Supporting Information

Photochemistry of 2-Formylphenylnitrene: A Doorway to Heavy-Atom Tunneling of a Benzazirine to a Cyclic Ketenimine

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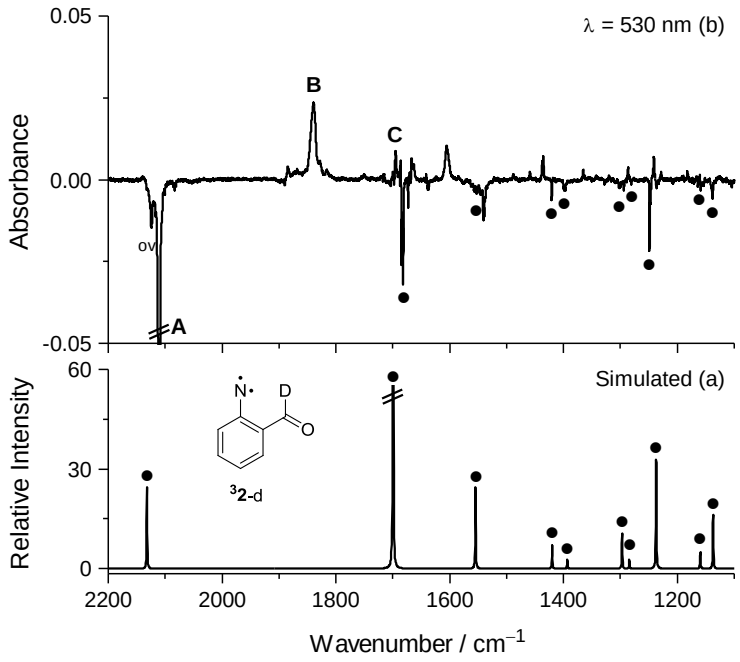


Figure S1. (a) IR spectrum of triplet deuterated 2-formylphenylnitrene ^{3}**2**-d simulated at the B3LYP/6-311++G(d,p) level. (b) Experimental difference IR spectrum showing changes after the second stage of irradiation at λ = 530 nm (120 min, 60 mW); subsequent to the first stage of irradiations at λ = 530 nm (40 min, 90 mW) shown in Figure 2. The negative bands are due to the consumed ^{3}**2**-d (at this stage ~95 %) and due to the consumed species **A**. The positive bands labeled as **B** and **C** are the most characteristic bands of the identified photoproducts that continue to accumulate.

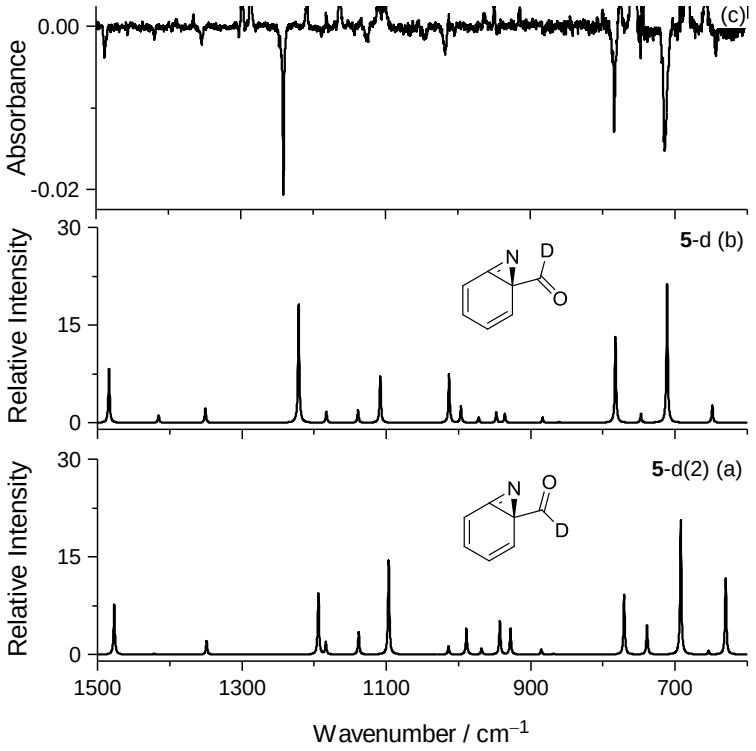


Figure S2. (a,b) IR spectra of deuterated formylbenzazirines **5**-d(2) (panel a) and **5**-d (panel b) simulated at the B3LYP/6-311++G(d,p) level. (c) Experimental difference IR spectrum showing the consumption (negative bands) of **C** assigned to benzazirine **5**-d. Positive bands (truncated) are due to the formation of **D** (Figure 4).

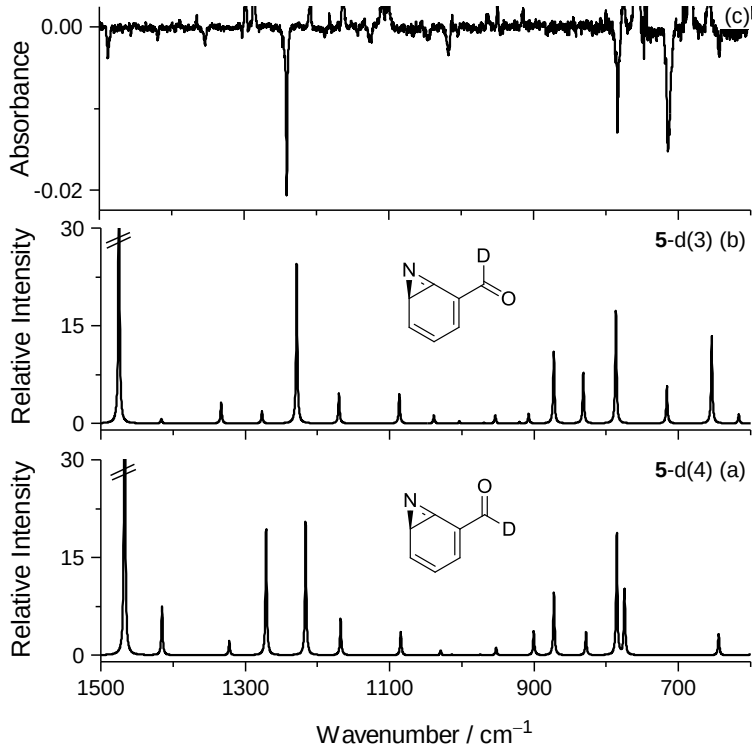


Figure S3. (a,b) IR spectra of deuterated formylbenzazirines **5**-d(4) (panel a) and **5**-d(3) (panel b) simulated at the B3LYP/6-311++G(d,p) level. (c) Experimental difference IR spectrum showing the consumption (negative bands) of **C** assigned to **5**-d (Figure S2). Positive bands (truncated) are due to the formation of **D** (Figure 4).

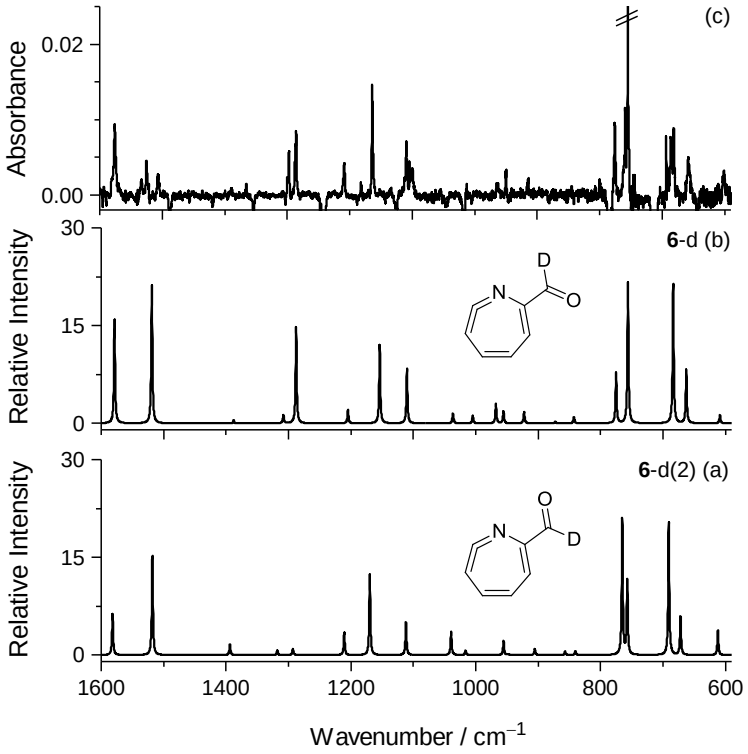


Figure S4. (a,b) IR spectra of deuterated formyl cyclic ketenimine **6**-d(2) (panel a) and **6**-d (panel b) simulated at the B3LYP/6-311++G(d,p) level. (c) Experimental difference IR spectrum showing the formation (positive bands) of **D** assigned to cyclic ketenimine **6**-d. Negative bands (truncated) are due to the consumption of **C** (Figure 4).

