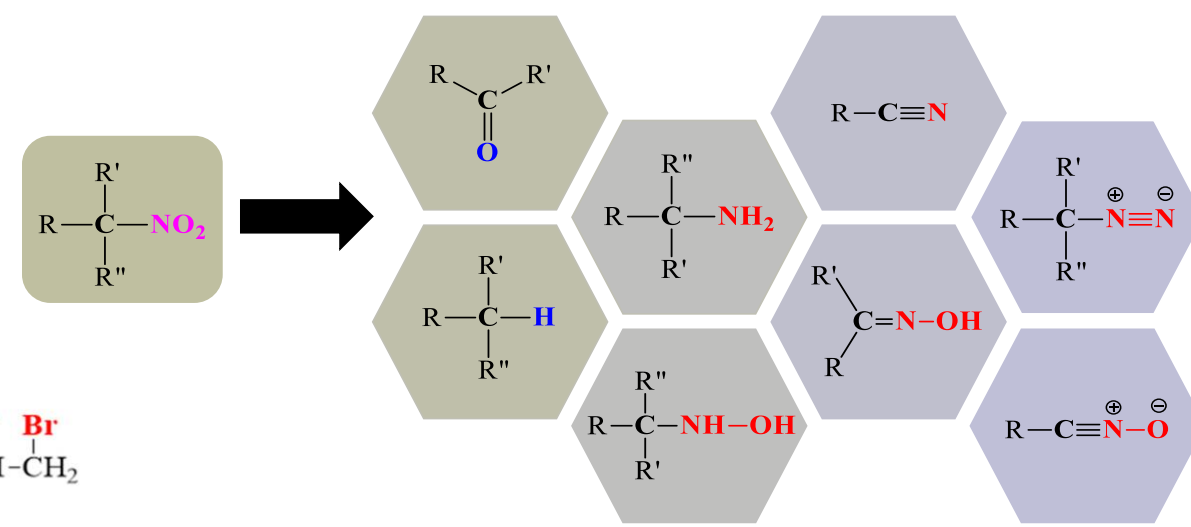
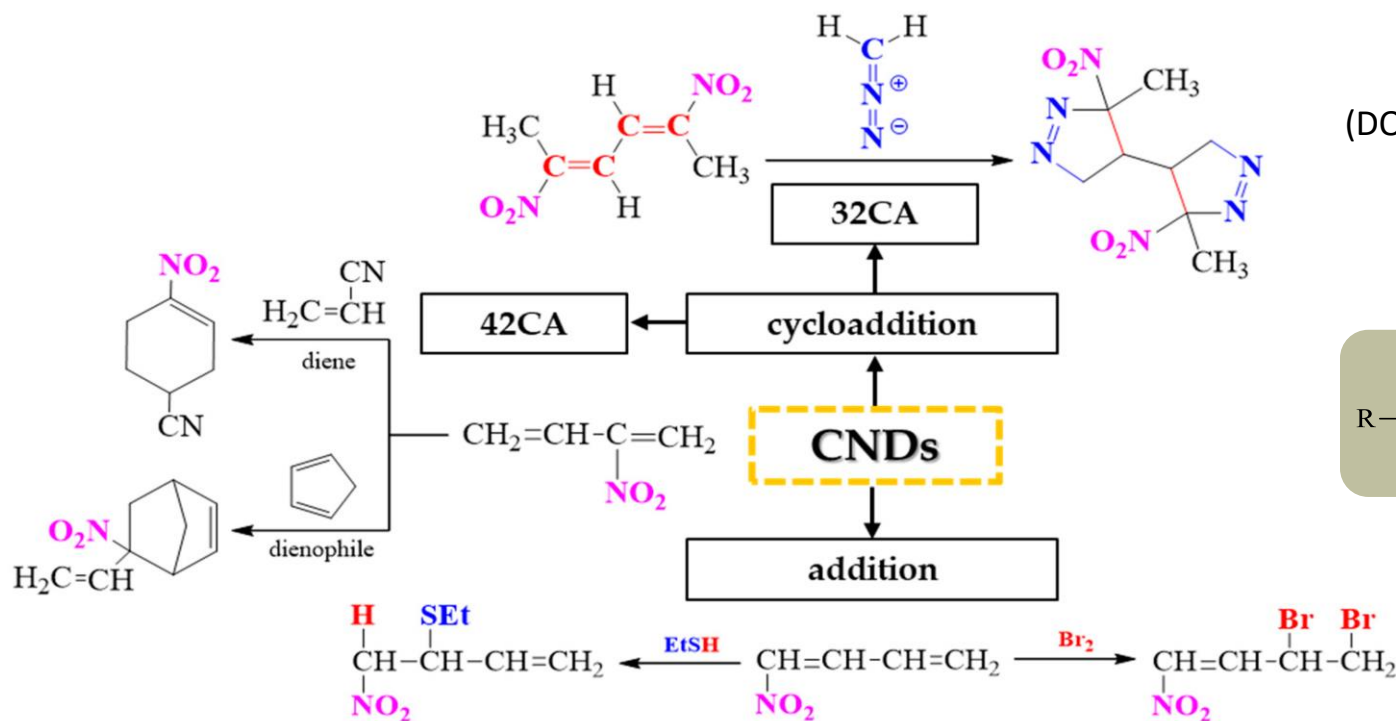
Nitro-functionalized analogues of 1,3-Butadiene: An overview of characteristic, synthesis, chemical transformations and biological activity

Mikołaj Sadowski^a and Karolina Kula^{a*}

^aDepartment of Organic Chemistry and Technology, Cracow University of Technology, Warszawska 24, 31-155, Cracow, Poland

Sadowski M., Kula K.
Curr. Chem. Lett. **2023**
 (DOI: 10.5267/j.ccl.2023.9.003)

61 publications
 (1961 → 65 years ago)





ELSEVIER

Contents lists available at [ScienceDirect](http://www.sciencedirect.com)

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Keywords:
4,4'-Bipyrazoles
Nitroolefins
Diazomethane
Dipolar cycloaddition
Crystal structures

Preparative synthesis of 3(5),3'(5')-dimethyl-4,4'-bipyrazole

Anastasiya V. Sharko^a, Ganna A. Senchyk^a, Eduard B. Rusanov^b, Konstantin V. Domasevitch^{a,*}



^a Inorganic Chemistry Department, National Taras Shevchenko University of Kyiv, Volodymyrska Street 64, Kyiv 01033, Ukraine

^b Institute of Organic Chemistry, Murmanska Str. 5, Kyiv 02660, Ukraine

ARTICLE INFO

Article history:

Received 8 July 2015

Revised 16 September 2015

Accepted 17 September 2015

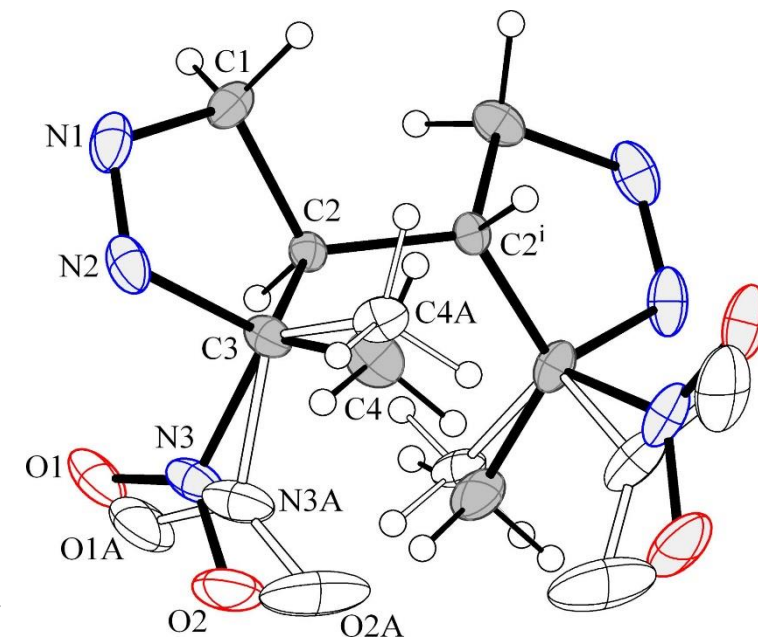
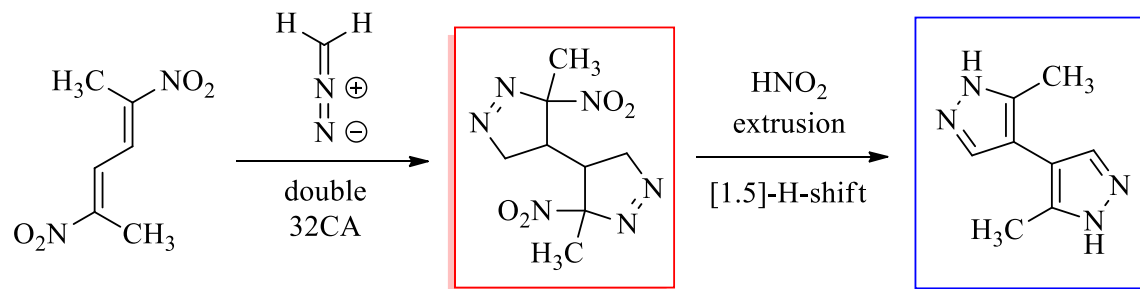
Available online 21 September 2015

Tetrahedron Letters 56 (2015) 6089–6092

ABSTRACT

An efficient, high-yielding preparative synthesis of 3(5),3'(5')-dimethyl-4,4'-bipyrazole, a new multi-purpose tecton for the supramolecular synthesis of metal–organic polymers and hydrogen-bonded frameworks, is described. Reactions include a double dipolar cycloaddition of diazomethane and 2,5-dinitro-2,4-hexadiene, followed by aromatization of isomeric bipyrazolines by alkali in aqueous methanol. Both *meso*- and *DL*-forms of the latter compounds were characterized by single crystal X-ray crystallography.

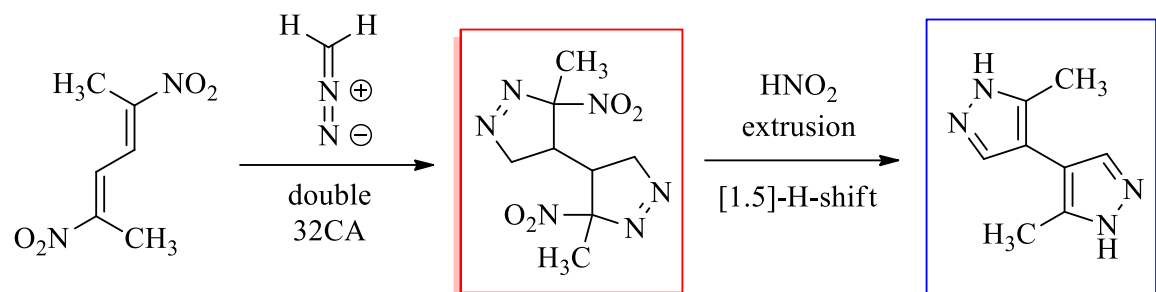
© 2015 Published by Elsevier Ltd.



