PHYSICAL CHEMISTRY

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Electronic Supplementary Information

Nitrene formation is the first step of the thermal and photochemical decomposition reactions of organic azides

by

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Table S1. Vertical excitation (VE) energies in eV of the singlet and triplet states of isopropyl azide (C_s, MS-CASPT2).[a,b]

State	VE	f_{OSC}[c]	Configuration[d]	W[e]
$2^1A'$	5.90	$4.22\ 10^{-4}$	$[n\pi]^1[\pi_\sigma*]^1$	39
			$[\pi(NNN)]^1[\pi*(NNN)]]^1$	48
$1^1A''$	4.49	$8.47\ 10^{-4}$	$[n\pi]^1[\pi*(NNN)]^1$	89
$2^1A''$	7.26	$7.12\ 10^{-3}$	$[\pi(NNN)]^1[\pi_\sigma*]^1$	89
		SOC[f]		
$1^3A'$	4.68	0	$[n\pi]^1[\pi_\sigma*]^1$	75
			$[\pi(NNN)]^1[\pi*(NNN)]]^1$	15
$2^3A'$	5.38	0	$[n\pi]^1[\pi_\sigma*]^1$	15
			$[\pi(NNN)]^1[\pi*(NNN)]]^1$	73
$1^3A''$	4.19	16.82	$[n\pi]^1[\pi*(NNN)]^1$	88
$2^3A''$	6.89	16.52	$[\pi(NNN)]^1[\pi_\sigma*]^1$	89

[a]C_s MP2/def2-TZVPP optimized geometry. [b]SA2-CASSCF(14e, 12o)/ANO-RCC reference wave function, IPEA=0.25. Imaginary shift = 0.1. [c]Oscillator strength. [d]MS-CASPT2 main electronic configurations of the excited states referred to the ground state configuration. [e]Weight of the configuration in %. Only contributions greater than 15% are included. [f]Spin orbit coupling constant in cm^{-1}.

Table S2. Vertical excitation (VE) energies in eV of the singlet and triplet states of isopropyl azide (C_s, MS-CASPT2).[a,b]

State	VE	f_{OSC}[c]	Configuration[d]	W[e]
$2^1A'$	5.90	$6.75\ 10^{-4}$	$[n\pi]^1[\pi_\sigma*]^1$	40
			$[\pi(NNN)]^1[\pi*(NNN)]]^1$	48
$1^1A''$	4.49	$8.93\ 10^{-4}$	$[n\pi]^1[\pi*(NNN)]^1$	88
$2^1A''$	7.24	$5.88\ 10^{-3}$	$[\pi(NNN)]^1[\pi_\sigma*]^1$	85
		SOC[f]		
$1^3A'$	4.66	0	$[n\pi]^1[\pi_\sigma*]^1$	75
			$[\pi(NNN)]^1[\pi*(NNN)]]^1$	15
$2^3A'$	5.38	0	$[n\pi]^1[\pi_\sigma*]^1$	15
			$[\pi(NNN)]^1[\pi*(NNN)]]^1$	75
$1^3A''$	4.18	16.22	$[n\pi]^1[\pi*(NNN)]^1$	87
$2^3A''$	6.87	16.22	$[\pi(NNN)]^1[\pi_\sigma*]^1$	86

[a]C_s MP2/def2-TZVPP optimized geometry. [b]SA2-CASSCF(16e, 14o)/ANO-R reference wave function, IPEA=0.25. Imaginary shift = 0.1. [c]Oscillator strength. [d]MS-CASPT2 main electronic configurations of the excited states referred to the ground state configuration. [e]Weight of the configuration in %. Only contributions greater than 15% are included. [f]Spin orbit coupling constant in cm^{-1}.

Table S3. Vertical excitation (VE) energies in eV of the singlet and triplet states of isopropyl azide (C_s, MS-CASPT2).[a,b]

State	VE	f_OSC[c]	Configuration[d]	W[e]
$2^1A'$	5.92	4.52×10^{-4}	$[n\pi]^1[\pi_\sigma{}^*]^1$	40
			$[\pi(NNN)]^1[\pi^*(NNN)]]^1$	48
$1^1A''$	4.49	8.65×10^{-4}	$[n\pi]^1[\pi^*(NNN)]^1$	88
$2^1A''$	7.27	7.07×10^{-3}	$[\pi(NNN)]^1[\pi_\sigma{}^*]^1$	85
		SOC[f]		
$1^3A'$	4.69	0	$[n\pi]^1[\pi_\sigma{}^*]^1$	75
			$[\pi(NNN)]^1[\pi^*(NNN)]]^1$	15
$2^3A'$	5.40	0	$[n\pi]^1[\pi_\sigma{}^*]^1$	15
			$[\pi(NNN)]^1[\pi^*(NNN)]]^1$	74
$1^3A''$	4.19	16.29	$[n\pi]^1[\pi^*(NNN)]^1$	88
$2^3A''$	6.90	16.23	$[\pi(NNN)]^1[\pi_\sigma{}^*]^1$	87

[a]C_s MP2/def2-TZVPP optimized geometry. [b]SA2-CASSCF(14e, 12o)/ANO-R reference wave function, IPEA=0.25. Imaginary shift = 0.1. [c]Oscillator strength. [d]MS-CASPT2 main electronic configurations of the excited states referred to the ground state configuration. [e]Weight of the configuration in %. Only contributions greater than 15% are included. [f]Spin orbit coupling constant in cm^{-1}.