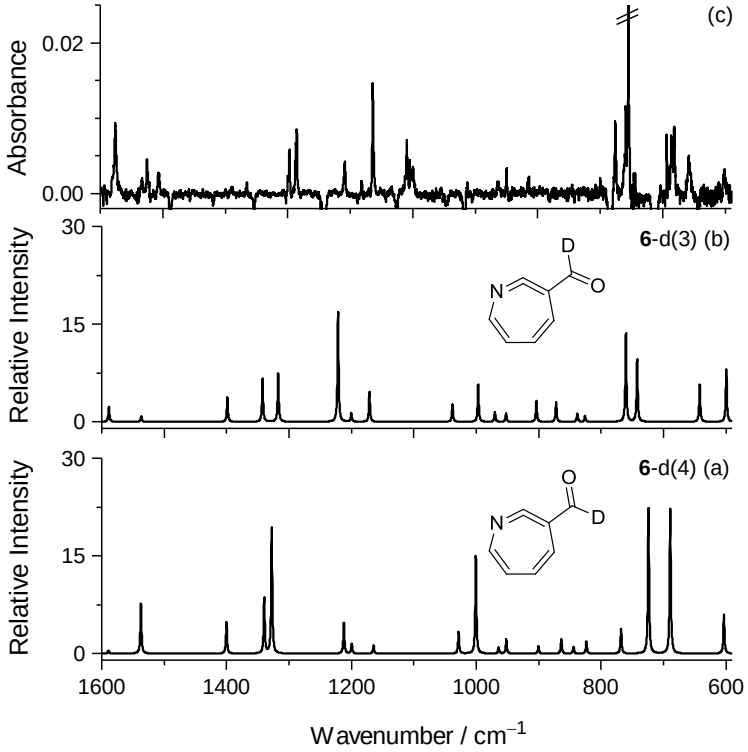


Figure S5. (a,b) IR spectra of deuterated formyl cyclic ketenimine **6**-d(4) (panel a) and **6**-d(3) (panel b) simulated at the B3LYP/6-311++G(d,p) level. (c) Experimental difference IR spectrum showing the formation (positive bands) of **D** assigned to **6**-d (Figure S4). Negative bands (truncated) are due to the consumption of **C** (Figure 4).

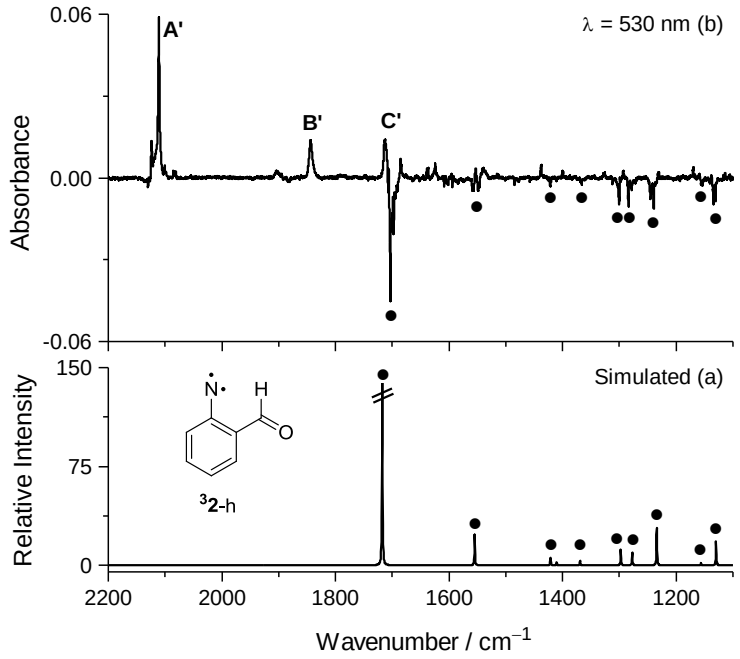


Figure S6. (a) IR spectrum of triplet 2-formylphenylnitrene ^{3}**2**-h simulated at the B3LYP/6-311++G(d,p) level. (b) Experimental difference IR spectrum showing changes after irradiation at λ = 530 nm (130 mW, 5 min), subsequent to irradiation at λ = 308 nm.[1] The negative bands are due to the consumed ^{3}**2**-h (at this stage ~25 %). The positive bands labeled at **A′**, **B′** and **C′** are the most characteristic bands of the identified photoproducts.

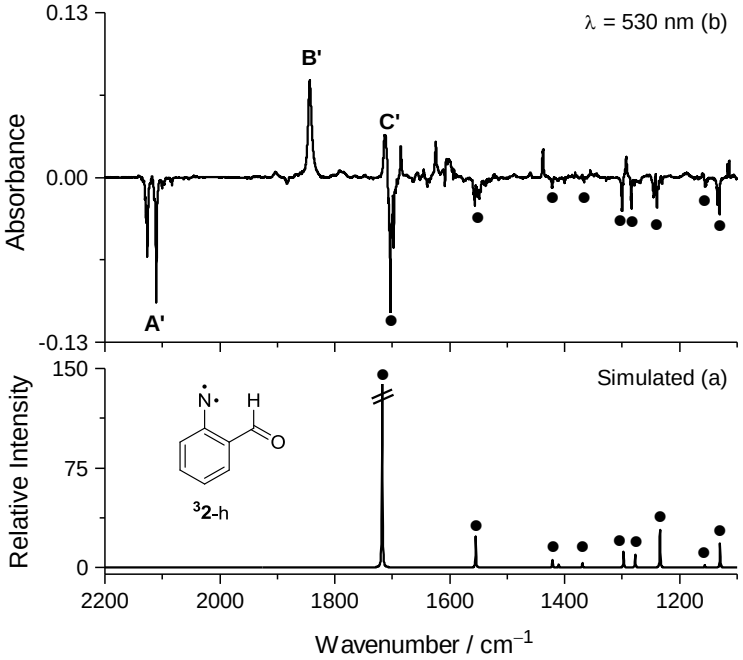


Figure S7. (a) IR spectrum of triplet 2-formylphenylnitrene ^{3}**2**-h simulated at the B3LYP/6-311++G(d,p) level. (b) Experimental difference IR spectrum showing changes after irradiation at λ = 530 nm (130 mW, 60 min), subsequent to irradiation at λ = 308 nm.[1] The negative bands are due to the consumed ^{3}**2**-h (at this stage > 90 %) and due to the consumed species **A′** (two different conformers). The positive bands labeled as **B′** and **C′** are the most characteristic bands of the identified photoproducts that continue to accumulate.

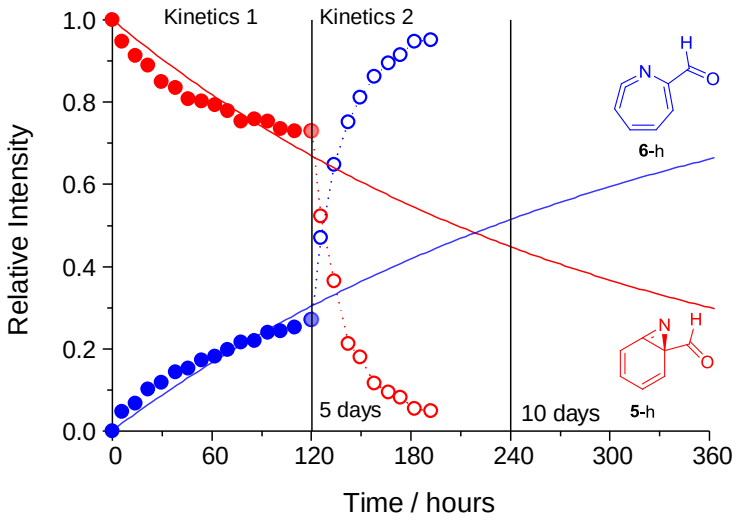


Figure S8. Kinetics of rearrangement of benzazirine **5**-h to cyclic ketenimine **6**-h in an argon matrix at 10 K. Kinetics 1 (initial 5 days, left): rearrangement of **5**-h (solid red circles (●), consumption) into **6**-h (solid blue circles (●), production) with the sample kept in the dark, except when the spectra were recorded, the sample was exposed to an infrared long-pass cutoff filter transmitting only wavelengths below 2200 cm^{-1}. Kinetics 2 (after 5 days in the dark, right): rearrangement of **5**-h (empty red circles (○), consumption) into **6**-h (empty blue circles (○), production) with the sample permanently exposed to the IR light source of the FTIR spectrometer. Blue and red solid lines represent best fits obtained using first-order single exponential kinetics equations, and adjustments were made using only the amounts of the reactant **5**-h and the product **6**-h during the first 5 days of observation (sample in the dark), corresponding to ~27% of the conversion. The rate constants are $k_{\mathbf{5}\text{-h}} = 9.3 \times 10^{-7}\ s^{-1}$ and $k_{\mathbf{6}\text{h}} = 8.3 \times 10^{-7}\ s^{-1}$. Blue and red dotted lines (right) are presented to guide the eye only.