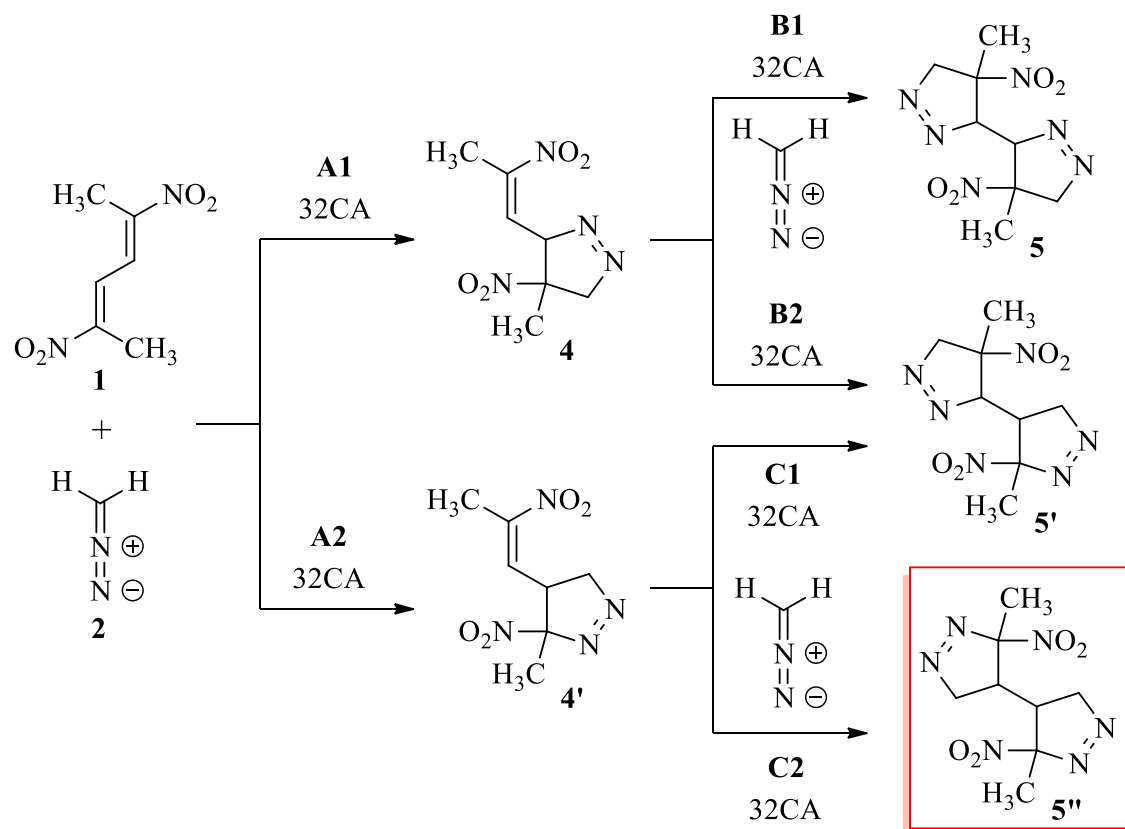
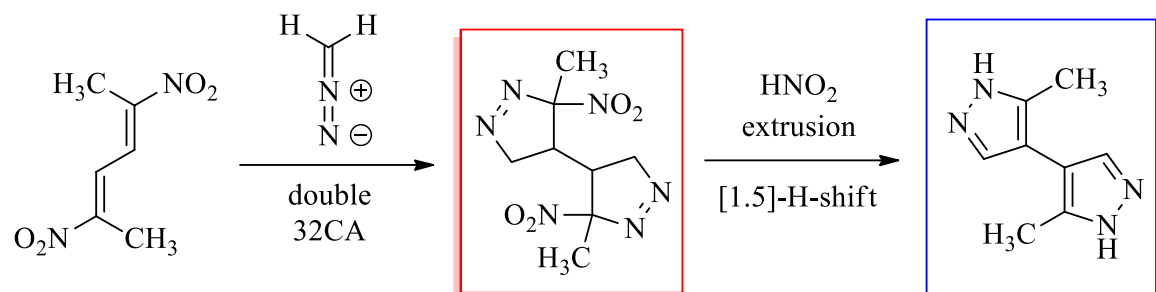
Molecular structures of isomeric bipyrazoline, adapted from Sharko *et al.*

Sharko A.V., Senchyk G.A.,
Rusanov E.B., Domasevitch K.V.*
Tetrahedron Lett. **2015**
(DOI: 10.1016/j.tetlet.2015.09.072)

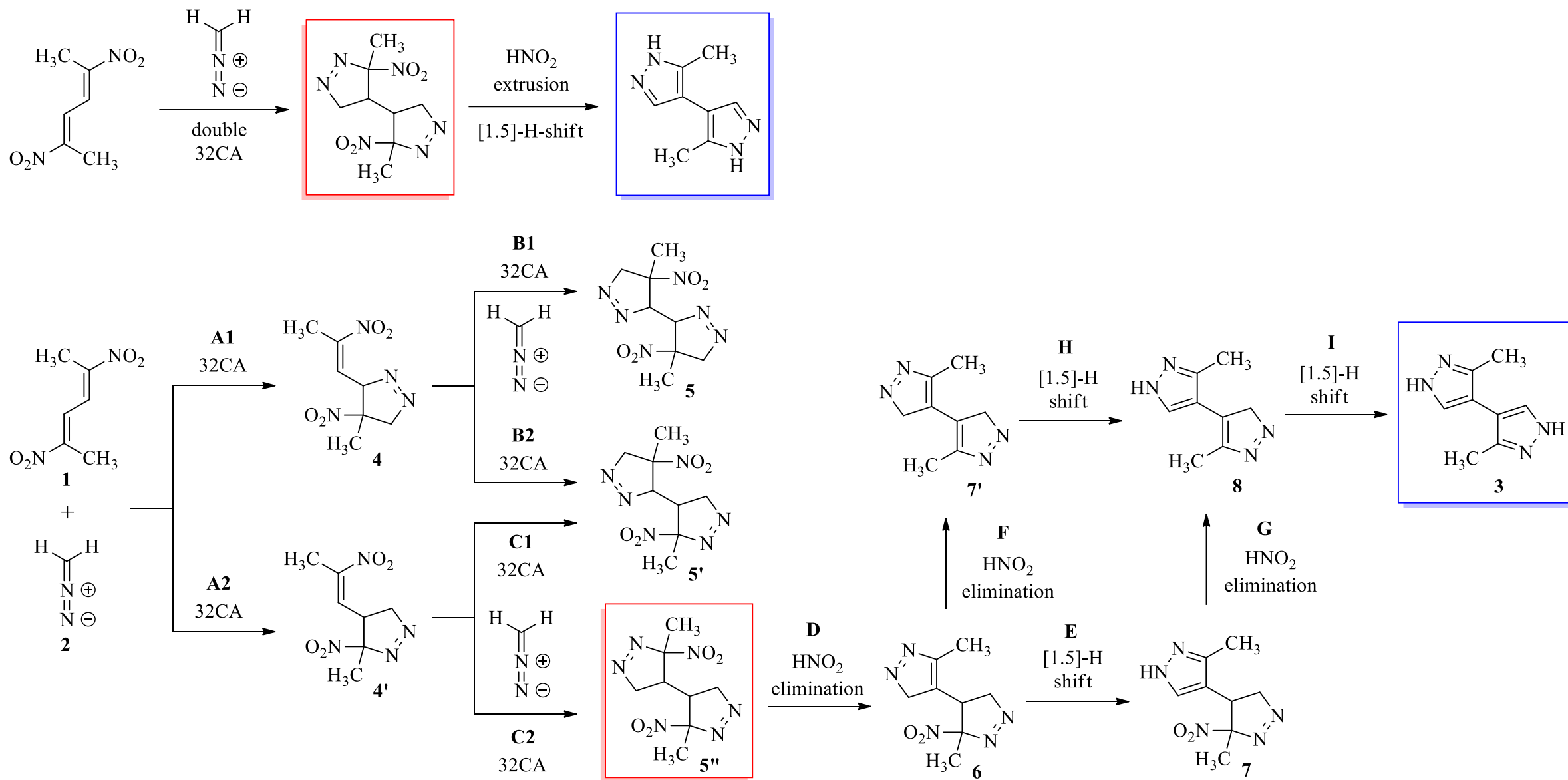
Possible Reaction Pathways: A Comprehensive Analysis



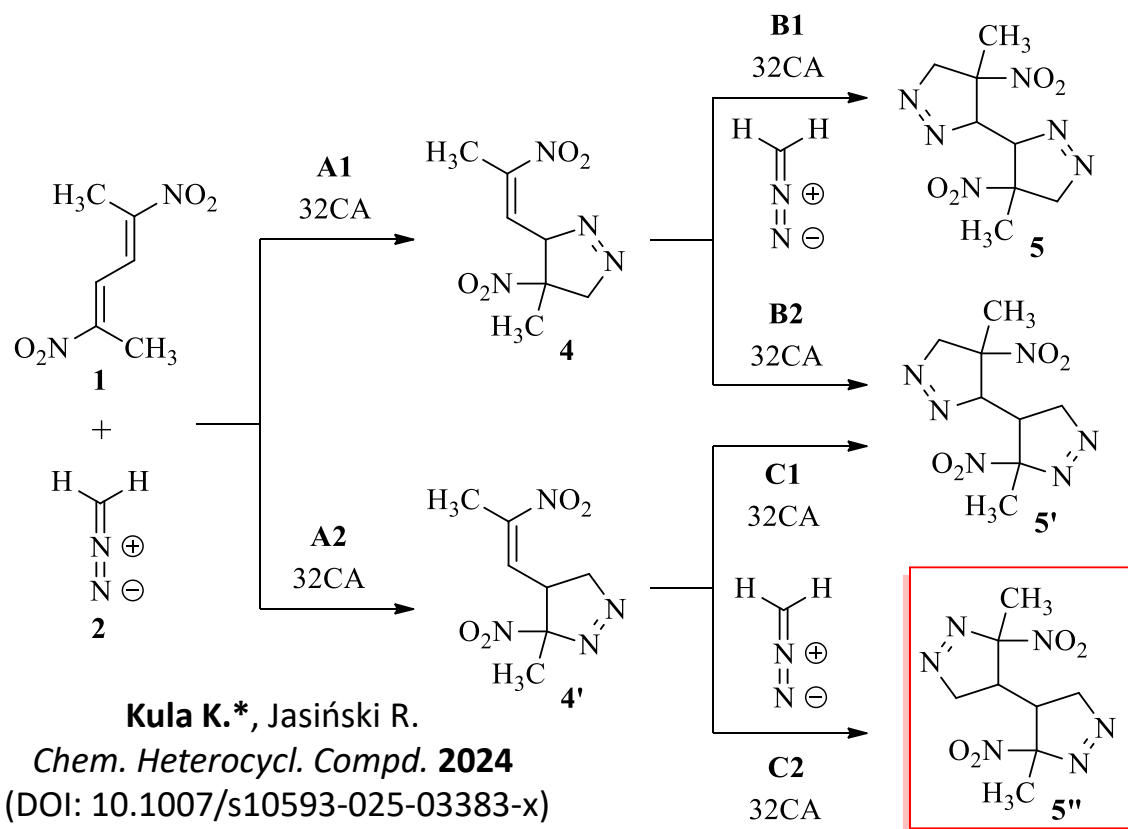
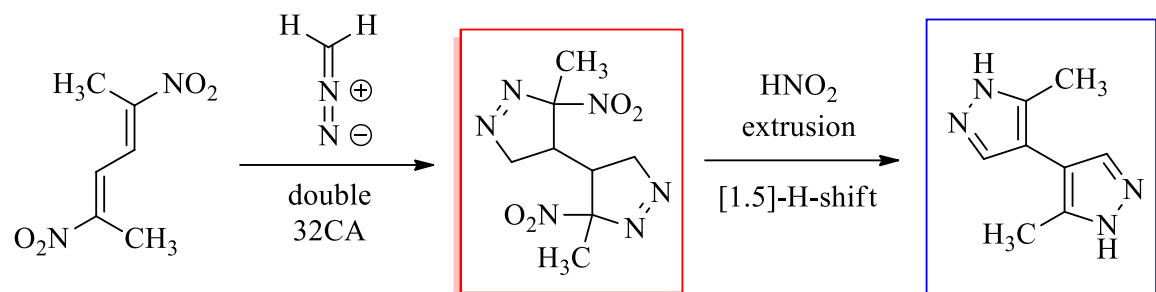
Possible Reaction Pathways: A Comprehensive Analysis



Possible Reaction Pathways: A Comprehensive Analysis



Possible Reaction Pathways: A Comprehensive Analysis



Kula K.*, Jasiński R.