Table S4. Internal coordinates of the species represented in Figure 3.

Coordinate	M0	M1	TS1	TS0	ISC1
R2,1	1.519	1.499	1.488	1.448	1.445
R3,1	1.102	1.106	1.110	1.125	1.124
A3,1,2	102.1	102.6	102.5	91.6	91.4
R4,1	1.521	1.524	1.525	1.524	1.525
A4,1,2	111.4	111.3	111.7	116.1	116.2
Dh4,1,2,3	116.1	116.1	115.8	111.5	111.5
R5,1	1.521	1.524	1.525	1.524	1.525
A5,1,2	111.4	111.3	111.7	116.1	116.2
Dh5,1,2,3	−116.1	−116.1	−115.8	−111.5	−111.5
R6,4	1.084	1.082	1.082	1.085	1.086
A6,4,1	111.3	111.4	111.3	110.3	110.4
Dh6,4,1,2	66.8	69.2	71.6	75.1	75.7
R7,5	1.084	1.082	1.082	1.085	1.086
A7,5,1	111.3	111.4	111.3	110.3	110.4
Dh7,5,1,6	35.8	34.2	33.0	37.8	37.6
R8,4	1.083	1.083	1.083	1.084	1.084
A8,4,1	110.1	109.5	109.6	111.3	111.3
Dh8,4,1,6	119.5	119.7	119.8	119.2	119.2
R9,5	1.083	1.083	1.083	1.084	1.084
A9,5,1	110.1	109.5	109.6	111.3	111.3
Dh9,5,1,7	−119.5	−119.7	−119.8	−119.2	−119.2
R10,4	1.082	1.083	1.083	1.081	1.081
A10,4,1	110.8	111.0	111.0	110.6	110.6
Dh10,4,1,6	−120.7	−121.0	−121.0	−119.7	−119.7
R11,5	1.082	1.083	1.083	1.081	1.081
A11,5,1	110.8	111.0	111.0	110.6	110.6
Dh11,5,1,7	120.7	121.0	121.0	119.7	119.7
R12,2	1.241	1.463	1.651	1.876	1.889
A12,2,1	114.2	108.0	106.2	105.0	104.4
Dh12,2,1,3	180.0	180.0	180.0	180.0	180.0
R13,12	1.141	1.188	1.159	1.105	1.104
A13,12,2	173.3	119.6	117.8	160.3	164.1
Dh13,12,2,	180.0	180.0	180.0	180.0	180.0

[a]CASSCF(16e, 14o)/ANO-RCC optimized geometry. R in Å; A and Dh in degrees. Numbering in Fig. S3.

Table S5. Internal coordinates of the species represented in Figure 3.

Coordinate	M0	M1	TS1	TS0	ISC1
R2,1	1.517	1.498	1.488	1.447	1.449
R3,1	1.103	1.107	1.111	1.127	1.123
A3,1,2	102.1	102.7	102.5	91.3	92.1
R4,1	1.521	1.524	1.525	1.524	1.525
A4,1,2	111.4	111.3	111.7	116.2	116.1
Dh4,1,2,3	116.1	116.0	115.7	111.4	111.7
R5,1	1.521	1.524	1.525	1.524	1.525
A5,1,2	111.4	111.3	111.7	116.2	116.1
Dh5,1,2,3	−116.1	−116.0	−115.7	−111.4	−111.7
R6,4	1.085	1.083	1.083	1.086	1.086
A6,4,1	111.3	111.4	111.3	110.3	110.4
Dh6,4,1,2	66.9	69.2	70.1	75.7	75.4
R7,5	1.085	1.083	1.083	1.086	1.086
A7,5,1	111.3	111.4	111.3	110.3	110.4
Dh7,5,1,6	35.8	34.2	34.1	37.6	37.4
R8,4	1.084	1.084	1.084	1.085	1.085
A8,4,1	110.1	109.6	109.6	111.3	111.2
Dh8,4,1,6	119.4	119.7	119.7	119.2	119.2
R9,5	1.084	1.084	1.084	1.085	1.085
A9,5,1	110.1	109.6	109.6	111.3	111.2
Dh9,5,1,7	−119.4	−119.7	−119.7	−119.2	−119.2
R10,4	1.083	1.084	1.084	1.082	1.082
A10,4,1	110.8	111.0	111.0	110.6	110.6
Dh10,4,1,6	−120.7	−121.0	−120.9	−119.7	−119.8
R11,5	1.083	1.084	1.084	1.082	1.082
A11,5,1	110.8	111.0	111.0	110.6	110.6
Dh11,5,1,7	120.7	121.0	120.9	119.7	119.8
R12,2	1.241	1.457	1.660	1.887	1.883
A12,2,1	114.3	108.1	106.1	105.1	104.4
Dh12,2,1,3	180.0	180.0	180.0	180.0	180.0
R13,12	1.141	1.189	1.158	1.106	1.105
A13,12,2	173.3	119.8	117.8	159.3	163.2
Dh13,12,2,	180.0	180.0	180.0	180.0	180.0