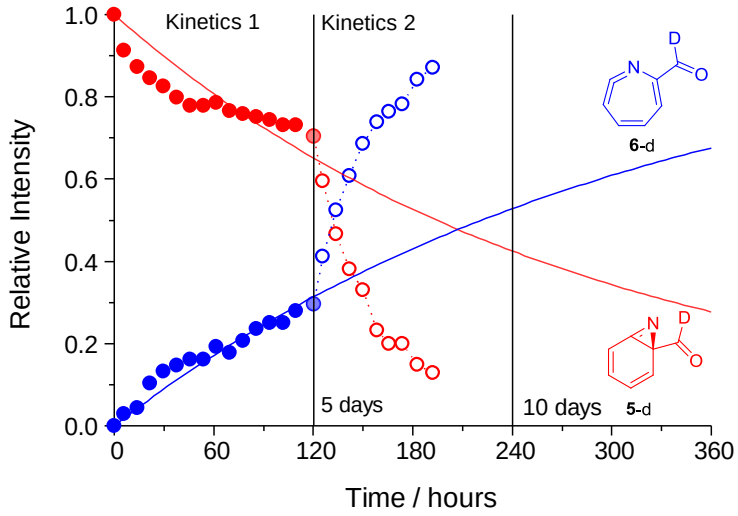


Figure S9. Kinetics of rearrangement of benzazirine **5**-d to cyclic ketenimine **6**-d in an argon matrix at 20 K. Kinetics 1 (initial 5 days, left). Kinetics 2 (after 5 days in the dark, right). See for other details the caption of Figure S8. Blue and red solid lines represent best fits obtained using first-order single exponential kinetics equations, and adjustments were made using only the amounts of the reactant **5**-d and the product **6**-d during the first 5 days of observation (sample in the dark), corresponding to ~29% of the conversion. The rate constants are $k_{\mathbf{5}\text{-d}} = 9.9 \times 10^{-7}\ s^{-1}$ and $k_{\mathbf{6}\text{-d}} = 8.7 \times 10^{-7}\ s^{-1}$. Blue and red dotted lines (right) are presented to guide the eye only.

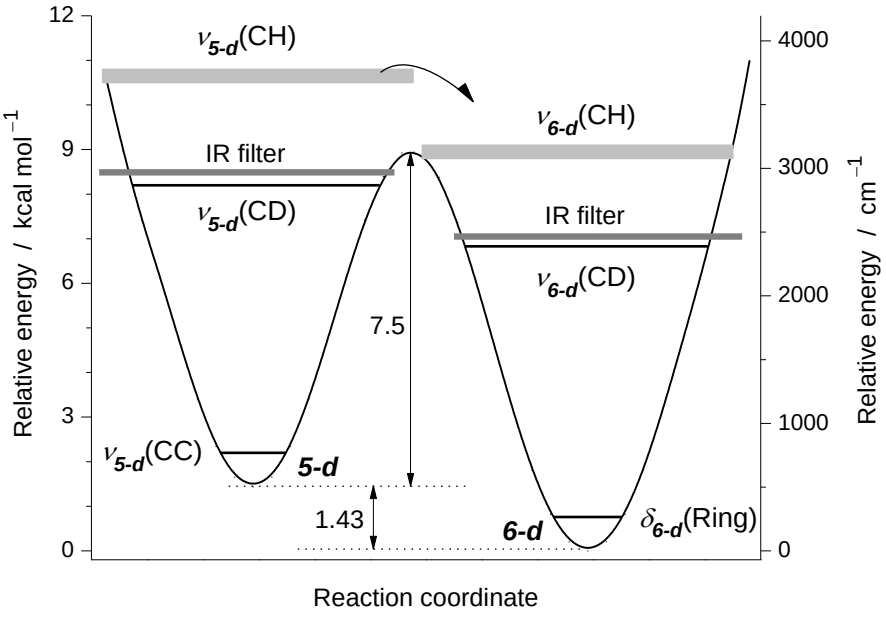


Figure S10. Potential energy profile connecting benzazirine **5**-d (left) and cyclic ketenimine **6**-d (right). Single point energy values of the stationary points (the two minima and the transition state) were computed at the CCSD(T)-F12/cc-pVTZ-F12//M06-2X/6-311+G(2d,p) level. Energy of **6**-d was set to relative zero. Energies of the most relevant vibrational modes are shown as black horizontal lines (below the "IR filter" cutoff). The grey horizontal bars have an energy span of ca. 100 cm^{-1}, and cover the range centered around 3000 cm^{-1} where four CH stretching modes (both in **5**-d and in **6**-d) appear. The curved arrow designates the direction of expected IR-induced isomerization when the sample is exposed to the unfiltered irradiation coming from the FTIR spectrometer light source (over-the-barrier mechanism). When the matrix sample is protected with the long-pass cutoff filter, transmitting only below 2200 cm^{-1}, all accessible energy levels in the system are below the barrier (on each side) and isomerization from **5**-d to **6**-d is only feasible via tunneling.

Table S1. Experimental IR spectral data (argon matrix at 10 K), B3LYP/6-311++G(d,p) calculated vibrational frequencies (ν, cm^{-1}), absolute infrared intensities (A^{th}, km mol^{-1}), and vibrational assignment of triplet deuterated 2-formylphenylnitrene ^{3}**2**-d.[a]

Ar matrix[b]		Calculated[c]		Sym.	Approx. assignment[d,e]
ν	I	ν	A^{th}		
2032/2024	ov	2132	39.2	A'	ν(C−D)
1685/1683/1682	m/m/s	1700	274.4	A'	ν(C=O)
1563/1556/1552/1546	w/w/w/w	1555	42.2	A'	ν(C6C5) + ν(C2C3)
1421	w	1420	11.1	A'	δ1(C–H)
1401/1400/1398	vw/vw/vw	1393	4.7	A'	δ2(C–H)
1302/1300/1294	w/vw/vw	1297	18.1	A'	ν(CN) + ν1(CC)ring
1281	vw	1284	4.8	A'	ν(CN) – ν1(CC)ring
1249/1236	m	1237	63.8	A'	ν(OC−C)
1159	w	1160	8.8	A'	δ3(C–H)
1141/1140/1138	w/w/w	1137	29.5	A'	δ4(C–H)
-	-	1089	3.9	A'	ν2(CC)ring
846	vw	840	2.8	A'	δ1(ring)
775	m	770	29.5	A'	δ(OC−C)
752/751/749	m/m/m	746	63.4	A"	γ1(C–H)
684	vw	680	7.6	A'	τ1(ring)
617	w	614	17.7	A'	δ2(ring)
533	vw	533	4.7	A'	δ2(ring)

[a]Triplet deuterated 2-formylphenylnitrene ^{3}**2**-d was generated by irradiation of deuterated 2-formylphenylazide **1**-d at λ = 308 nm in an argon matrix at 10 K. Only bands in the 2500–500 cm^{-1} region having calculated intensities above 2 km mol^{-1} are included. [b]Experimental intensities are presented in qualitative terms: s = strong, m = medium, w = weak, vw = very weak, and ov = overlapped. [c]B3LYP/6-311++G(d,p) calculated scaled frequencies. [d]Assignments made by inspection of Chemcraft animation. Abbreviations: ν = stretching, δ = bending, γ = rocking, τ = torsion, s = symmetric, and as = antisymmetric. Signs "+" and "–" designate combinations of vibrations occurring in "syn"-phase ("+") and in "anti"-phase ("–"). [e]For atom numbering see Scheme S1.