Chem. Heterocycl. Compd. 2024

(DOI: 10.1007/s10593-025-03383-x)

Home > Chemistry of Heterocyclic Compounds > Article

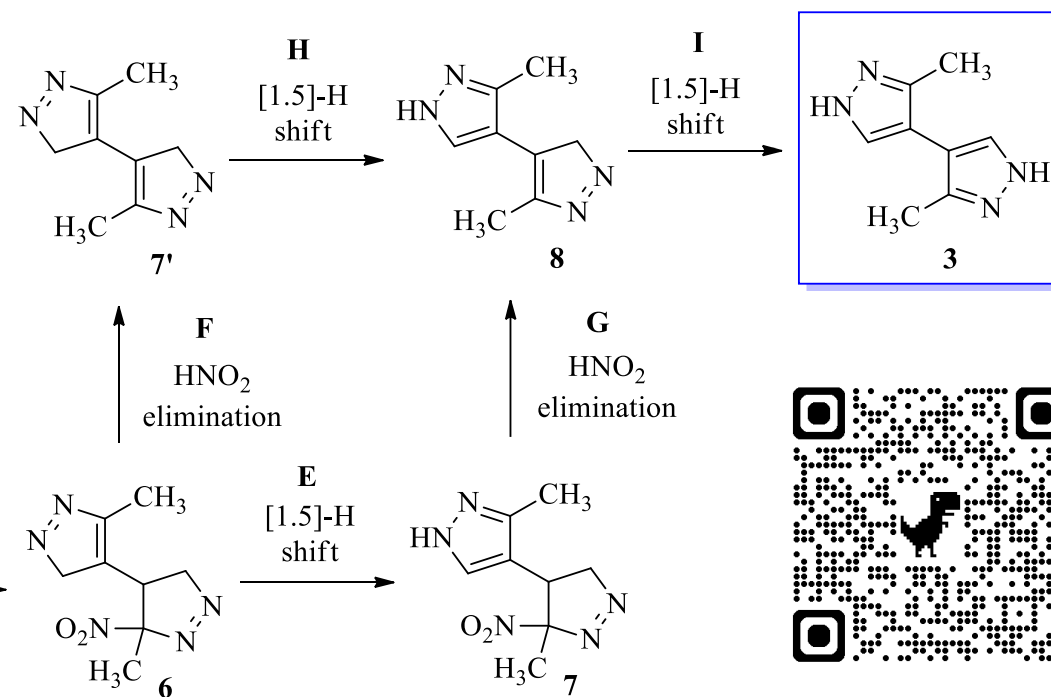
Synthesis of bis(het)aryl systems via domino reaction involving (2E,4E)-2,5-dinitrohexa-2,4-diene: DFT mechanistic considerations

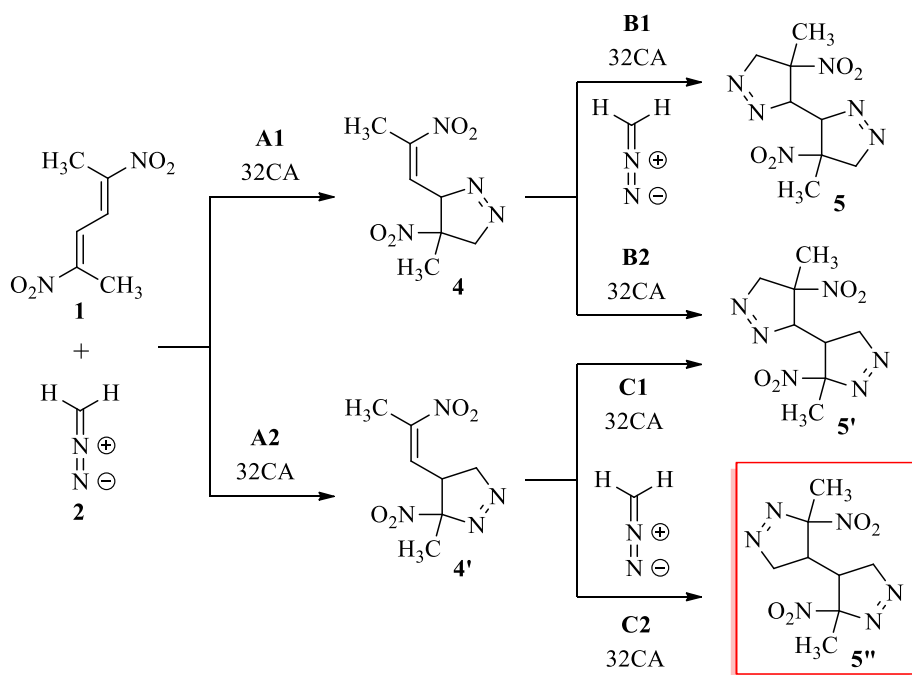
Published: 20 February 2025

Volume 60, pages 600–610, (2024) [Cite this article](#)

Karolina Kula ✉ & Radomir Jasiński

202 Accesses 17 Citations [Explore all metrics](#) →





Open Access Review

Applications of the Conceptual Density Functional Theory Indices to Organic Chemistry Reactivity

by Luis R. Domingo ^{1,*}, Mar Ríos-Gutiérrez ¹ and Patricia Pérez ²

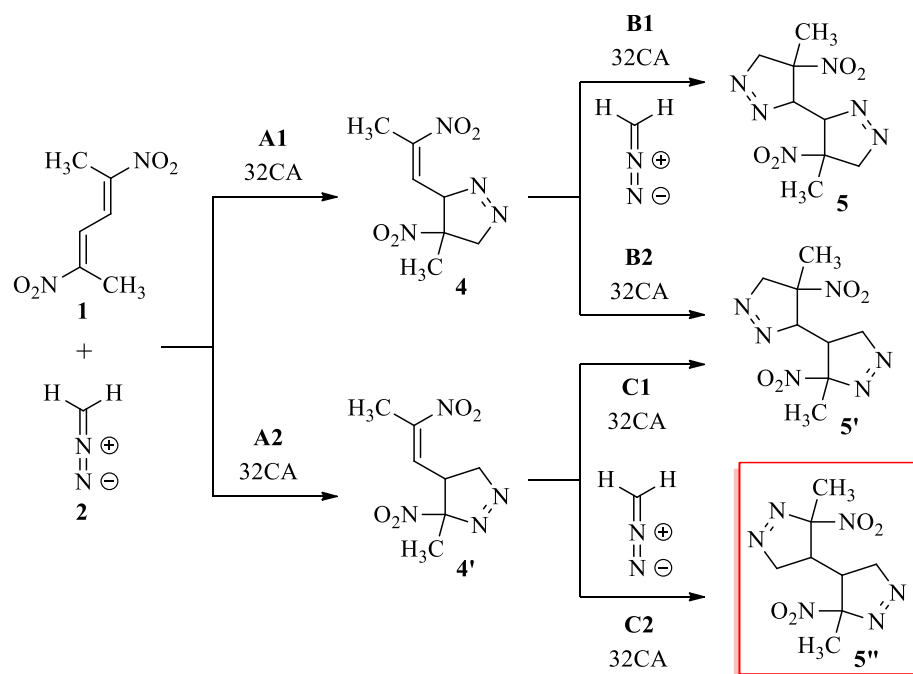
¹ Department of Organic Chemistry, University of Valencia, Dr. Moliner 50, E-46100 Burjassot, Valencia, Spain

² Facultad de Ciencias Exactas, Departamento de Ciencias Químicas, Universidad Andres Bello, Av. República 498, 8370146 Santiago, Chile

* Author to whom correspondence should be addressed.

Molecules **2016**, *21*(6), 748; <https://doi.org/10.3390/molecules21060748>

Submission received: 12 May 2016 / Revised: 1 June 2016 / Accepted: 2 June 2016 / Published: 9 June 2016



Open Access Review

Applications of the Conceptual Density Functional Theory Indices to Organic Chemistry Reactivity

by Luis R. Domingo ^{1,*}, Mar Ríos-Gutiérrez ¹ and Patricia Pérez ²

¹ Department of Organic Chemistry, University of Valencia, Dr. Moliner 50, E-46100 Burjassot, Valencia, Spain

² Facultad de Ciencias Exactas, Departamento de Ciencias Químicas, Universidad Andres Bello, Av. República 498, 8370146 Santiago, Chile

* Author to whom correspondence should be addressed.

Molecules **2016**, *21*(6), 748; <https://doi.org/10.3390/molecules21060748>

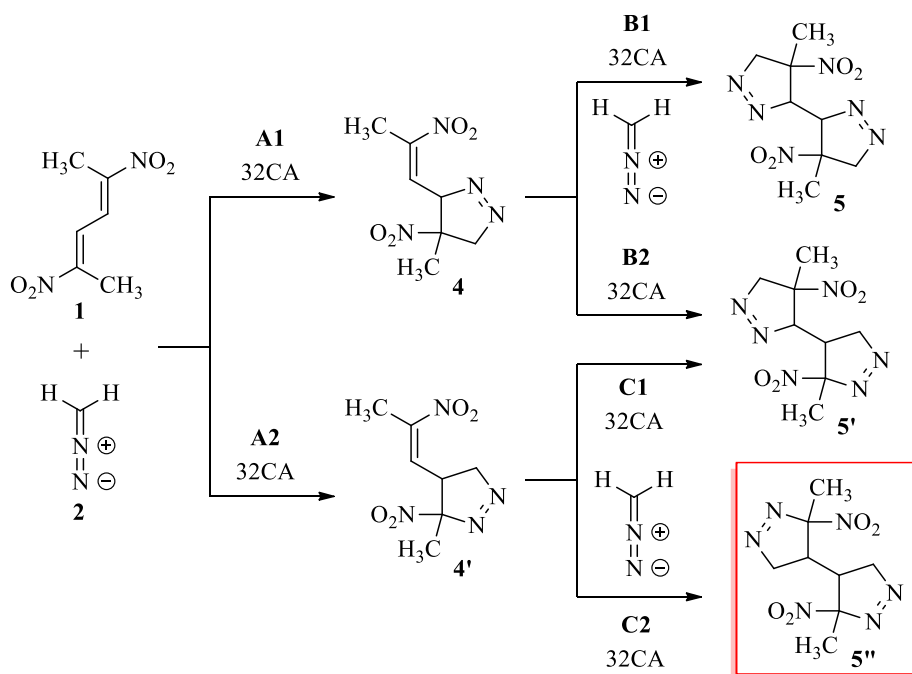
Submission received: 12 May 2016 / Revised: 1 June 2016 / Accepted: 2 June 2016 / Published: 9 June 2016

$$\mu \approx \frac{1}{2} \cdot (E_{\text{HOMO}} + E_{\text{LUMO}})$$

$$\omega = \mu^2 / 2 \cdot \eta$$

$$\eta \approx E_{\text{LUMO}} - E_{\text{HOMO}}$$

$$N = E_{\text{HOMO}} - E_{\text{HOMO (TCE)}}$$



Open Access Review

Applications of the Conceptual Density Functional Theory Indices to Organic Chemistry Reactivity

by Luis R. Domingo ^{1,*}, Mar Ríos-Gutiérrez ¹ and Patricia Pérez ²

¹ Department of Organic Chemistry, University of Valencia, Dr. Moliner 50, E-46100 Burjassot, Valencia, Spain

² Facultad de Ciencias Exactas, Departamento de Ciencias Químicas, Universidad Andres Bello, Av. República 498, 8370146 Santiago, Chile

* Author to whom correspondence should be addressed.