[a]CASSCF(16e, 14o)/ANO-R optimized geometry. R in Å; A and Dh in degrees. Numbering in Fig. S3.

Table S6. Internal coordinates of the species represented in Figure 3.

Coordinate	M0	M1	TS1	TS0	ISC1
R2,1	1.522	1.502	1.493	1.454	1.464
R3,1	1.079	1.082	1.085	1.098	1.095
A3,1,2	102.1	102.7	102.4	93.5	94.9
R4,1	1.521	1.524	1.525	1.525	1.525
A4,1,2	111.2	111.1	111.5	115.6	115.1
Dh4,1,2,3	116.4	116.4	116.1	112.5	113.0
R5,1	1.521	1.524	1.525	1.525	1.525
A5,1,2	111.2	111.1	111.5	115.6	115.1
Dh5,1,2,3	−116.4	−116.4	−116.1	−112.5	−113.0
R6,4	1.084	1.082	1.082	1.085	1.085
A6,4,1	111.4	111.4	111.4	110.5	110.6
Dh6,4,1,2	66.5	69.0	69.8	74.3	73.5
R7,5	1.084	1.082	1.082	1.085	1.085
A7,5,1	111.4	111.4	111.4	110.5	110.6
Dh7,5,1,6	35.6	34.0	33.9	37.1	36.9
R8,4	1.084	1.083	1.083	1.084	1.084
A8,4,1	110.0	109.5	109.6	111.1	111.1
Dh8,4,1,6	119.5	119.7	119.8	119.3	119.3
R9,5	1.084	1.083	1.083	1.084	1.084
A9,5,1	110.0	109.5	109.6	111.1	111.1
Dh9,5,1,7	−119.5	−119.7	−119.8	−119.3	−119.3
R10,4	1.082	1.083	1.083	1.081	1.082
A10,4,1	110.8	111.0	111.0	110.6	110.6
Dh10,4,1,6	−120.7	−121.1	−121.0	−119.8	−119.9
R11,5	1.082	1.083	1.083	1.081	1.082
A11,5,1	110.8	111.0	111.0	110.6	110.6
Dh11,5,1,7	120.7	121.1	121.0	119.8	119.9
R12,2	1.240	1.460	1.658	1.909	1.865
A12,2,1	114.2	108.1	106.1	104.6	104.7
Dh12,2,1,3	180.0	180.0	180.0	180.0	180.0
R13,12	1.141	1.188	1.158	1.104	1.105
A13,12,2	173.2	119.7	117.9	159.4	158.0
Dh13,12,2,	180.0	180.0	180.0	180.0	180.0

[a]CASSCF(14e, 12o)/ANO-RCC optimized geometry. R in Å; A and Dh in degrees. Numbering in Fig. S3.

Table S7. Internal coordinates of the species represented in Figure 3.