Table S2. Experimental IR spectral data (argon matrix at 10 K), B3LYP/6-311++G(d,p) calculated vibrational frequencies (ν, cm^{-1}), absolute infrared intensities (A^{th}, km mol^{-1}), and vibrational assignment of N-deuterated iminoketene **3**-d.[a]

Ar matrix[b]		Calculated[c]		Sym.	Approx. assignment[d,e]
ν	I	ν	A^{th}		
2419	vw	2454	10.1	A′	ν(N–D)
2112/2109	vs	2149	1180.4	A′	$\nu(C{=}C{=}O)_{as}$
1637	m	1645	63.2	A′	$\nu(C{=}C)_{as}$
1547	s	1555	123.2	A′	ν(C=N)
1541/1539	s/s	1541	141.9	A′	$\nu(C{=}C)_{s}$
1397/1396	m/m	1385	23.0	A′	δ1(C–H), $\nu(C3–C2–C7)_{s}$ + ν(C3–C4)
1310/1308	w/w	1295	23.8	A′	$\nu(C{=}C{=}O)_{s}$
1230/1229	vw/vw	1233	7.6	A′	$\nu(C3–C2–C7)_{as}$ – ν(C3–C4), δ2(C–H)
1207	vw	1205	6.6	A′	δ3(C–H)
1157/1154	w/m	1150	17.6	A′	δ4(C–H)
-	-	1124	4.5	A′	δ(C1–C2–C7), δ3(C–H)
916	m	910	35.1	A′	δ(C=N–D), δ1(ring)
826	vw	818	5.2	A″	γ1(C–H)
814	m	810	23.6	A′	δ(C=N–D), δ2(ring)
727/723	m/w	722	53.6	A″	γ2(C–H)
688/686	w/w	682	15.8	A′	δ(C=C=O), δ3(ring)
621/616	m/m	607	41.0	A″	τ(N–D)

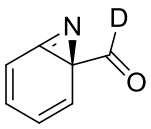
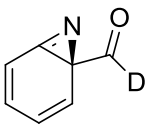
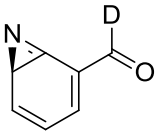
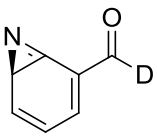
[a]N-Deuterated iminoketene **3**-d was generated during irradiation of deuterated triplet 2-formylphenylnitrene ^{3}**2**-d at λ = 530 nm in an argon matrix at 10 K. Only bands in the 2600–600 cm^{-1} region having calculated intensities above 3 km mol^{-1} are included. [b]Experimental intensities are presented in qualitative terms: vs = very strong, s = strong, m = medium, w = weak, vw = very weak. [c]B3LYP/6-311++G(d,p) calculated scaled frequencies. [d]Assignments made by inspection of Chemcraft animations. Abbreviations: ν = stretching, δ = bending, γ = rocking, τ = torsion, s = symmetric, and as = antisymmetric. Signs "+" and "–" designate combinations of vibrations occurring in "syn"-phase ("+") and in "anti"-phase ("–"). [e]For atom numbering see Scheme S1.

Table S3. Experimental IR spectral data (argon matrix at 10 K), B3LYP/6-311++G(d,p) calculated vibrational frequencies (ν, cm^{-1}), absolute infrared intensities (A^{th}, km mol^{-1}), and vibrational assignment of N-deuterated benzoazetinone **4**-d.[a]

Ar matrix[b]		Calculated[c]		Approx. assignment[d]
ν	I	ν	A^{th}	
2543/2533	w/br	2535	24.6	ν(N–D)
1839	s/br	1852	587.1	ν(C=O)
1624	w	1636	11.3	ν(C4C3) – ν(C3C2) + ν(C2C7) + ν(C7C6) – ν(C6C5) + ν(C5C4)
1605	s	1608	201.1	ν(C4C3) – ν(C2C7) + ν(C7C6) – ν(C5C4) + ν(C2C1) – ν(C3N)
1459	w	1457	6.0	δ1(C–H) + ν(C7C6) – ν(C5C4)
1437/1436	m	1436	30.8	ν(C3C2) – ν(C6C5), δ2(C–H)
1365	w	1364	18.8	ν(C4C3) – ν(C3C2) + ν(C2C7) – ν(C7C6) + ν(C6C5) – ν(C5C4) – ν(C2C1) – ν(C3N)
1287	m	1284	28.2	δ3(C–H)
1167	w	1167	36.9	ν(C3N) + ν(C1N)
1160	vw	1161	7.2	δ4(C–H)
1069	w	1058	12.9	δ1(ring6)
1004/999	m/br	1004	41.2	δ(N–D), ν(C1N)
946	m	932	31.4	ν(C1N), γ1(C–H)
942	m	928	8.5	γ1(C–H)
-	-	859	4.1	γ2(C–H)
813	vw	804	9.9	δ3(ring6), δ(C=O)
800	w	797	12.8	τ(ring4)
750/745	m/m	744	45.5	γ3(C–H) + δ(ring4)
736	m	735	40.0	γ3(C–H) – δ(ring4)
662	w	661	15.8	γ(C=O), τ1(ring6)

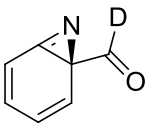
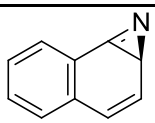
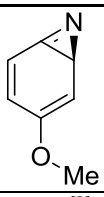
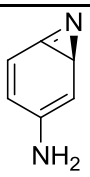
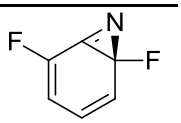
[a] *N*-Deuterated benzoazetinone **4**-d was generated by irradiation of deuterated iminoketene **3**-d at λ = 500 nm in an argon matrix at 10 K. Only bands in the 2600–600 cm^{-1} region having calculated intensities above 3 km mol^{-1} are included. [b] Experimental intensities are presented in qualitative terms: s = strong, m = medium, w = weak, vw = very weak, and br = broad. [c] B3LYP/6-311++G(d,p) calculated scaled frequencies. [d] Assignments made by inspection of Chemcraft animations. Abbreviations: ν = stretching, δ = bending, γ = rocking, and τ = torsion. Signs "+" and "–" designate combinations of vibrations occurring in "syn"-phase ("+") and in "anti"-phase ("–"). [e] For atom numbering see Scheme S1.

Table S4. Relative zero point corrected energies (kJ mol^{-1}) calculated at the B3LYP/6-311++G(d,p) level of theory for different structures of deuterated formylbenzazirine **5**.[a]

Structure				
Name	**5**-d	**5**-d(2)	**5**-d(3)	**5**-d(4)
Relative energy	0.0	10.4	6.6	9.7

[a]Conformers **5**-d and **5**-d(2) can be formed by cyclization of deuterated 2-formylphenynitrene **2**-d "towards" the formyl group. Conformers **5**-d(3) and **5**-d(4) can be formed by cyclization of deuterated 2-formylphenynitrene **2**-d "away" from the formyl group.

Table S5. Comparison between the experimental and the B3LYP/6-311++G(d,p) calculated ν(C=N) vibrational frequencies (cm^{-1}) of different benzazirines.

Structure					
Experimental[a]	1751[this work]	1731[2]	1717[3]	1710[4]	1679[5]
Calculated[b]	1802	1771	1763	1762	1725
Δ[cal.-exp.]	+51	+40	+46	+52	+46

[a]Corresponding to benzazirines isolated in argon matrices: See ref. 2-5. [b]All calculated values were scaled by a common factor of 0.98.

Table S6. Relative zero point corrected energies (kJ mol^{-1}) calculated at the B3LYP/6-311++G(d,p) level of theory for different structures of deuterated formyl cyclic ketenimine **6**.