Molecules **2016**, *21*(6), 748; <https://doi.org/10.3390/molecules21060748>

Submission received: 12 May 2016 / Revised: 1 June 2016 / Accepted: 2 June 2016 / Published: 9 June 2016

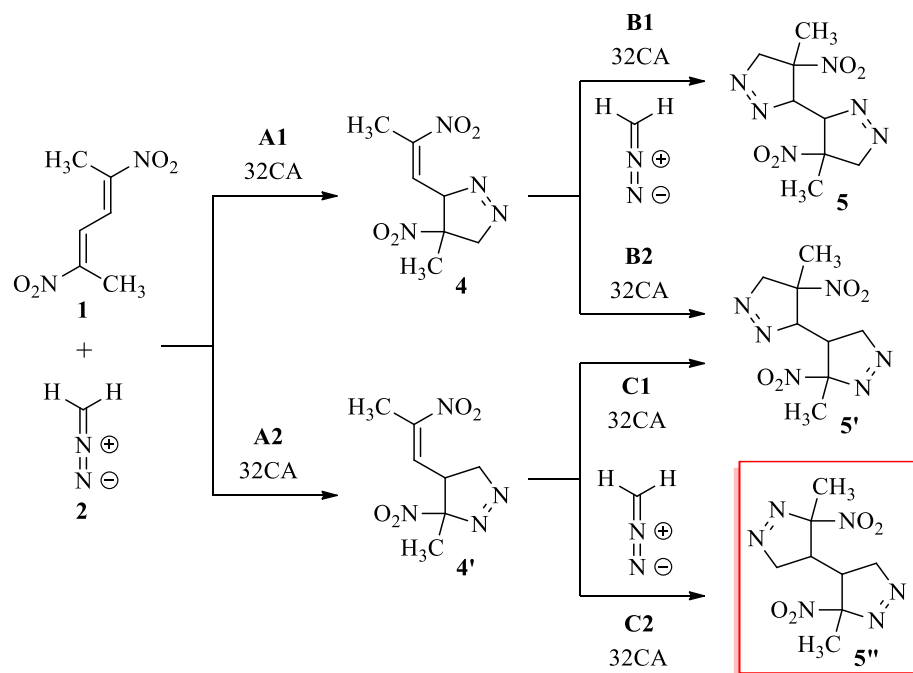
$$\mu \approx \frac{1}{2} \cdot (E_{\text{HOMO}} + E_{\text{LUMO}})$$

$$\omega = \mu^2 / 2 \cdot \eta$$

$$\eta \approx E_{\text{LUMO}} - E_{\text{HOMO}}$$

$$N = E_{\text{HOMO}} - E_{\text{HOMO (TCE)}}$$

b3lyp/6-31g(d) / gas phase



Origin of Nitropyrazoline Formation *via* 32CA: A CDFT Study

Open Access Review

Applications of the Conceptual Density Functional Theory Indices to Organic Chemistry Reactivity

by Luis R. Domingo ^{1,*}, Mar Ríos-Gutiérrez ¹ and Patricia Pérez ²

¹ Department of Organic Chemistry, University of Valencia, Dr. Moliner 50, E-46100 Burjassot, Valencia, Spain

² Facultad de Ciencias Exactas, Departamento de Ciencias Químicas, Universidad Andres Bello, Av. República 498, 8370146 Santiago, Chile

* Author to whom correspondence should be addressed.

Molecules **2016**, *21*(6), 748; <https://doi.org/10.3390/molecules21060748>

Submission received: 12 May 2016 / Revised: 1 June 2016 / Accepted: 2 June 2016 / Published: 9 June 2016

$$\mu \approx \frac{1}{2} \cdot (E_{\text{HOMO}} + E_{\text{LUMO}})$$

$$\omega = \frac{\mu^2}{2 \cdot \eta}$$

$$\eta \approx E_{\text{LUMO}} - E_{\text{HOMO}}$$

$$N = E_{\text{HOMO}} - E_{\text{HOMO (TCE)}}$$

ELECTROPHILE

b3lyp/6-31g(d) / gas phase

NUCLEOPHILE

Marginal

Moderate

Strong

Marginal

Moderate

Strong

$0.8 > \omega$

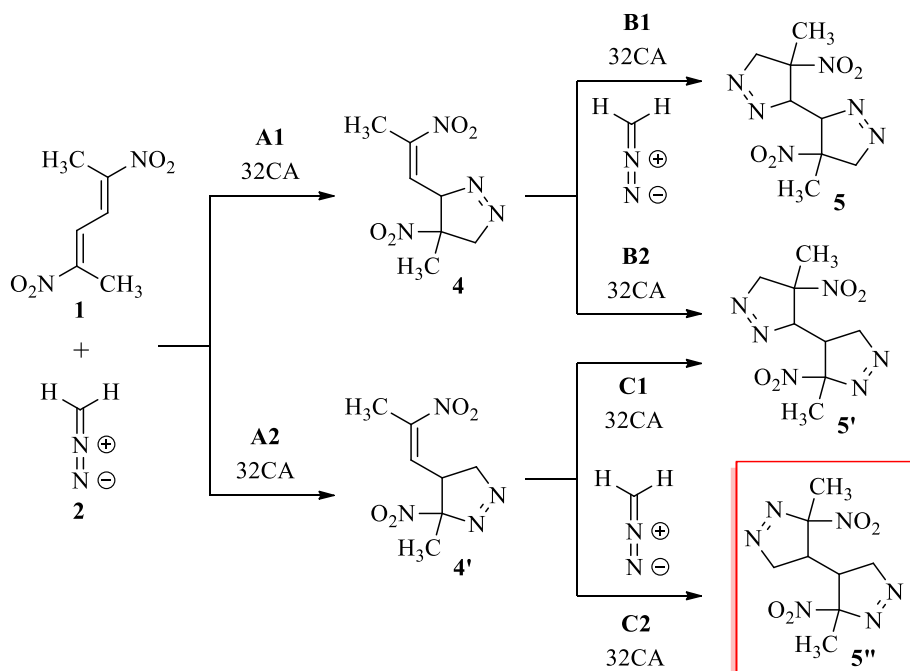
$0.8 < \omega < 1.5$

$\omega \geq 1.5$

$2.0 > N$

$2.0 < N < 3.0$

$N \geq 3.0$



Origin of Nitropyrazoline Formation *via* 32CA: A CDFT Study

Open Access Review

Applications of the Conceptual Density Functional Theory Indices to Organic Chemistry Reactivity

by Luis R. Domingo ^{1,*}, Mar Ríos-Gutiérrez ¹ and Patricia Pérez ²

¹ Department of Organic Chemistry, University of Valencia, Dr. Moliner 50, E-46100 Burjassot, Valencia, Spain

² Facultad de Ciencias Exactas, Departamento de Ciencias Químicas, Universidad Andres Bello, Av. República 498, 8370146 Santiago, Chile

* Author to whom correspondence should be addressed.

Molecules 2016, 21(6), 748; <https://doi.org/10.3390/molecules21060748>

Submission received: 12 May 2016 / Revised: 1 June 2016 / Accepted: 2 June 2016 / Published: 9 June 2016

$$\mu \approx \frac{1}{2} \cdot (E_{\text{HOMO}} + E_{\text{LUMO}})$$

$$\omega = \frac{\mu^2}{2 \cdot \eta}$$

$$\eta \approx E_{\text{LUMO}} - E_{\text{HOMO}}$$

$$N = E_{\text{HOMO}} - E_{\text{HOMO (TCE)}}$$

ELECTROPHILE

b3lyp/6-31g(d) / gas phase

NUCLEOPHILE

Marginal

Moderate

Strong

Marginal

Moderate

Strong

$0.8 > \omega$

$0.8 < \omega < 1.5$

$\omega \geq 1.5$

$2.0 > N$

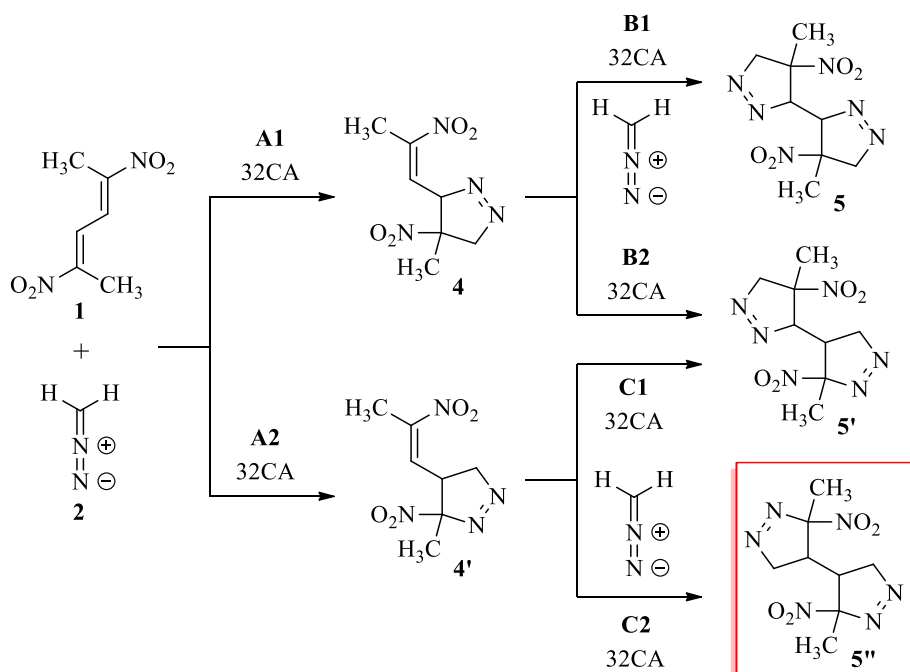
$2.0 < N < 3.0$

$N \geq 3.0$

polar/non-polar

$$\Delta\omega = \omega_{\text{El.}} - \omega_{\text{Nu.}}$$

$$\Delta\omega \geq 1 \text{ eV}$$



Origin of Nitropyrazoline Formation *via* 32CA: A CDFT Study

Open Access Review

Applications of the Conceptual Density Functional Theory Indices to Organic Chemistry Reactivity

by Luis R. Domingo ^{1,*}, Mar Ríos-Gutiérrez ¹ and Patricia Pérez ²

¹ Department of Organic Chemistry, University of Valencia, Dr. Moliner 50, E-46100 Burjassot, Valencia, Spain

² Facultad de Ciencias Exactas, Departamento de Ciencias Químicas, Universidad Andres Bello, Av. República 498, 8370146 Santiago, Chile

* Author to whom correspondence should be addressed.