Coordinate	M0	M1	TS1	TS0	ISC1
R2,1	1.520	1.502	1.492	1.454	1.466
R3,1	1.080	1.083	1.086	1.098	1.096
A3,1,2	102.1	102.7	102.4	93.5	95.2
R4,1	1.521	1.524	1.525	1.525	1.525
A4,1,2	111.2	111.1	111.5	115.6	115.1
Dh4,1,2,3	116.4	116.3	116.0	112.5	113.1
R5,1	1.521	1.524	1.525	1.525	1.525
A5,1,2	111.2	111.1	111.5	115.6	115.1
Dh5,1,2,3	−116.4	−116.3	−116.0	−112.5	−113.1
R6,4	1.085	1.083	1.083	1.085	1.086
A6,4,1	111.4	111.4	111.4	110.5	110.7
Dh6,4,1,2	66.6	68.9	69.9	74.3	73.4
R7,5	1.085	1.083	1.083	1.085	1.086
A7,5,1	111.4	111.4	111.4	110.5	110.7
Dh7,5,1,6	35.6	34.0	33.9	37.1	36.8
R8,4	1.084	1.084	1.084	1.084	1.085
A8,4,1	110.0	109.5	109.6	111.1	111.0
Dh8,4,1,6	119.4	119.7	119.8	119.3	119.3
R9,5	1.084	1.084	1.084	1.084	1.085
A9,5,1	110.0	109.5	109.6	111.1	111.0
Dh9,5,1,7	−119.4	−119.7	−119.8	−119.3	−119.3
R10,4	1.083	1.084	1.084	1.081	1.082
A10,4,1	110.8	111.0	111.0	110.6	110.6
Dh10,4,1,6	−120.7	−121.1	−121.0	−119.8	−119.9
R11,5	1.083	1.084	1.084	1.081	1.082
A11,5,1	110.8	111.0	111.0	110.6	110.6
Dh11,5,1,7	120.7	121.1	121.0	119.8	119.9
R12,2	1.240	1.454	1.667	1.909	1.863
A12,2,1	114.3	108.2	106.0	104.6	104.7
Dh12,2,1,3	180.0	180.0	180.0	180.0	180.0
R13,12	1.141	1.189	1.157	1.104	1.106
A13,12,2	173.2	119.9	117.9	159.4	157.2
Dh13,12,2,	180.0	180.0	180.0	180.0	180.0

[a]CASSCF(14e, 12o)/ANO-R optimized geometry. R in Å; A and Dh in degrees. Numbering in Fig. S3.

Table S8. Internal coordinates of the nitrene species represented in Figure 3.

Coordinate	Nitrene T0	Nitrene S0	Nitrene S1
R2,1	1.472	1.445	1.448
R3,1	1.113	1.120	1.116
A3,1,2	106.0	106.0	104.5
R4,1	1.525	1.529	1.530
A4,1,2	109.8	110.4	110.8
Dh4,1,2,3	117.4	117.0	116.7
R5,1	1.525	1.529	1.530
A5,1,2	109.8	110.4	110.8
Dh5,1,2,3	−117.4	−117.0	−116.7
R6,4	1.084	1.083	1.083
A6,4,1	110.7	110.6	110.5
Dh6,4,1,2	63.7	64.4	64.7
R7,5	1.084	1.083	1.083
A7,5,1	110.7	110.6	110.5
Dh7,5,1,6	35.4	35.8	36.2
R8,4	1.083	1.083	1.083
A8,4,1	110.4	110.1	110.2
Dh8,4,1,6	119.8	119.8	119.7
R9,5	1.083	1.083	1.083
A9,5,1	110.4	110.1	110.2
Dh9,5,1,7	−119.8	−119.8	−119.7
R10,4	1.083	1.082	1.082
A10,4,1	111.0	110.9	110.9
Dh10,4,1,6	−120.2	−120.2	−120.1
R11,5	1.083	1.082	1.082
A11,5,1	111.0	110.9	110.9
Dh11,5,1,7	120.2	120.2	120.1

[a]CASSCF(8e, 7o)/ANO-RCC optimized geometry. R in Å; A and Dh in degrees. Numbering of atoms in Fig. S3.

Table S9. Set of nonredundant internal coordinates of isopropyl azide.[a]