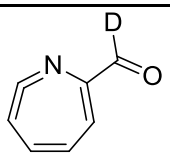
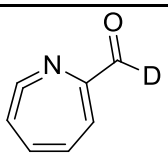
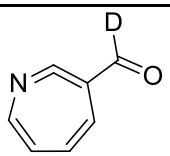
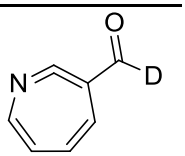
Structure				
Name	**6**-d	**6**-d(2)	**6**-d(3)	**6**-d(4)
Relative energy	14.4	15.6	0.0	9.2

Table S7. Experimental IR spectral data (argon matrix at 10 K), B3LYP/6-311++G(d,p) calculated vibrational frequencies (ν, cm^{-1}), absolute infrared intensities (A^{th}, km mol^{-1}), and vibrational assignment of formylbenzazirine **5**-h.[a]

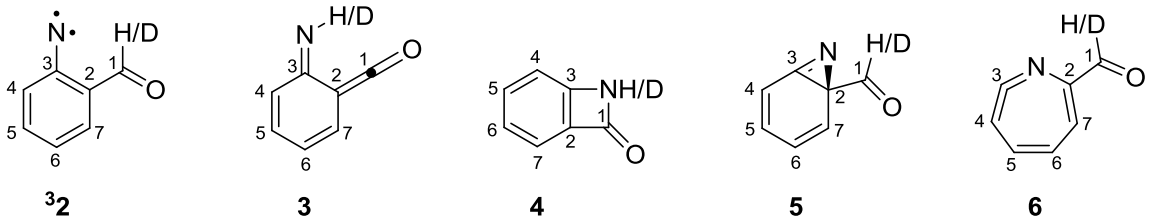
Ar matrix[b]		Calculated[c]		Approx. assignment[d]
ν	I	ν	A^{th}	
2837/2820	ov/br/w	2854	75.1	ν(OC–H)
1765/1747	w/w	1802	34.3	ν(C=N)
1716/1713/1710/1697	m/s/br	1725	337.6	ν(C=O)
1595/1598	ov	1586	3.7	$\nu(C{=}C)_{as}$
1488	w	1484	25.0	$\nu(C{=}C)_{s}$
1418	vw	1416	4.2	δ1(C–H)
1355	m	1350	8.2	δ2(C–H)
1242	s	1226	58.6	ν(C2–C1)
1185	w	1180	4.5	δ3(C–H)
1126	vw	1138	4.5	δ4(C–H)
1091	ov	1077	30.9	$\nu(C3–C2–C1)_{as}$, δ(C–H)
1020	m	1014	24.0	δ1(6-ring)
-	-	946	5.4	γ1(C–H) + ν(C6–C5)
-	-	935	5.3	γ1(C–H) – ν(C6–C5)
802/798	s	796	45.6	γ2(C–H)
775	w	769	7.2	δ2(6-ring)
716/714	s	712	63.7	γ3(C–H)
648	m	654	11.1	τ1(6-ring)

[a]Formylbenzazirine **5**-h was generated by irradiation of triplet 2-formylphenylnitrene ^{3}**2**-h in an argon matrix at 10 K. Only bands in the 2900–600 cm^{-1} region having calculated intensities above 3 km mol^{-1} are included. [b]Experimental intensities are presented in qualitative terms: s = strong, m = medium, w = weak, vw = very weak, br = broad, and ov = overlapped. [c]B3LYP/6-311++G(d,p) calculated scaled frequencies. [d]Assignments made by inspection of Chemcraft animations. Abbreviations: ν = stretching, δ = bending, γ = rocking,, τ = torsion, s = symmetric, and as = antisymmetric. Signs "+" and "–" designate combinations of vibrations occurring in "syn"-phase ("+") and in "anti"-phase ("–"). [e]For atom numbering see Scheme S1.

Table S8. Experimental IR spectral data (argon matrix at 10 K), B3LYP/6-311++G(d,p) calculated vibrational frequencies (ν, cm^{-1}), absolute infrared intensities (A^{th}, km mol^{-1}), and vibrational assignment of formyl cyclic ketenimine **6**-h.[a]

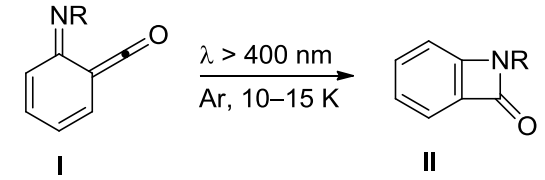
Ar matrix[b]		Calculated[c]		Approx. assignment[d]
ν	I	ν	A^{th}	
2858/2846	w/br/ov	2879	84.5	ν(OC–H)
1883	s	1913	173.9	$\nu(C{=}C{=}N)_{as}$
-	ov	1729	219.1	ν(C=O)
1576	m	1579	54.5	$\nu(C{=}C)_{as}$
1530/1528	m/m	1519	68.1	$\nu(C{=}C)_{s}$
1398	vw	1396	3.4	δ1(C–H) – δ(OC–H)
1378	vw	1373	2.2	δ1(C–H) + δ(OC–H)
1309	vw	1308	4.3	δ2(C–H)
1290/1279	w/m	1281	62.0	δ3(C–H)
1142	w	1130	11.3	ν(C2–C1)
1100	m	1103	44.0	δ4(C–H)
-	-	1035	6.5	ν(C7C6) – ν(C5C4)
969	w	970	15.0	ν(C7C6) + ν(C5C4)
950	w	954	6.1	γ1(C–H)
905	vw	914	5.5	δ1(ring)
-	-	855	3.4	δ2(ring)
791	m	791	18.6	γ2(C–H)
762	s	763	88.7	γ3(C–H)
695/689/648	w/m/m	686	62.7	γ4(C–H)
667	w	674	23.5	δ(C=C=N)
609	vw	616	4.1	τ1(ring)

[a]Formyl cyclic ketenimine **6**-h was generated by spontaneous decay of formylbenzazirine **5**-h in an argon matrix at 10 K. Only bands in the 2900–600 cm^{-1} region having calculated intensities above 2 km mol^{-1} are included. [b]Experimental intensities are presented in qualitative terms: s = strong, m = medium, w = weak, vw = very weak, br = broad, and ov = overlapped. [c]B3LYP/6-311++G(d,p) calculated scaled frequencies. [d]Assignments made by inspection of Chemcraft animations. Abbreviations: ν = stretching, δ = bending, γ = rocking, τ = torsion, s = symmetric, and as = antisymmetric. Signs "+" and "–" designate combinations of vibrations occurring in "syn"-phase ("+") and in "anti"-phase ("–"). [e]For atom numbering see Scheme S1.



^{3}2 **3** **4** **5** **6**

Scheme S1. Atom numbering of triplet 2-formylphenylnitrene **2**, iminoketene **3**, benzoazetinone **4**, formylbenzazirine **5**, and formyl cyclic ketenimine **6**, adopted in this work.



I **II**

R = Me, 2125 cm^{-1} R = Me, 1843 cm^{-1}

R = OMe, 2118 cm^{-1} R = OMe,1857 cm^{-1}

Scheme S2. Previous examples described for photocyclization in argon matrix of iminoketenes **I** into benzoazetinones **II** (R = Me and OMe).[6,7] The frequencies presented correspond to the characteristic $\nu(C{=}C{=}O)_{as}$ and $\nu(C{=}O)$ modes of **I** and **II**, respectively.

Computational Data:

B3LYP/6-311++G(d,p) Calculations

2-Formylphenylnitrene ^{3}**2**-h

Energy = -399.7375001 Ha, ZPE = 0.099968 Ha

C	-1.783368000	0.791600000	-0.000066000
C	-0.373313000	1.075195000	-0.000087000
C	0.547911000	-0.041091000	0.000003000
C	0.052036000	-1.339356000	0.000109000
C	-1.320661000	-1.584394000	0.000131000
C	-2.230365000	-0.511885000	0.000042000
H	-2.472472000	1.626692000	-0.000135000
H	0.763970000	-2.156650000	0.000177000
H	-1.688236000	-2.603555000	0.000215000
H	-3.296069000	-0.711210000	0.000060000
C	2.007217000	0.212559000	-0.000018000
N	0.038007000	2.326835000	-0.000195000
O	2.841097000	-0.667196000	0.000058000
H	2.301234000	1.278684000	-0.000106000

$\tilde{\nu}$	A	$\tilde{\nu}$	A
3203	4.9	1027	1.4
3197	4.2	995	0.4
3186	1.9	979	1.1
3174	2.3	870	0.0
2944	45.7	862	8.2
1753	263.5	816	33.9
1587	43.6	762	63.5
1543	0.1	701	5.2
1450	10.6	632	15.9
1439	4.0	544	4.4
1397	6.2	496	0.0
1324	20.2	477	2.1
1303	16.7	433	4.5
1259	50.8	345	0.5
1180	3.1	247	1.1
1153	30.2	205	7.3
1084	12.9	163	14.8
1038	0.1	112	2.0