Molecules **2016**, *21*(6), 748; <https://doi.org/10.3390/molecules21060748>

Submission received: 12 May 2016 / Revised: 1 June 2016 / Accepted: 2 June 2016 / Published: 9 June 2016

$$\mu \approx \frac{1}{2} \cdot (E_{\text{HOMO}} + E_{\text{LUMO}})$$

$$\omega = \mu^2 / 2 \cdot \eta$$

$$\eta \approx E_{\text{LUMO}} - E_{\text{HOMO}}$$

$$N = E_{\text{HOMO}} - E_{\text{HOMO}}(\text{TCE})$$

ELECTROPHILE

Marginal

$$0.8 > \omega$$

Moderate

$$0.8 < \omega < 1.5$$

Strong

$$\omega \geq 1.5$$

b3lyp/6-31g(d) / gas phase

Marginal

$$2.0 > N$$

Moderate

$$2.0 < N < 3.0$$

Strong

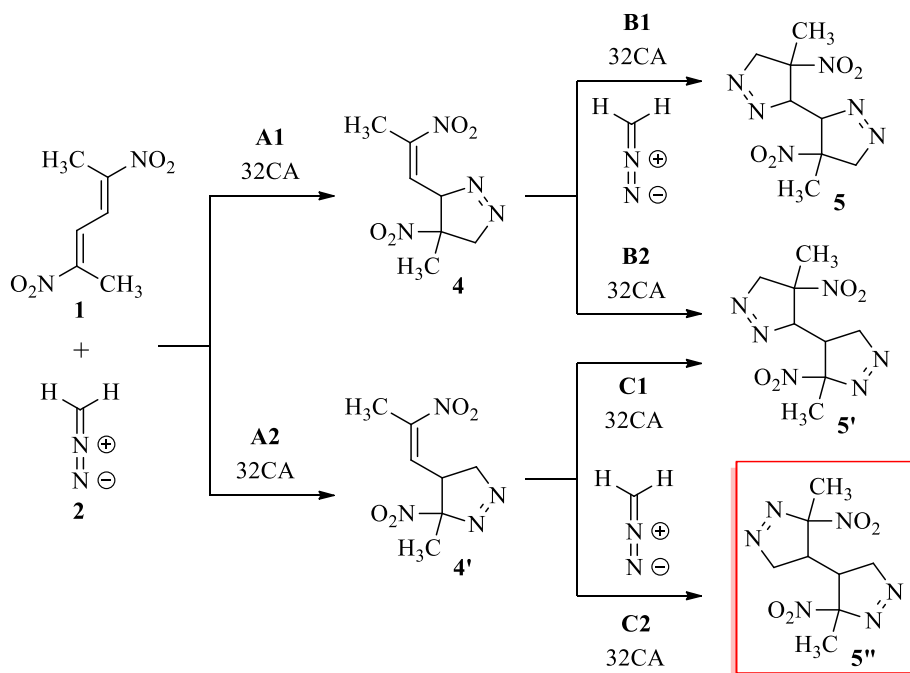
$$N \geq 3.0$$

polar/non-polar

$$\Delta\omega = \omega_{\text{El.}} - \omega_{\text{Nu.}}$$

$$\Delta\omega \geq 1 \text{ eV}$$

molecule	μ [eV]	η [eV]	ω [eV]	N [eV]
1	-5.55	4.01	3.84	1.57
2	-3.64	4.73	1.41	3.11
4	-5.22	4.45	3.07	1.67
4'	-5.28	4.43	3.15	1.63



Origin of Nitropyrazoline Formation *via* 32CA: A CDFT Study

Open Access Review

Applications of the Conceptual Density Functional Theory Indices to Organic Chemistry Reactivity

by Luis R. Domingo ^{1,*}, Mar Ríos-Gutiérrez ¹ and Patricia Pérez ²

¹ Department of Organic Chemistry, University of Valencia, Dr. Moliner 50, E-46100 Burjassot, Valencia, Spain

² Facultad de Ciencias Exactas, Departamento de Ciencias Químicas, Universidad Andres Bello, Av. República 498, 8370146 Santiago, Chile

* Author to whom correspondence should be addressed.

Molecules 2016, 21(6), 748; <https://doi.org/10.3390/molecules21060748>

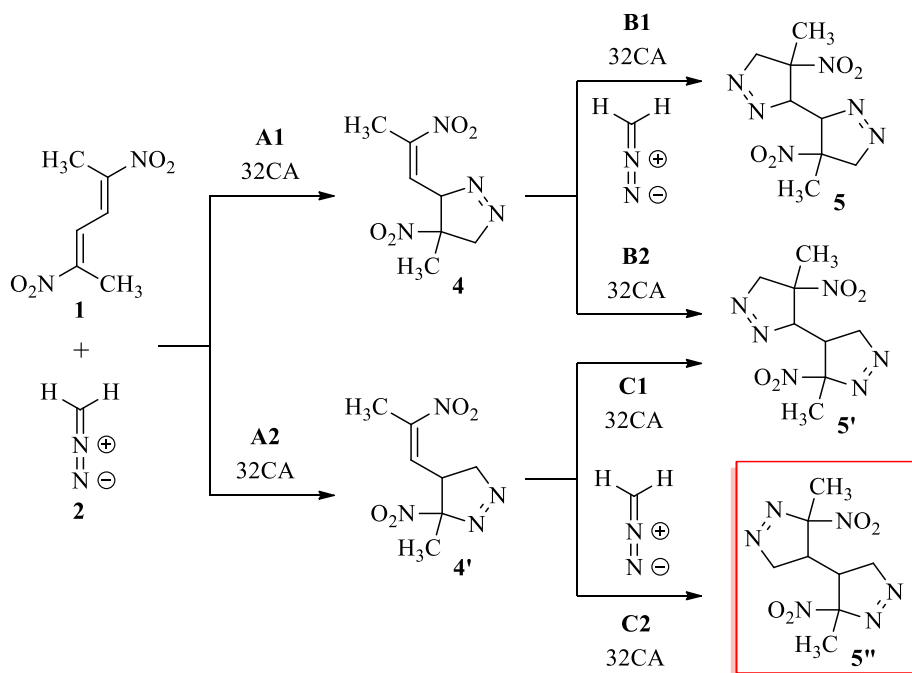
Submission received: 12 May 2016 / Revised: 1 June 2016 / Accepted: 2 June 2016 / Published: 9 June 2016

$$\mu \approx \frac{1}{2} \cdot (E_{\text{HOMO}} + E_{\text{LUMO}})$$

$$\omega = \frac{\mu^2}{2 \cdot \eta}$$

$$\eta \approx E_{\text{LUMO}} - E_{\text{HOMO}}$$

$$N = E_{\text{HOMO}} - E_{\text{HOMO}}(\text{TCE})$$



ELECTROPHILE

b3lyp/6-31g(d) / gas phase

NUCLEOPHILE

Marginal

Moderate

Strong

Marginal

Moderate

Strong

$0.8 > \omega$

$0.8 < \omega < 1.5$

$\omega \geq 1.5$

$2.0 > N$

$2.0 < N < 3.0$

$N \geq 3.0$

Path

$\Delta\omega$ [eV]

molecule

μ [eV]

η [eV]

ω [eV]

N [eV]

2 + 1 (A)

2.43

polar/non-polar

1

-5.55

4.01

3.84

1.57

2 + 4 (B)

1.66

$\Delta\omega = \omega_{\text{El.}} - \omega_{\text{Nu.}}$

2

-3.64

4.73

1.41

3.11

2 + 4' (C)

1.74

$\Delta\omega \geq 1$ eV

4

-5.22

4.45

3.07

1.67

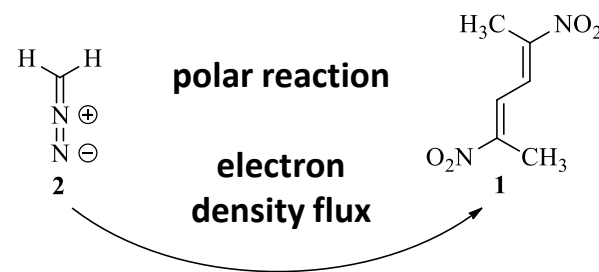
4'

-5.28

4.43

3.15

1.63



Origin of Nitropyrazoline Formation *via* 32CA: A CDFT Study

Open Access Review

Applications of the Conceptual Density Functional Theory Indices to Organic Chemistry Reactivity

by Luis R. Domingo ^{1,*}, Mar Ríos-Gutiérrez ¹ and Patricia Pérez ²

¹ Department of Organic Chemistry, University of Valencia, Dr. Moliner 50, E-46100 Burjassot, Valencia, Spain

² Facultad de Ciencias Exactas, Departamento de Ciencias Químicas, Universidad Andres Bello, Av. República 498, 8370146 Santiago, Chile

* Author to whom correspondence should be addressed.

Molecules 2016, 21(6), 748; <https://doi.org/10.3390/molecules21060748>

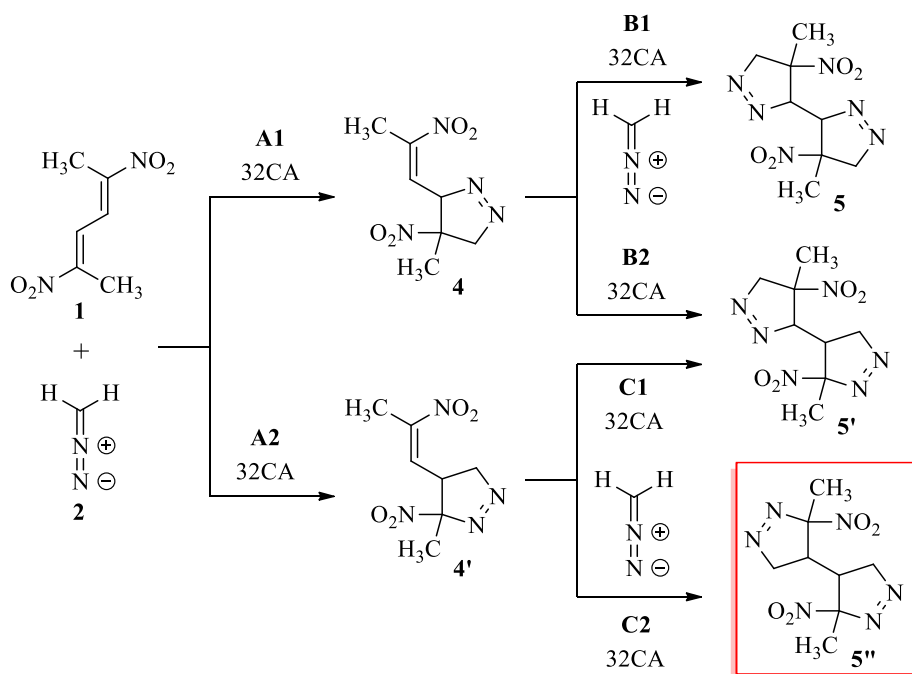
Submission received: 12 May 2016 / Revised: 1 June 2016 / Accepted: 2 June 2016 / Published: 9 June 2016

$$\mu \approx \frac{1}{2} \cdot (E_{\text{HOMO}} + E_{\text{LUMO}})$$

$$\omega = \frac{\mu^2}{2 \cdot \eta}$$

$$\eta \approx E_{\text{LUMO}} - E_{\text{HOMO}}$$

$$N = E_{\text{HOMO}} - E_{\text{HOMO}}(\text{TCE})$$



ELECTROPHILE

b3lyp/6-31g(d) / gas phase

NUCLEOPHILE

Marginal

Moderate

Strong

Marginal

Moderate

Strong

$0.8 > \omega$

$0.8 < \omega < 1.5$

$\omega \geq 1.5$

$2.0 > N$

$2.0 < N < 3.0$

$N \geq 3.0$

Path

$\Delta\omega$ [eV]