Nº	Symbol	Definition	Description
1	$\nu(NN)$	$R_{2,12}$	N-N$_w$ stretching
2	$\nu(NN)$	$R_{12,13}$	N-N stretching
3	$\nu(CN)$	$R_{1,2}$	C-N stretching
4	$\nu(CH)$	$R_{1,3}$	C-Hα stretching
5	$\nu(CC)$	$\frac{1}{\sqrt{2}}(R_{1,4} - R_{1,5})$	C-C stretching
6	$\nu(CC)$	$\frac{1}{\sqrt{2}}(R_{1,4} + R_{1,5})$	C-C stretching
7	$\nu_{as}(CH_2)$	$\frac{1}{\sqrt{2}}(R_{4,6} - R_{4,8})$	CH$_2$ asym stretching
8	$\nu_{as}(CH_3)$	$\frac{1}{\sqrt{6}}(2R_{4,10} - R_{4,6} - R_{4,8})$	CH$_3$ asym stretching
9	$\nu_s(CH_3)$	$\frac{1}{\sqrt{3}}(R_{4,10} + R_{4,6} + R_{4,8})$	CH$_3$ sym stretching
10	$\nu_{as}(CH_2)$	$\frac{1}{\sqrt{2}}(R_{5,7} - R_{5,9})$	CH$_2$ asym stretching
11	$\nu_{as}(CH_3)$	$\frac{1}{\sqrt{6}}(2R_{5,11} - R_{5,7} - R_{5,9})$	CH$_3$ asym stretching
12	$\nu_s(CH_3)$	$\frac{1}{\sqrt{3}}(R_{5,11} + R_{5,7} + R_{5,9})$	CH$_3$ sym stretching
13	$\delta(CCH)$	$\alpha_{2,3}^{1}$	CCHα def
14	$\delta_{sym}(CH_3)$	$\frac{1}{\sqrt{6}}(\alpha_{4,10}^{4} + \alpha_{6,8}^{4} + \alpha_{6,10}^{4} - \alpha_{6,1}^{4} - \alpha_{10,1}^{4} - \alpha_{8,1}^{4})$	CH$_3$ sym def
15	$\delta_{asym}(CH_3)$	$\frac{1}{\sqrt{6}}(2\alpha_{8,10}^{4} - \alpha_{6,8}^{4} - \alpha_{6,10}^{4})$	CH$_3$ asym def
16	$\delta'_{asym}(CH_3)$	$\frac{1}{\sqrt{2}}(\alpha_{6,10}^{4} - \alpha_{6,8}^{4})$	CH$_3$ asym def
17	$\delta_{rock}(CH_3)$	$\frac{1}{\sqrt{6}}(2\alpha_{6,1}^{4} - \alpha_{10,1}^{4} - \alpha_{8,1}^{4})$	CH$_3$ rocking
18	$\delta'_{rock}(CH_3)$	$\frac{1}{\sqrt{2}}(\alpha_{10,1}^{4} - \alpha_{8,1}^{4})$	CH$_3$ rocking
19	$\delta_{sym}(CH_3)$	$\frac{1}{\sqrt{6}}(\alpha_{5,11}^{5} + \alpha_{7,9}^{5} + \alpha_{7,11}^{5} - \alpha_{7,1}^{5} - \alpha_{11,1}^{5} - \alpha_{9,1}^{5})$	CH$_3$ sym def
20	$\delta_{asym}(CH_3)$	$\frac{1}{\sqrt{6}}(2\alpha_{9,11}^{5} - \alpha_{7,9}^{5} - \alpha_{7,11}^{5})$	CH$_3$ asym def
21	$\delta'_{asym}(CH_3)$	$\frac{1}{\sqrt{2}}(\alpha_{7,11}^{5} - \alpha_{7,9}^{5})$	CH$_3$ asym def
22	$\delta_{rock}(CH_3)$	$\frac{1}{\sqrt{6}}(2\alpha_{7,1}^{5} - \alpha_{11,1}^{5} - \alpha_{9,1}^{5})$	CH$_3$ rocking
23	$\delta'_{rock}(CH_3)$	$\frac{1}{\sqrt{2}}(\alpha_{11,1}^{5} - \alpha_{9,1}^{5})$	CH$_3$ rocking
24	$\delta(CCH)$	$\frac{1}{\sqrt{2}}(\alpha_{3,4}^{1} - \alpha_{3,5}^{1})$	CCH def
25	$\delta(CNN)$	$\alpha_{1,12}^{2}$	CNN def

#			
26	$\delta(NNN)$	$\alpha_{2,13}^{12}$	NNN def
27	$\delta(CCC)$	$\alpha_{5,4}^{1}$	CCC def
28	$\delta(CCN)$	$\alpha_{4,2}^{1}$	CCN def
29	$\delta(CCN)$	$\alpha_{5,2}^{1}$	CCN def
30	$\Gamma(CN)$	Γ_{1-2}	torsion of $N-N_2$ bond
31	$\Gamma(CC)$	Γ_{1-2}	torsion of C-N bond
32	$\Gamma(CS)$	Γ_{1-4}	torsion of CH_3
33	$\Gamma(CH_3)$	Γ_{1-5}	torsion of CH_3

[a] Atom numbering in Figure S3.

Table S10a. Assignment of the calculated fundamental modes of TS1.[a]