2-Formylphenylnitrene ^{3}**2**-d

Energy = -399.7375001 Ha, ZPE = 0.096861 Ha

C	-1.783368000	0.791600000	-0.000066000
C	-0.373313000	1.075195000	-0.000087000
C	0.547911000	-0.041091000	0.000003000
C	0.052036000	-1.339356000	0.000109000
C	-1.320661000	-1.584394000	0.000131000
C	-2.230365000	-0.511885000	0.000042000
H	-2.472472000	1.626692000	-0.000135000
H	0.763970000	-2.156650000	0.000177000
H	-1.688236000	-2.603555000	0.000215000
H	-3.296069000	-0.711210000	0.000060000
C	2.007217000	0.212559000	-0.000018000
N	0.038007000	2.326835000	-0.000195000
O	2.841097000	-0.667196000	0.000058000
D	2.301234000	1.278684000	-0.000106000

$\tilde{\nu}$	A	$\tilde{\nu}$	A
3203	4.9	997	1.2
3197	4.3	985	1.3
3186	1.9	895	0.0
3174	2.3	857	2.8
2176	39.2	854	0.0
1734	274.4	786	29.5
1586	42.2	762	63.4
1541	0.1	694	7.6
1449	11.1	626	17.7
1422	4.7	543	4.7
1324	18.1	495	0.1
1311	4.8	471	2.1
1263	63.8	426	2.8
1183	8.8	344	0.5
1160	29.5	237	0.1
1112	3.9	202	7.2
1039	0.6	148	11.7
1025	0.4	110	3.0

Iminoketene **3**-h

Energy = -399.7773394 Ha, ZPE = 0.102190 Ha

C	-0.029200000	-1.869851000	0.000000000
C	-0.829362000	-0.648096000	0.000000000
C	0.000000000	0.601990000	0.000000000
C	1.455604000	0.554917000	0.000000000
C	2.086875000	-0.638549000	0.000000000
C	1.322823000	-1.865335000	0.000000000
H	-0.596489000	-2.792686000	0.000000000
H	2.008743000	1.486281000	0.000000000
H	3.168904000	-0.681031000	0.000000000
H	1.859053000	-2.808138000	0.000000000
C	-0.615293000	1.783474000	0.000000000
N	-2.114949000	-0.745620000	0.000000000
O	-1.174496000	2.793096000	0.000000000
H	-2.588270000	0.158845000	0.000000000

$\tilde{\nu}$	A	$\tilde{\nu}$	A
3456	7.5	992	14.6
3201	7.6	956	0.0
3196	5.9	866	6.9
3180	1.2	846	0.7
3168	8.9	805	24.1
2193	1180.1	731	82.6
1679	64.8	697	15.9
1600	112.4	688	20.5
1573	123.2	640	1.8
1460	1.7	574	3.4
1419	32.2	546	7.0
1333	47.3	479	15.5
1294	17.2	464	3.6
1249	6.3	382	9.5
1195	36.2	373	0.9
1164	1.5	190	0.5
1072	51.8	136	2.1
1003	0.0	57	0.1

Iminoketene **3**-d

Energy = -399.7773394 Ha, ZPE = 0.098859 Ha

C	-0.029200000	-1.869851000	0.000000000
C	-0.829362000	-0.648096000	0.000000000
C	0.000000000	0.601990000	0.000000000
C	1.455604000	0.554917000	0.000000000
C	2.086875000	-0.638549000	0.000000000
C	1.322823000	-1.865335000	0.000000000
H	-0.596489000	-2.792686000	0.000000000
H	2.008743000	1.486281000	0.000000000
H	3.168904000	-0.681031000	0.000000000
H	1.859053000	-2.808138000	0.000000000
C	-0.615293000	1.783474000	0.000000000
N	-2.114949000	-0.745620000	0.000000000
O	-1.174496000	2.793096000	0.000000000
D	-2.588270000	0.158845000	0.000000000

$\tilde{\nu}$	A	$\tilde{\nu}$	A
3201	7.6	956	0.0
3196	5.9	929	35.1
3180	1.2	834	5.2
3168	8.9	826	23.6
2530	10.1	737	53.6
2193	1 180.4	703	0.8
1678	63.2	696	15.8
1587	123.2	637	2.0
1572	141.9	619	41.0
1460	1.8	572	3.3
1414	23.0	544	4.9
1321	23.8	469	20.3
1258	7.6	444	3.2
1229	6.6	374	10.2
1174	17.6	366	2.4
1147	4.5	188	0.4
1003	0.0	134	2.2
998	0.9	55	0.2

Benzoazetinone **4**-h

Energy = -399.7945314 Ha, ZPE = 0.103625 Ha

C	1.270778000	1.352883000	0.025798000
C	-0.001781000	0.837697000	-0.021422000
C	-0.271712000	-0.535775000	-0.038920000
C	0.718436000	-1.489242000	-0.033321000
C	2.038195000	-0.991370000	0.007681000
C	2.295609000	0.378922000	0.040689000
H	1.497040000	2.411246000	0.048736000
H	0.516264000	-2.553351000	-0.044268000
H	2.870072000	-1.685283000	0.021125000
H	3.326517000	0.713878000	0.075486000
C	-1.748563000	-0.178320000	-0.019941000
N	-1.384179000	1.223136000	-0.135318000
O	-2.811241000	-0.706002000	0.084570000
H	-1.836486000	1.950801000	0.406204000

$\tilde{\nu}$	A	$\tilde{\nu}$	A
3564	29.8	983	0.3
3200	5.0	971	31.8
3197	12.4	949	1.8
3185	6.5	877	3.4
3170	2.2	836	22.6
1891	596.1	814	12.1
1671	10.9	772	9.8
1642	201.6	755	72.3
1487	4.9	680	38.3
1468	29.9	662	13.2
1397	21.7	609	6.0
1318	34.0	521	49.1
1245	9.5	501	21.8
1206	28.4	455	166.9
1184	4.7	392	7.4
1128	1.1	280	0.2
1080	8.7	248	8.2
1010	5.1	138	0.5

Benzoazetinone **4**-d

Energy = -399.7945314 Ha, ZPE = 0.100351 Ha

C	1.270778000	1.352883000	0.025798000
C	-0.001781000	0.837697000	-0.021422000
C	-0.271712000	-0.535775000	-0.038920000
C	0.718436000	-1.489242000	-0.033321000
C	2.038195000	-0.991370000	0.007681000
C	2.295609000	0.378922000	0.040689000
H	1.497040000	2.411246000	0.048736000
H	0.516264000	-2.553351000	-0.044268000
H	2.870072000	-1.685283000	0.021125000
H	3.326517000	0.713878000	0.075486000
C	-1.748563000	-0.178320000	-0.019941000
N	-1.384179000	1.223136000	-0.135318000
O	-2.811241000	-0.706002000	0.084570000
D	-1.836486000	1.950801000	0.406204000

$\tilde{\nu}$	A	$\tilde{\nu}$	A
3200	5.0	983	0.4
3197	12.4	951	31.4
3185	6.5	947	8.5
3170	2.2	876	4.1
2613	24.6	821	9.9
1890	587.1	814	12.8
1669	11.3	759	45.5
1641	201.1	750	40.0
1487	6.0	675	15.8
1465	30.8	650	2.4
1392	18.8	578	2.4
1310	28.2	509	11.7
1191	36.9	489	8.3
1185	7.2	398	19.6
1129	2.8	362	105.6
1080	12.9	279	0.1
1025	41.2	235	15.4
1008	3.3	138	0.5

Benzazirine **5**-h

Energy = -399.712182 Ha, ZPE = 0.100195 Ha

C	-1.753831000	-0.858366000	-0.629140000
C	-0.500584000	-1.139680000	0.002561000
C	0.603487000	-0.152449000	0.239401000
C	0.038774000	1.156567000	0.544643000
C	-1.275408000	1.392321000	0.269049000
C	-2.123683000	0.434046000	-0.413753000
H	-2.337819000	-1.587078000	-1.173729000
H	0.696632000	1.963359000	0.848285000
H	-1.690459000	2.375225000	0.460200000
H	-3.091266000	0.772119000	-0.768733000
C	1.958591000	-0.311421000	-0.319014000
N	0.115351000	-1.453549000	1.042472000
O	2.709406000	0.611357000	-0.541675000
H	2.256127000	-1.365747000	-0.492406000