2 + 1 (A)

2.43

polar/non-polar

2 + 4 (B)

1.66

$\Delta\omega = \omega_{\text{El.}} - \omega_{\text{Nu.}}$

2 + 4' (C)

1.74

$\Delta\omega \geq 1$ eV

molecule

μ [eV]

η [eV]

ω [eV]

N [eV]

1

-5.55

4.01

3.84

1.57

2

-3.64

4.73

1.41

3.11

4

-5.22

4.45

3.07

1.67

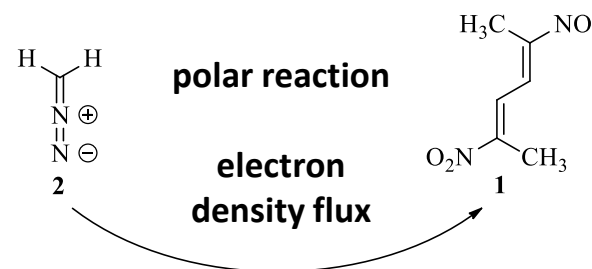
4'

-5.28

4.43

3.15

1.63



local electrophilicity

$$\omega_k = \omega \cdot P_k^+$$

radical cation

radical anion

local nucleophilicity

$$N_k = N \cdot P_k^-$$

Origin of Nitropyrazoline Formation *via* 32CA: A CDFT Study

Open Access Review

Applications of the Conceptual Density Functional Theory Indices to Organic Chemistry Reactivity

by Luis R. Domingo ^{1,*}, Mar Ríos-Gutiérrez ¹ and Patricia Pérez ²

¹ Department of Organic Chemistry, University of Valencia, Dr. Moliner 50, E-46100 Burjassot, Valencia, Spain

² Facultad de Ciencias Exactas, Departamento de Ciencias Químicas, Universidad Andres Bello, Av. República 498, 8370146 Santiago, Chile

* Author to whom correspondence should be addressed.

Molecules 2016, 21(6), 748; <https://doi.org/10.3390/molecules21060748>

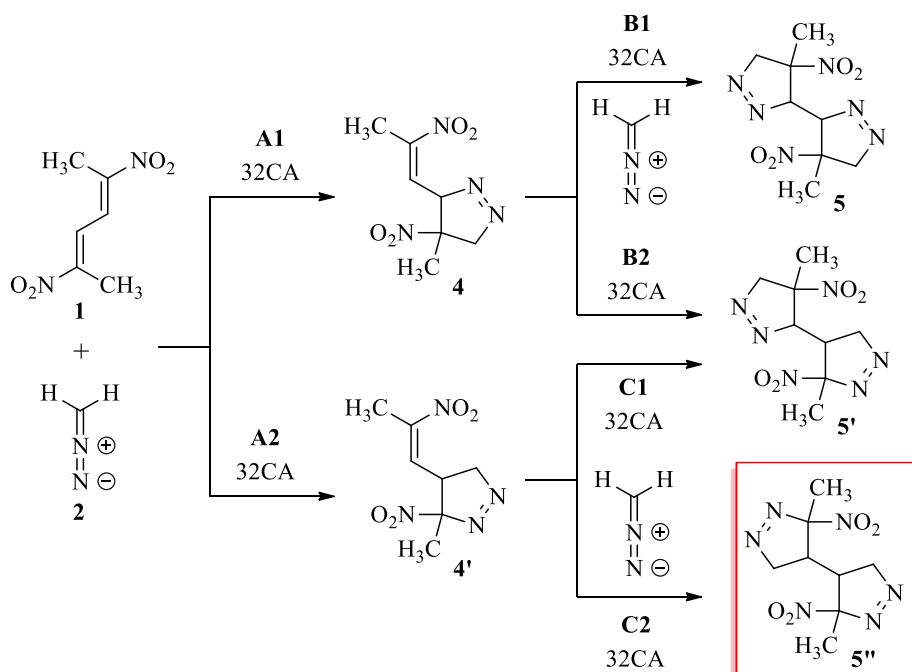
Submission received: 12 May 2016 / Revised: 1 June 2016 / Accepted: 2 June 2016 / Published: 9 June 2016

$$\mu \approx \frac{1}{2} \cdot (E_{\text{HOMO}} + E_{\text{LUMO}})$$

$$\omega = \frac{\mu^2}{2 \cdot \eta}$$

$$\eta \approx E_{\text{LUMO}} - E_{\text{HOMO}}$$

$$N = E_{\text{HOMO}} - E_{\text{HOMO}}(\text{TCE})$$



ELECTROPHILE

b3lyp/6-31g(d) / gas phase

NUCLEOPHILE

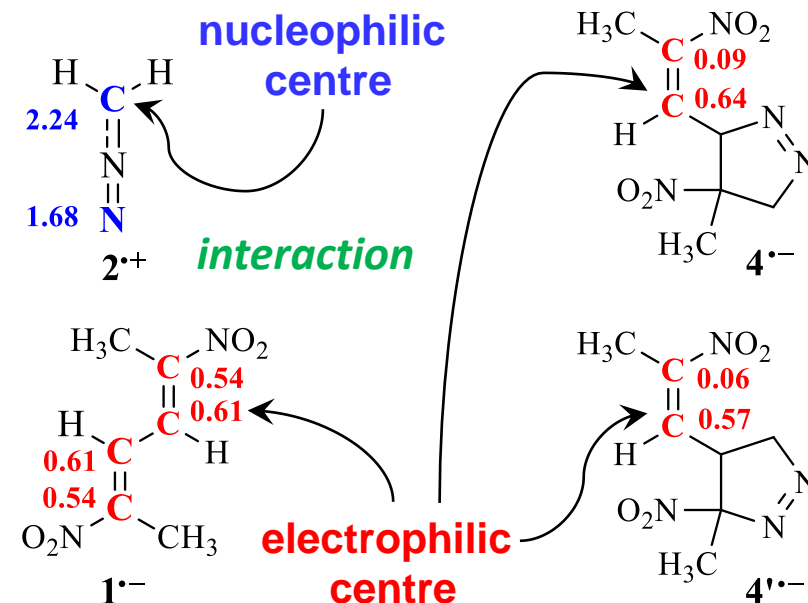
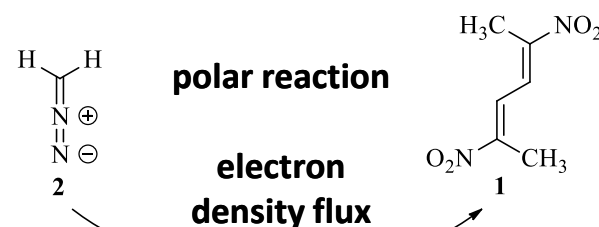
Marginal	Moderate	Strong	Marginal	Moderate	Strong
$0.8 > \omega$	$0.8 < \omega < 1.5$	$\omega \geq 1.5$	$2.0 > N$	$2.0 < N < 3.0$	$N \geq 3.0$

Path	$\Delta\omega$ [eV]
------	---------------------

2 + 1 (A)	2.43	polar/non-polar
2 + 4 (B)	1.66	$\Delta\omega = \omega_{\text{El.}} - \omega_{\text{Nu.}}$
2 + 4' (C)	1.74	$\Delta\omega \geq 1$ eV

molecule	μ [eV]	η [eV]	ω [eV]	N [eV]
----------	------------	-------------	---------------	--------

1	-5.55	4.01	3.84	1.57
2	-3.64	4.73	1.41	3.11
4	-5.22	4.45	3.07	1.67
4'	-5.28	4.43	3.15	1.63



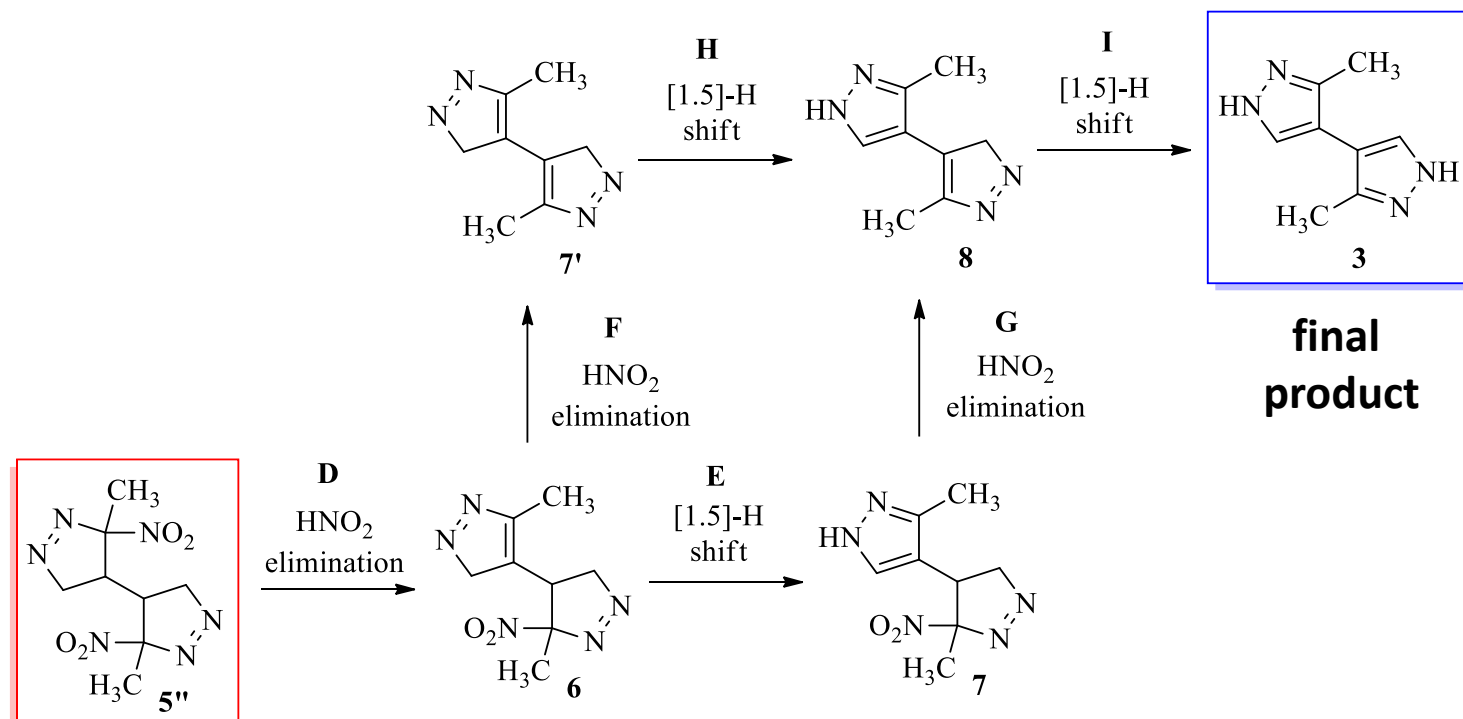
local electrophilicity
 $\omega_k = \omega \cdot P_k^+$