TS1[b]	PED[c]	TS1[d]	PED[c]	Assignment
3240	48(8)+48(11)	3239	48(8)+48(11)	CH_3 asym stretching
3238	48(8)+48(11)	3236	48(8)+48(11)	CH_3 asym stretching
3210	49(7)+49(10)	3211	49(7)+49(10)	CH_2 asym stretching
3201	49(7)+49(10	3201	49(7)+49(10	CH_2 asym stretching
3156	47(9)+47(12)	3155	47(9)+47(12)	CH_3 sym stretching
3149	47(9)+47(12)	3148	47(9)+47(12)	CH_3 sym stretching
2795	99(4)	3065	98(4)	C-Hα stretching
2301	99(2)	2312	99(2)	N-N stretching
1618	23(15)+23(16)+23(20)+23(21)	1619	19(15)+27(16)+19(20)+27(21)	CH_3 asym def
1612	23(15)+23(16)+23(20)+23(21)	1613	27(15)+19(16)+27(20)+19(21)	CH_3 asym def
1602	38(16)+38(21)	1601	39(16)+39(21)	CH_3 asym def
1599	38(15)+38(20)	1599	39(15)+39(20)	CH_3 asym def
1537	46(14)+46(19)	1537	46(14)+46(19	CH_3 sym def
1523	44(14)+44(19)	1522	44(14)+44(19)	CH_3 sym def
1370	20(3)+29(13)	1413	16(3)+47(13)	CCHα def
1354	21(5)+50(24)	1396	13(5)+64(24)	CCH def
1286	29(17)+29(22)+11(28)	1294	11(6)+22(17)+22(22)+16(27)	CCN def
1211	30(5)+11(18)+11(23)+16(24)	1221	38(5)+12(18)+12(23)+10(28)+10(29	CCH def
1113	28(13)+22(18)+22(23)	1130	29(13)+21(18)+21(23)	CH_3 rocking
1005	37(5)+28(18)+28(23)	1006	33(5)+22(18)+22(23)	CH_3 rocking
986	33(17)+33(22)+25(24)	993	29(17)+29(22)+18(24)	CH_3 rocking
941	17(3)+32(6)+25(13)	958	26(3)+33(6)+16(13)	C-C stretching
783	46(3)+35(6)+14(13)	790	49(3)+36(6)	C-C stretching
568	24(25)+22(28)+22(29)	577	24(25)+22(28)+22(29)	CCN def
479	44(28)+44(29)	476	44(28)+44(29)	CCN def
398	73(27)	399	72(27)	CCC def
279	22(25)+24(26)+15(32)+15(33)	276	21(25)+18(26)+22(32)+22(33)	CNN + NNN def
252	14(26)+27(32)+27(33)	253	19(26)+21(32)+21(33)	torsion of CH_3
242	59(30)+20(31)	232	34(30)+14(31)+18(32)+18(33)	torsion of $N-N_2$ bond
220	47(32)+47(33)	220	20(30)+37(32)+37(33)	torsion of CH_3
114	45(25)+45(26)	113	45(25)+46(26)	CNN + NNN def
86	39(30)+58(31)	85	39(30)+60(31)	torsion of C-N bond
421 i	60(1)+13(3)+11(13)+8(25)	**369 i**	68(1)+11(3)+6(13)+8(25)	

[a]Assignment of vibrational modes according to the set of internal coordinates given in Table S9. [b]Frequencies of TS1 in cm^{-1} [CASSCF(16e,14o)]. [c]Weight of the potential energy distribution; in parenthesis: coordinate number. [d]Frequencies of TS1 in cm^{-1} CASSCF(14e,12o).

Table S10b. Assignment of the calculated fundamental modes of TSx.[a]

TSx[b]	PED[c]	TSx[d]	PED[c]	Assignment
3124	48(8)+48(11)	3191	47(8)+47(11)	CH_3 asym stretching
3123	48(8)+48(11)	3190	47(8)+47(11)	CH_3 asym stretching
3089	48(7)+48(10)	3155	47(7)+47(10)	CH_2 asym stretching
3082	48(7)+48(10	3150	48(7)+48(10	CH_2 asym stretching
3029	47(9)+47(12)	3070	48(9)+48(12)	CH_3 sym stretching
3023	47(9)+47(12)	3066	48(9)+48(12)	CH_3 sym stretching
2705	99(4)	2762	99(4)	C-Hα stretching
2366	99(2)	2116	92(2)	N-N stretching
1498	38(15)+38(20)	1511	24(15)+21(16)+24(20)+21(21)	CH_3 asym def
1494	37(16)+37(21)	1508	22(15)+21(16)+22(20)+21(21)	CH_3 asym def
1479	46(15)+46(20)	1490	40(15)+40(20)	CH_3 asym def
1477	46(16)+46(21)	1490	39(16)+39(21)	CH_3 asym def
1404	47(14)+47(19)	1403	47(14)+47(19)	CH_3 sym def
1386	47(14)+47(19)	1390	44(14)+44(19)	CH_3 sym def
1335	43(3)+11(6)+14(25)	1374	45(3)+12(6)+13(27)	CCHα def
1182	34(5)+14(24)+15(28)+15(29)	1219	39(5)+13(24)+14(28)+14(29)	CCH def
1167	34(17)+34(22)	1175	33(17)+33(21)	CCN def
1079	13(17)+13(22)+53(2	1093	12(17)+12(22)+57(24)	CCH def
1056	18(3)+33(18)+33(23)	1068	14(3)+34(18)+34(23)	CH_3 rocking
915	32(5)+21(18)+21(23)	931	32(5)+30(18)+30(23)	CH_3 rocking
897	23(17)+23(22)+25(2	900	29(17)+29(22)+29(24)	CH_3 rocking
829	44(6)+25(13)+11(17)+11(22)	839	70(6)+10(13)	C-C stretching
721	14(3)+36(13)	698	13(3)+13(6)+39(13)	C-C stretching
503	16(25)+20(28)+20(2	508	11(3)+23(13)+16(29)+19(28)+19(29)	CCN def
491	43(28)+43(29)	502	42(28)+42(29)	CCN def
378	72(27)	376	72(27)	CCC def
255	24(25)+34(26)	259	21(25)+18(26)+23(32)+23(33)	CNN + NNN def
242	12(28)+12(29)+48(30)+20(3 1)	244	14(28)+14(29)+41(30)+23(31)	torsion of CH_3
219	20(26)+29(32)+29(3	225	25(26)+ 20(32)+20(33)	torsion of N-N$_2$ bond
182	43(32)+43(33)	187	42(32)+42(33)	torsion of CH_3
118	53(32)+30(33)	109	49(25)+33(26)	CNN + NNN def
75	46(30)+51(31)	77	47(30)+48(31)	torsion of C-N bond
418 *i*	14(1)+18 (3)+39(13)	**604 *i***	16(1)+17(3)+10(4)+38(13)	