$\tilde{\nu}$	A	$\tilde{\nu}$	A
3215	0.8	992	3.0
3191	7.1	965	5.4
3178	1.9	955	5.3
3169	2.6	901	2.1
2912	75.1	813	45.6
1839	34.3	785	7.2
1761	337.6	727	63.7
1619	3.7	668	11.1
1515	25.0	602	3.4
1445	4.2	599	3.4
1399	2.5	539	2.7
1378	8.2	463	7.8
1251	58.6	419	0.1
1204	4.5	379	3.8
1161	4.5	291	19.2
1099	30.9	222	14.7
1034	24.0	184	1.2
1008	2.9	101	4.2

Benzazirine **5**-d

Energy = -399.712182 Ha, ZPE = 0.097105 Ha

C	-1.753831000	-0.858366000	-0.629140000
C	-0.500584000	-1.139680000	0.002561000
C	0.603487000	-0.152449000	0.239401000
C	0.038774000	1.156567000	0.544643000
C	-1.275408000	1.392321000	0.269049000
C	-2.123683000	0.434046000	-0.413753000
H	-2.337819000	-1.587078000	-1.173729000
H	0.696632000	1.963359000	0.848285000
H	-1.690459000	2.375225000	0.460200000
H	-3.091266000	0.772119000	-0.768733000
C	1.958591000	-0.311421000	-0.319014000
N	0.115351000	-1.453549000	1.042472000
O	2.709406000	0.611357000	-0.541675000
D	2.256127000	-1.365747000	-0.492406000

$\tilde{\nu}$	A	$\tilde{\nu}$	A
3215	0.8	967	5.0
3191	7.1	955	4.4
3178	1.9	901	2.5
3169	2.6	878	0.6
2152	59.8	799	41.2
1839	34.8	763	4.3
1745	341.3	726	67.4
1619	3.7	662	8.5
1514	26.3	600	1.0
1444	3.9	593	6.3
1378	7.0	538	2.9
1246	57.4	457	6.7
1207	5.5	412	0.4
1162	6.0	375	2.8
1131	22.5	280	22.4
1034	23.3	201	9.0
1017	7.8	181	1.7
992	2.7	101	4.4

Cyclic ketenimine **6**-h

Energy = -399.7187303 Ha, ZPE = 0.100218 Ha

C	-2.132270000	-0.743717000	0.534028000
C	-1.057493000	-1.293120000	0.001548000
C	0.791268000	-0.181057000	-0.146364000
C	0.203914000	1.043037000	-0.030989000
C	-1.192795000	1.397881000	-0.231663000
C	-2.284361000	0.619165000	0.003534000
H	-2.738677000	-1.168828000	1.320383000
H	0.890426000	1.862565000	0.161208000
H	-1.366346000	2.419692000	-0.556161000
H	-3.276997000	1.024158000	-0.177063000
C	2.251140000	-0.391736000	0.013230000
N	0.024372000	-1.308490000	-0.602972000
O	3.032644000	0.467578000	0.354130000
H	2.583421000	-1.421498000	-0.220543000

$\tilde{\nu}$	A	$\tilde{\nu}$	A
3214	0.6	990	15.0
3169	4.6	974	6.1
3157	13.0	932	5.5
3138	5.6	872	3.4
2938	84.5	807	18.6
1952	173.9	778	88.7
1764	219.1	700	62.7
1611	54.5	688	23.5
1550	68.1	628	4.1
1424	3.4	542	5.7
1402	2.2	534	7.3
1335	4.3	441	3.3
1307	62.0	393	0.3
1226	1.5	382	13.9
1153	11.3	310	0.5
1125	44.0	207	5.2
1056	6.5	161	16.3
1025	0.9	104	2.4

Cyclic ketenimine **6**-d

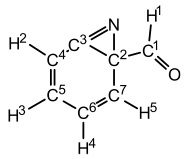
Energy = -399.7187303 Ha, ZPE = 0.097136 Ha

C	-2.132270000	-0.743717000	0.534028000
C	-1.057493000	-1.293120000	0.001548000
C	0.791268000	-0.181057000	-0.146364000
C	0.203914000	1.043037000	-0.030989000
C	-1.192795000	1.397881000	-0.231663000
C	-2.284361000	0.619165000	0.003534000
H	-2.738677000	-1.168828000	1.320383000
H	0.890426000	1.862565000	0.161208000
H	-1.366346000	2.419692000	-0.556161000
H	-3.276997000	1.024158000	-0.177063000
C	2.251140000	-0.391736000	0.013230000
N	0.024372000	-1.308490000	-0.602972000
O	3.032644000	0.467578000	0.354130000
D	2.583421000	-1.421498000	-0.220543000

$\tilde{\nu}$	A	$\tilde{\nu}$	A
3214	0.6	975	5.8
3169	4.7	941	5.5
3157	13.0	890	0.7
3138	5.6	860	3.1
2171	65.6	791	24.2
1952	175.0	772	68.1
1746	236.7	698	67.7
1611	50.5	676	25.9
1550	66.6	621	3.9
1416	1.4	541	5.5
1335	3.9	533	8.1
1314	46.3	430	3.2
1229	6.7	390	1.1
1177	38.0	380	13.2
1133	26.2	309	0.4
1058	4.9	203	4.5
1025	3.7	142	12.2
987	9.4	103	3.1

Tunneling Calculations

Rate constants computed at several temperatures (using *Polyrate* software) for the parent molecule **5** and the respective isotopic substitutions.



Parent

T(K)	TST	CVT	CVT/ZCT	CVT/SCT
6	2.01E-177	1.80E-177	3.41E-08	3.47E-05
8	2.39E-130	2.20E-130	3.41E-08	3.47E-05
10	4.43E-102	4.15E-102	3.41E-08	3.47E-05
20	1.95E-45	1.88E-45	3.66E-08	3.56E-05
30	1.77E-26	1.73E-26	7.62E-08	4.76E-05
40	5.85E-17	5.76E-17	4.67E-07	1.10E-04
50	3.21E-11	3.17E-11	7.82E-06	4.88E-04
75	1.68E-03	1.66E-03	4.81E-02	1.53E-01
100	1.38E+01	1.38E+01	5.82E+01	7.92E+01
125	3.36E+03	3.35E+03	7.51E+03	8.66E+03
150	1.39E+05	1.38E+05	2.31E+05	2.51E+05
175	2.05E+06	2.05E+06	2.91E+06	3.09E+06
200	1.60E+07	1.59E+07	2.06E+07	2.14E+07
225	8.06E+07	8.04E+07	9.73E+07	1.00E+08
250	3.00E+08	2.99E+08	3.46E+08	3.55E+08
273.15	8.26E+08	8.25E+08	9.27E+08	9.47E+08
275	8.90E+08	8.89E+08	9.97E+08	1.02E+09
298.15	2.09E+09	2.09E+09	2.30E+09	2.34E+09
300	2.23E+09	2.23E+09	2.44E+09	2.48E+09
325	4.90E+09	4.90E+09	5.27E+09	5.35E+09
350	9.70E+09	9.70E+09	1.03E+10	1.04E+10
375	1.77E+10	1.77E+10	1.86E+10	1.88E+10
400	3.00E+10	3.00E+10	3.13E+10	3.16E+10

D3

T(K)	TST	CVT	CVT/ZCT	CVT/SCT
6	1.14E-177	1.00E-177	1.16E-08	1.61E-05
8	1.57E-130	1.42E-130	1.16E-08	1.61E-05
10	3.16E-102	2.92E-102	1.16E-08	1.61E-05
20	1.64E-45	1.58E-45	1.26E-08	1.65E-05
30	1.58E-26	1.54E-26	2.93E-08	2.21E-05
40	5.38E-17	5.27E-17	2.17E-07	5.39E-05
50	3.00E-11	2.96E-11	4.57E-06	2.76E-04
75	1.61E-03	1.59E-03	3.97E-02	1.25E-01
100	1.34E+01	1.33E+01	5.08E+01	6.99E+01
125	3.29E+03	3.27E+03	6.59E+03	7.66E+03
150	1.36E+05	1.36E+05	2.04E+05	2.24E+05
175	2.02E+06	2.02E+06	2.61E+06	2.77E+06
200	1.58E+07	1.58E+07	1.86E+07	1.95E+07
225	7.99E+07	7.97E+07	8.91E+07	9.21E+07
250	2.98E+08	2.97E+08	3.20E+08	3.28E+08
273.15	8.22E+08	8.21E+08	8.64E+08	8.82E+08
275	8.86E+08	8.84E+08	9.29E+08	9.48E+08
298.15	2.09E+09	2.08E+09	2.15E+09	2.19E+09
300	2.22E+09	2.22E+09	2.29E+09	2.33E+09
325	4.89E+09	4.89E+09	4.98E+09	5.05E+09
350	9.70E+09	9.68E+09	9.78E+09	9.89E+09
375	1.77E+10	1.76E+10	1.77E+10	1.79E+10
400	3.00E+10	3.00E+10	2.99E+10	3.02E+10