radical anion

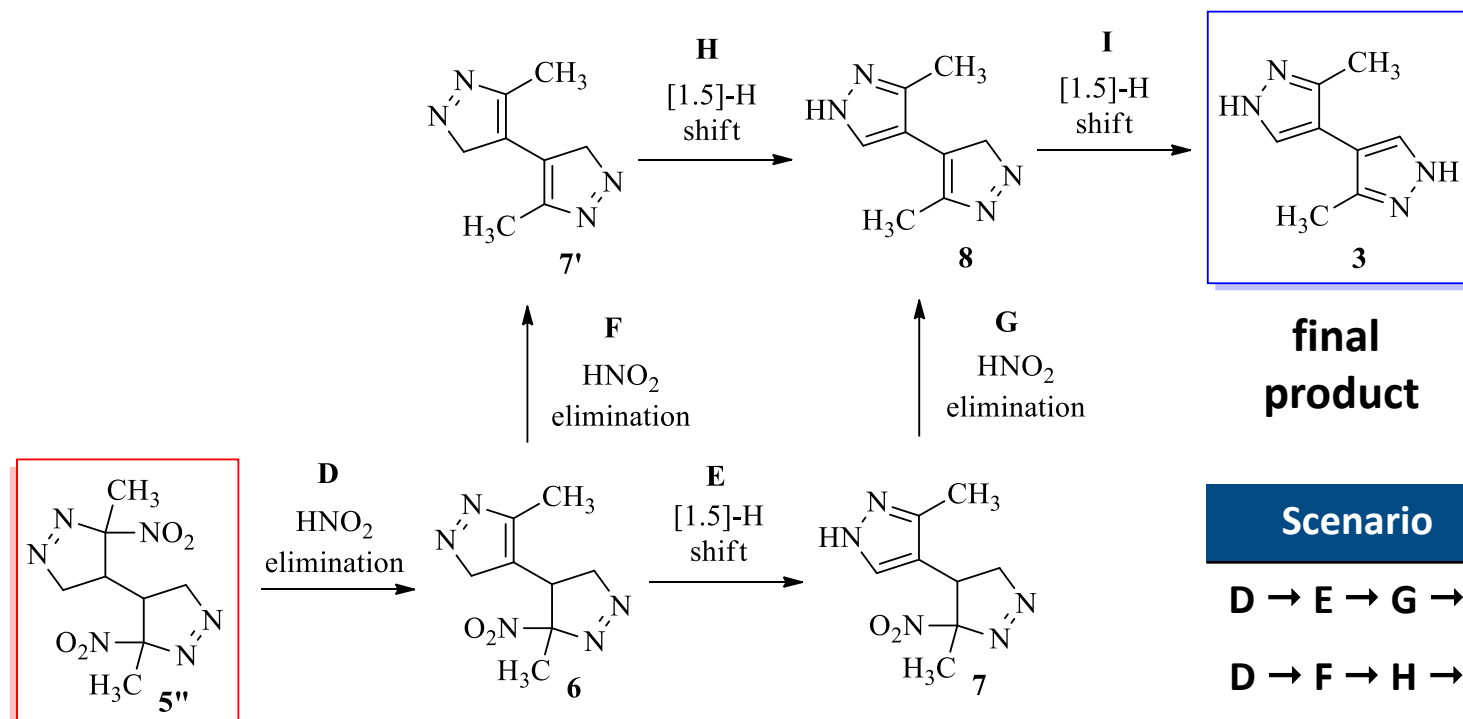
radical cation

local nucleophilicity
 $N_k = N \cdot P_k^-$

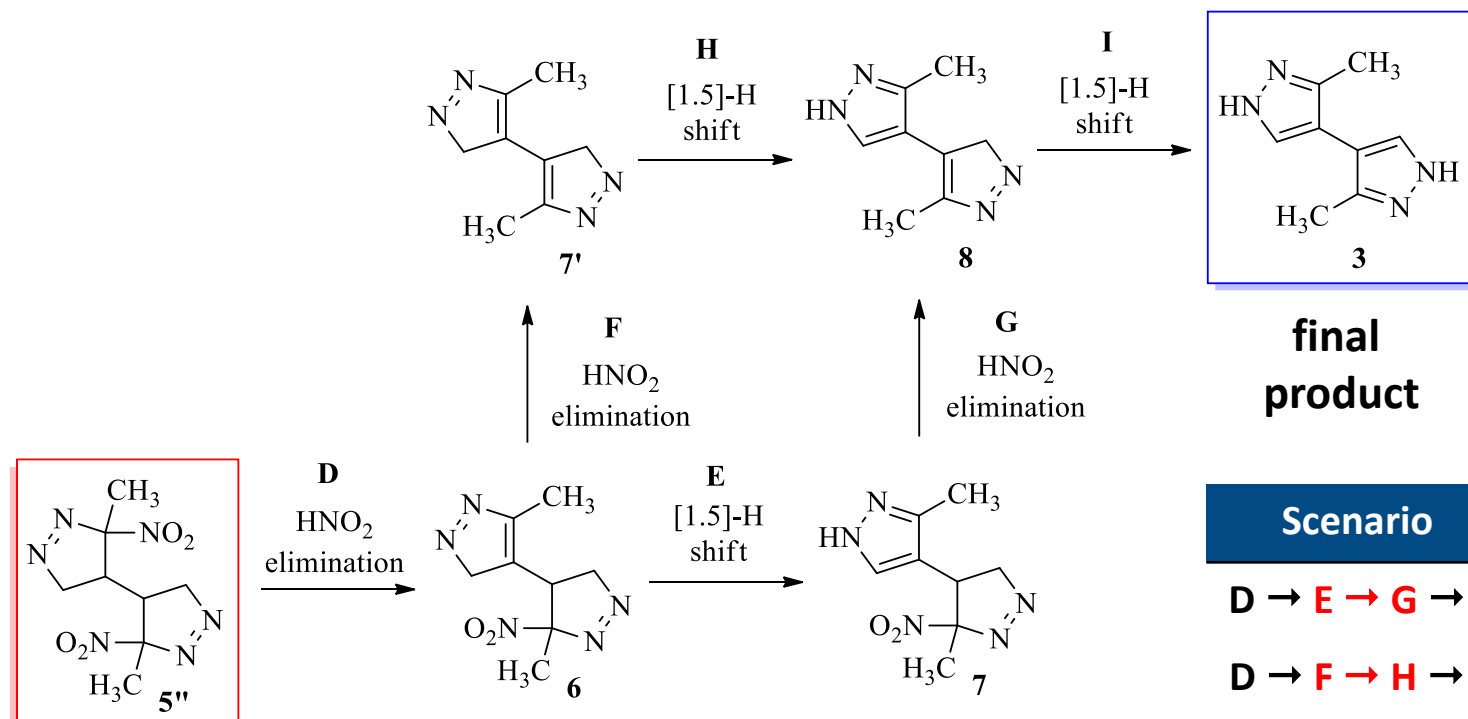
Mechanistic Origin of Bipyrazole Formation: A PES Analysis



Mechanistic Origin of Bipyrazole Formation: A PES Analysis



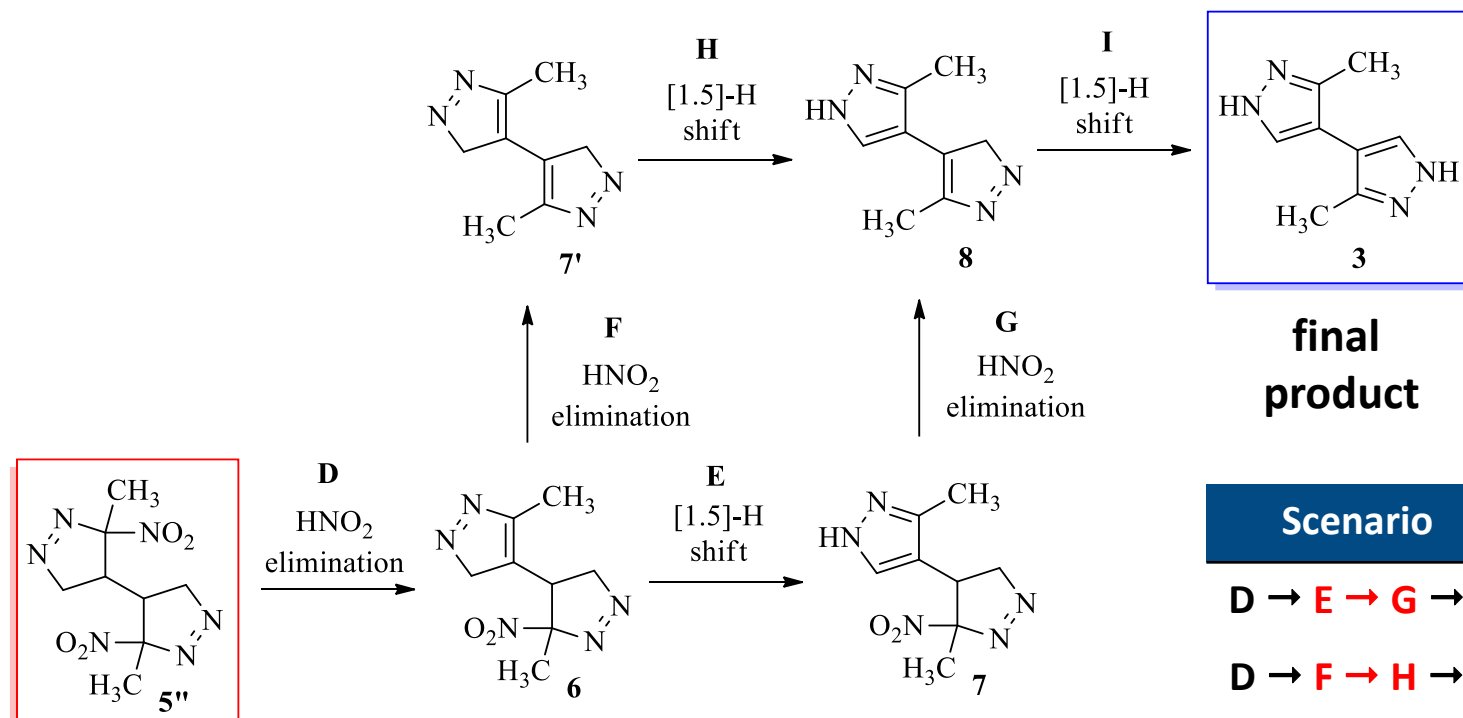
Mechanistic Origin of Bipyrazole Formation: A PES Analysis



Mechanistic Origin of Bipyrazole Formation: A PES Analysis

wb97xd/6-311g(d,p) / pcm (toluene)

		ΔH [kcal/mol]	ΔG [kcal/mol]	ΔS [cal/mol·K]
D	5'' → TS _D	36.89	36.01	2.96
	5'' → 7	9.40	-4.64	47.09
E	6 → TS _E	23.71	23.85	-0.46
	6 → 7'	-28.13	-27.92	-0.69
F	6 → TS _F	36.33	36.08	0.81
	6 → 7	4.78	-9.28	47.16
G	7' → TS _H	35.19	34.12	3.59
	7' → 8	5.85	-7.80	45.79
H	7 → TS _H	24.45	24.84	-1.30
	7 → 8	-27.06	-26.45	-2.06
I	8 → TS _I	25.11	25.84	-2.46
	8 → 3	-25.17	-25.06	-0.37