[a]Assignment of vibrational modes according to the set of internal coordinates given in Table S9. [b]Frequencies of TSx in cm^{-1} [B3LYP/def2-TZVPP)]. [c]Weight of the potential energy distribution; in parenthesis: coordinate number. [d]Frequencies of TSx in cm^{-1} MP2/def2-TZVPP.
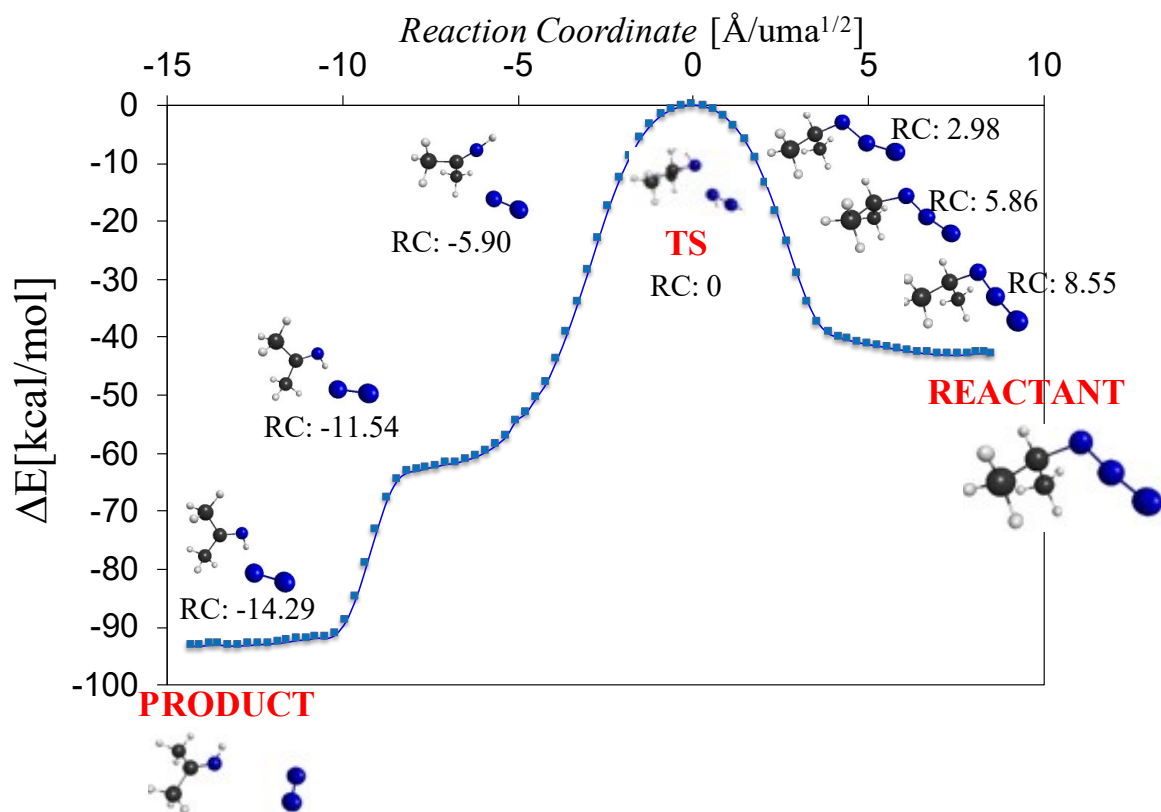
Fig. S1 Intrinsic reaction coordinate connecting reactant and products via the transition state **TSx**. IRC:B3LYP/def2-TZVPP.
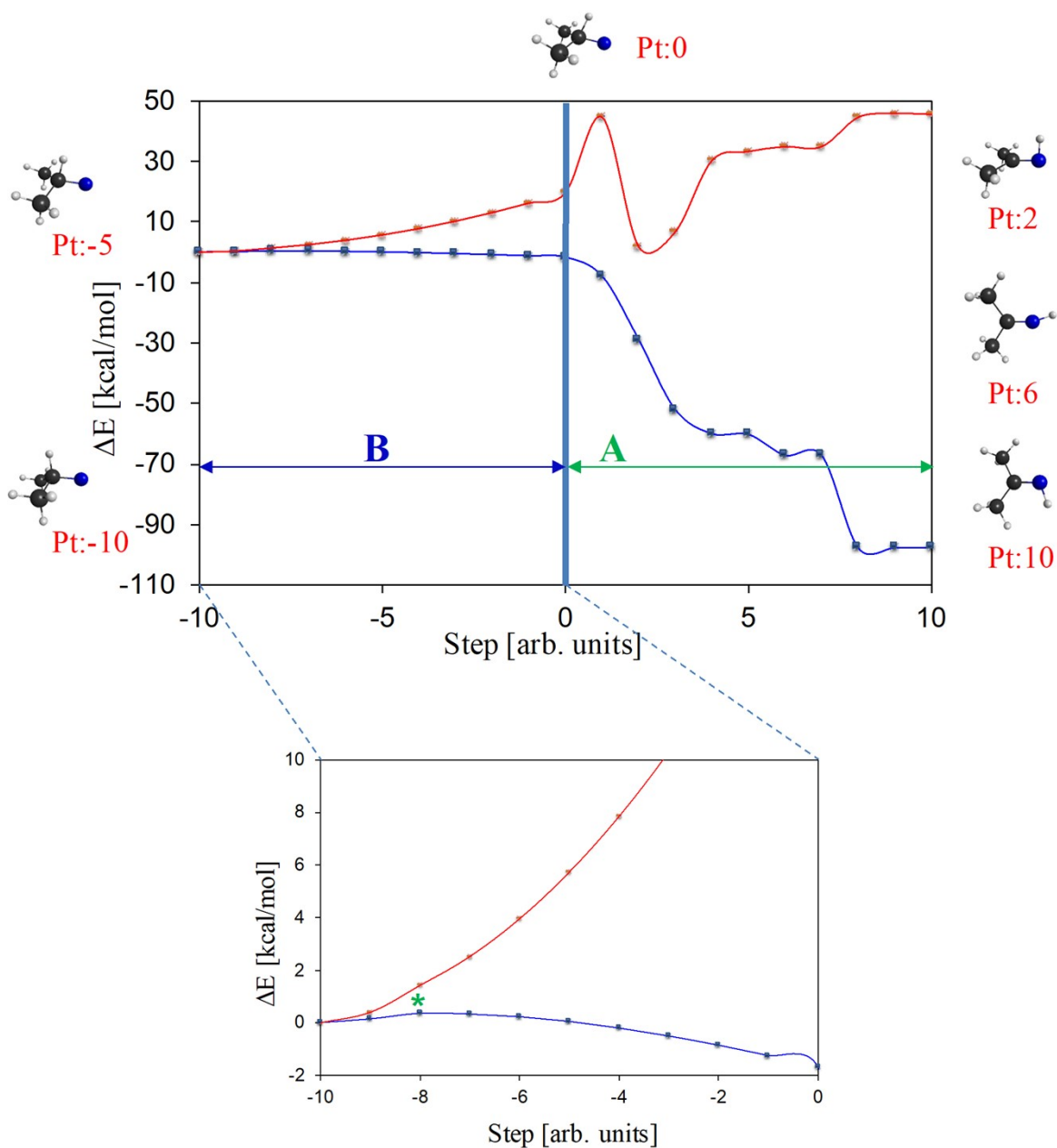
Fig. S2 SA2-CASSCF(8e, 7o)/ANO-RCC potential energy curves of the two low-lying singlet states of isopropyl nitrene leading to isomerization into imine. **A** section: energy profile obtained from the geometries of the IRC [dissociative direction] represented in Fig. S1(b) after removing the N_2 fragment. **B** section: linear interpolation starting at the $1^1A'$ minimum of isopropyl nitrene and ending at the first point of A section.
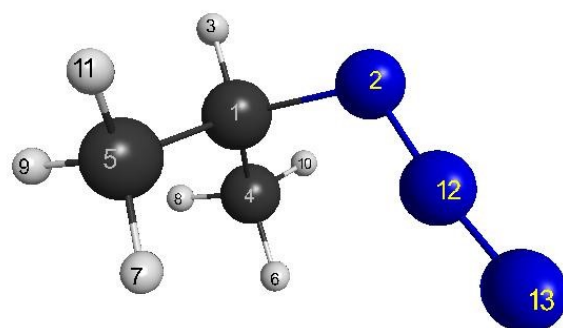
Fig S3 Atom numbering for Tables S4 to S10.