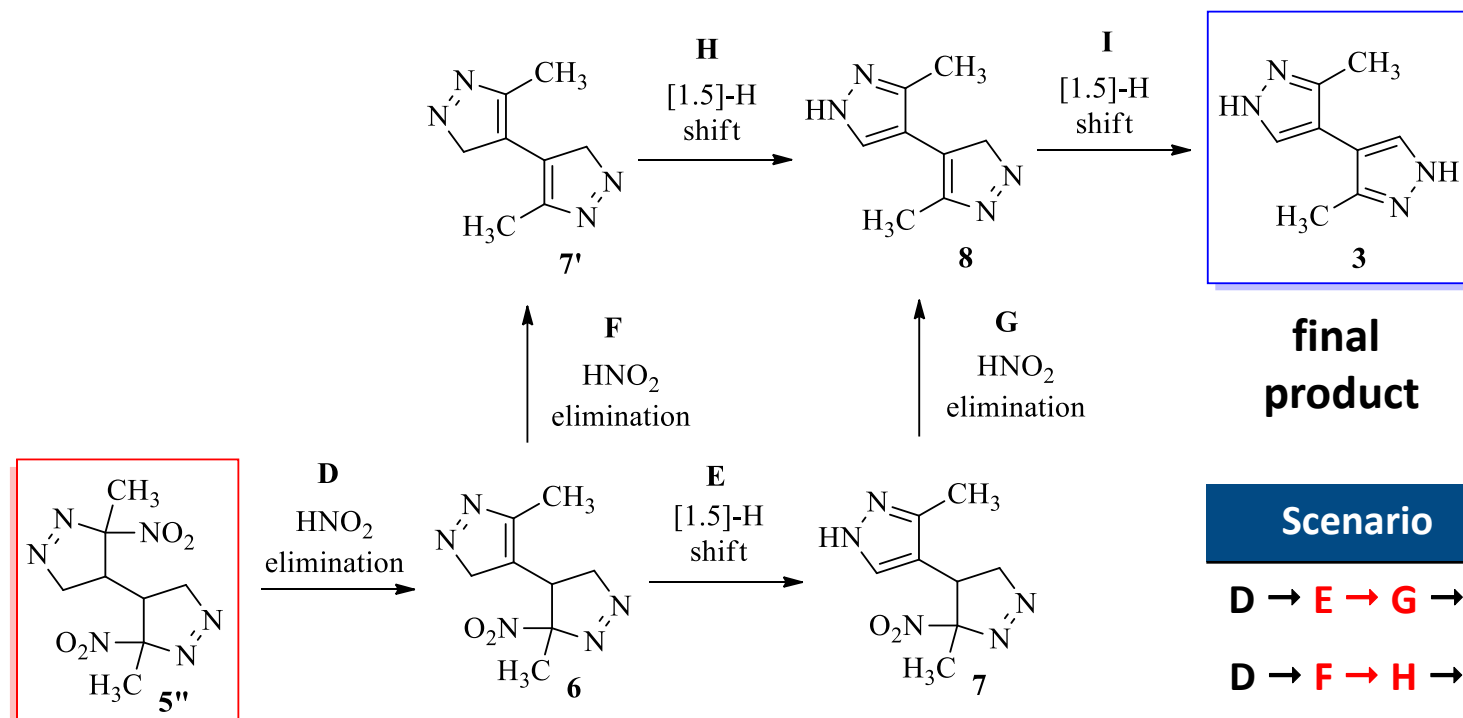


Mechanistic Origin of Bipyrazole Formation: A PES Analysis

wb97xd/6-311g(d,p) / pcm (toluene)

		ΔH [kcal/mol]	ΔG [kcal/mol]	ΔS [cal/mol·K]
D	5'' → TS _D	36.89	36.01	2.96
	5'' → 7	9.40	-4.64	47.09
E	6 → TS _E	23.71	23.85	-0.46
	6 → 7'	-28.13	-27.92	-0.69
F	6 → TS _F	36.33	36.08	0.81
	6 → 7	4.78	-9.28	47.16
G	7' → TS _H	35.19	34.12	3.59
	7' → 8	5.85	-7.80	45.79
H	7 → TS _H	24.45	24.84	-1.30
	7 → 8	-27.06	-26.45	-2.06
I	8 → TS _I	25.11	25.84	-2.46
	8 → 3	-25.17	-25.06	-0.37

ΔG^\ddagger for the **H-shift** is **lower** than that for the **HNO₂ elimination**.

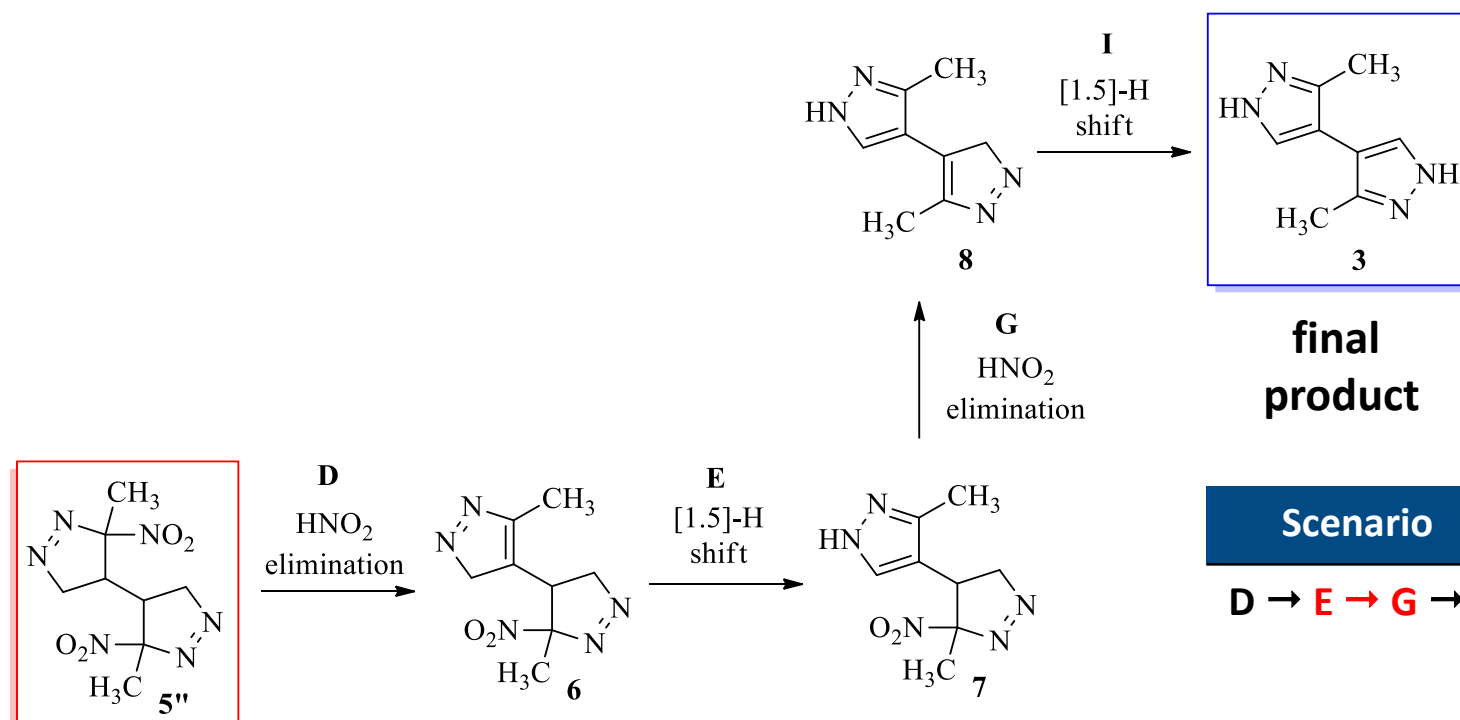


Mechanistic Origin of Bipyrazole Formation: A PES Analysis

wb97xd/6-311g(d,p) / pcm (toluene)

		ΔH [kcal/mol]	ΔG [kcal/mol]	ΔS [cal/mol·K]
D	5'' → TS _D	36.89	36.01	2.96
	5'' → 7	9.40	-4.64	47.09
E	6 → TS _E	23.71	23.85	-0.46
	6 → 7'	-28.13	-27.92	-0.69
F	6 → TS _F	36.33	36.08	0.81
	6 → 7	4.78	-9.28	47.16
G	7' → TS _H	35.19	34.12	3.59
	7' → 8	5.85	-7.80	45.79
H	7 → TS _H	24.45	24.84	-1.30
	7 → 8	-27.06	-26.45	-2.06
I	8 → TS _I	25.11	25.84	-2.46
	8 → 3	-25.17	-25.06	-0.37

ΔG^\ddagger for the **H-shift** is **lower** than that for the **HNO₂ elimination**.



Scenario
D → E → G → I

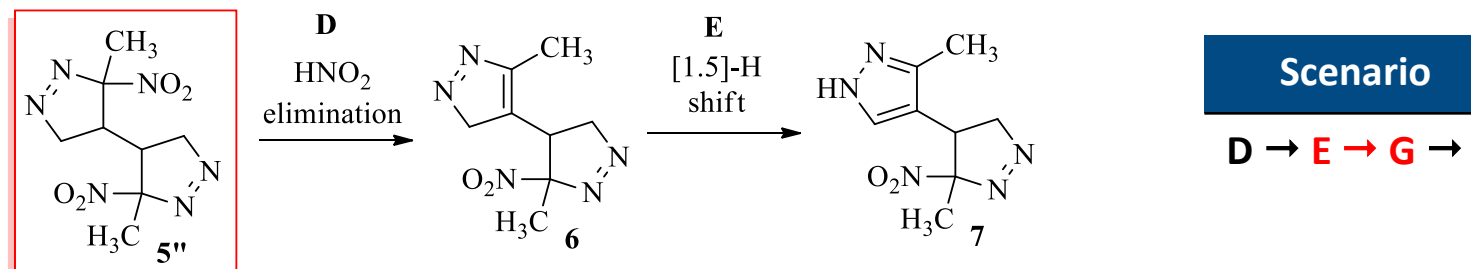
Mechanistic Origin of Bipyrazole Formation: A PES Analysis

wb97xd/6-311g(d,p) / pcm (toluene)

		ΔH [kcal/mol]	ΔG [kcal/mol]	ΔS [cal/mol·K]
D	5'' → TS _D	36.89	36.01	2.96
	5'' → 7	9.40	-4.64	47.09
E	6 → TS _E	23.71	23.85	-0.46
	6 → 7'	-28.13	-27.92	-0.69
F	6 → TS _F	36.33	36.08	0.81
	6 → 7	4.78	-9.28	47.16
G	7' → TS _H	35.19	34.12	3.59
	7' → 8	5.85	-7.80	45.79
H	7 → TS _H	24.45	24.84	-1.30
	7 → 8	-27.06	-26.45	-2.06
I	8 → TS _I	25.11	25.84	-2.46
	8 → 3	-25.17	-25.06	-0.37

ΔG^\ddagger for the **H-shift** is **lower** than that for the **HNO₂ elimination**.

The transformations proceed *via* weakly polar, asynchronous, one-step mechanisms without ionic and/or radical intermediates.



Scenario
D → E → G → I



ACKNOWLEDGMENTS

This research has been supported by PLGrid. The numerical experiment was possible through computing allocation on the Ares system at ACC Cyfronet AGH under the grants **PLG/2024/017868**.



HPC Users' Conference

Zakopane, 13-15 April 2026

Mechanistic Insights into the Cycloaddition of (2E,4E)-2,5-Dinitro-2,4-hexadiene with Diazomethane from Density Functional Theory

Karolina Kula, Radomir Jasiński

karolina.kula@pk.edu.pl



Cracow University of Technology
Faculty of Chemical Engineering
and Technology



HPC Users' Conference

Zakopane, 13-15 April 2026