D2

T(K)	TST	CVT	CVT/ZCT	CVT/SCT
6	8.21E-178	7.18E-178	1.73E-08	1.93E-05
8	1.22E-130	1.11E-130	1.73E-08	1.93E-05
10	2.59E-102	2.39E-102	1.73E-08	1.93E-05
20	1.49E-45	1.43E-45	1.87E-08	1.99E-05
30	1.48E-26	1.44E-26	4.09E-08	2.73E-05
40	5.12E-17	5.02E-17	2.88E-07	6.76E-05
50	2.89E-11	2.84E-11	5.63E-06	3.21E-04
75	1.57E-03	1.55E-03	4.03E-02	1.18E-01
100	1.32E+01	1.31E+01	5.09E+01	6.77E+01
125	3.23E+03	3.21E+03	6.65E+03	7.61E+03
150	1.34E+05	1.33E+05	2.07E+05	2.24E+05
175	1.99E+06	1.99E+06	2.64E+06	2.79E+06
200	1.56E+07	1.55E+07	1.88E+07	1.96E+07
225	7.88E+07	7.87E+07	8.99E+07	9.26E+07
250	2.94E+08	2.93E+08	3.22E+08	3.30E+08
273.15	8.12E+08	8.11E+08	8.69E+08	8.86E+08
275	8.74E+08	8.73E+08	9.34E+08	9.52E+08
298.15	2.06E+09	2.06E+09	2.16E+09	2.20E+09
300	2.20E+09	2.19E+09	2.30E+09	2.34E+09
325	4.83E+09	4.83E+09	5.00E+09	5.06E+09
350	9.58E+09	9.57E+09	9.80E+09	9.92E+09
375	1.75E+10	1.75E+10	1.77E+10	1.79E+10
400	2.97E+10	2.97E+10	3.00E+10	3.02E+10

D4

T(K)	TST	CVT	CVT/ZCT	CVT/SCT
6	3.52E-177	3.11E-177	3.21E-08	3.32E-05
8	3.65E-130	3.32E-130	3.21E-08	3.32E-05
10	6.21E-102	5.76E-102	3.21E-08	3.32E-05
20	2.30E-45	2.22E-45	3.45E-08	3.40E-05
30	1.98E-26	1.93E-26	7.22E-08	4.54E-05
40	6.37E-17	6.25E-17	4.49E-07	1.06E-04
50	3.43E-11	3.38E-11	7.63E-06	4.74E-04
75	1.75E-03	1.74E-03	4.88E-02	1.53E-01
100	1.43E+01	1.42E+01	5.96E+01	8.06E+01
125	3.45E+03	3.43E+03	7.69E+03	8.83E+03
150	1.41E+05	1.41E+05	2.36E+05	2.56E+05
175	2.09E+06	2.08E+06	2.97E+06	3.14E+06
200	1.62E+07	1.61E+07	2.09E+07	2.18E+07
225	8.15E+07	8.13E+07	9.87E+07	1.02E+08
250	3.02E+08	3.02E+08	3.51E+08	3.59E+08
273.15	8.33E+08	8.32E+08	9.38E+08	9.57E+08
275	8.97E+08	8.96E+08	1.01E+09	1.03E+09
298.15	2.11E+09	2.11E+09	2.32E+09	2.36E+09
300	2.25E+09	2.24E+09	2.47E+09	2.51E+09
325	4.93E+09	4.93E+09	5.32E+09	5.40E+09
350	9.76E+09	9.75E+09	1.04E+10	1.05E+10
375	1.78E+10	1.77E+10	1.87E+10	1.89E+10
400	3.02E+10	3.01E+10	3.15E+10	3.18E+10

D5

T(K)	TST	CVT	CVT/ZCT	CVT/SCT
6	5.49E-177	4.89E-177	1.23E-08	2.27E-05
8	5.09E-130	4.66E-130	1.23E-08	2.27E-05
10	8.10E-102	7.55E-102	1.23E-08	2.27E-05
20	2.63E-45	2.54E-45	1.34E-08	2.33E-05
30	2.16E-26	2.11E-26	3.13E-08	3.10E-05
40	6.80E-17	6.68E-17	2.44E-07	7.21E-05
50	3.62E-11	3.57E-11	5.20E-06	3.40E-04
75	1.82E-03	1.80E-03	4.32E-02	1.34E-01
100	1.47E+01	1.46E+01	5.57E+01	7.64E+01
125	3.51E+03	3.50E+03	7.22E+03	8.40E+03
150	1.43E+05	1.43E+05	2.22E+05	2.43E+05
175	2.11E+06	2.10E+06	2.80E+06	2.98E+06
200	1.63E+07	1.62E+07	1.98E+07	2.07E+07
225	8.18E+07	8.16E+07	9.38E+07	9.72E+07
250	3.03E+08	3.02E+08	3.34E+08	3.44E+08
273.15	8.33E+08	8.32E+08	8.96E+08	9.17E+08
275	8.97E+08	8.96E+08	9.63E+08	9.85E+08
298.15	2.11E+09	2.10E+09	2.22E+09	2.26E+09
300	2.24E+09	2.24E+09	2.36E+09	2.41E+09
325	4.92E+09	4.91E+09	5.11E+09	5.19E+09
350	9.72E+09	9.71E+09	9.99E+09	1.01E+10
375	1.77E+10	1.76E+10	1.80E+10	1.82E+10
400	3.00E+10	2.99E+10	3.04E+10	3.07E+10

D1

T(K)	TST	CVT	CVT/ZCT	CVT/SCT
6	2.06E-177	1.82E-177	1.26E-08	1.85E-05
8	2.44E-130	2.23E-130	1.26E-08	1.85E-05
10	4.50E-102	4.19E-102	1.26E-08	1.85E-05
20	1.96E-45	1.89E-45	1.38E-08	1.90E-05
30	1.78E-26	1.74E-26	3.28E-08	2.53E-05
40	5.88E-17	5.78E-17	2.42E-07	6.19E-05
50	3.23E-11	3.19E-11	5.19E-06	3.20E-04
75	1.69E-03	1.68E-03	4.56E-02	1.40E-01
100	1.40E+01	1.39E+01	5.69E+01	7.71E+01
125	3.41E+03	3.39E+03	7.34E+03	8.47E+03
150	1.40E+05	1.40E+05	2.26E+05	2.46E+05
175	2.08E+06	2.08E+06	2.86E+06	3.03E+06
200	1.62E+07	1.62E+07	2.02E+07	2.11E+07
225	8.18E+07	8.16E+07	9.59E+07	9.90E+07
250	3.04E+08	3.03E+08	3.42E+08	3.51E+08
273.15	8.38E+08	8.36E+08	9.17E+08	9.37E+08
275	9.02E+08	9.01E+08	9.86E+08	1.01E+09
298.15	2.12E+09	2.12E+09	2.27E+09	2.31E+09
300	2.26E+09	2.26E+09	2.42E+09	2.46E+09
325	4.97E+09	4.96E+09	5.23E+09	5.31E+09
350	9.83E+09	9.82E+09	1.02E+10	1.04E+10
375	1.79E+10	1.79E+10	1.84E+10	1.86E+10
400	3.04E+10	3.04E+10	3.11E+10	3.14E+10

^{13}C4

T(K)	TST	CVT	CVT/ZCT	CVT/SCT
6	1.47E-177	1.31E-177	2.93E-08	3.00E-05
8	1.89E-130	1.73E-130	2.93E-08	3.00E-05
10	3.67E-102	3.42E-102	2.93E-08	3.00E-05
20	1.77E-45	1.71E-45	3.16E-08	3.09E-05
30	1.66E-26	1.62E-26	6.68E-08	4.16E-05
40	5.58E-17	5.49E-17	4.19E-07	9.87E-05
50	3.09E-11	3.05E-11	7.26E-06	4.53E-04
75	1.64E-03	1.62E-03	4.64E-02	1.47E-01
100	1.36E+01	1.35E+01	5.62E+01	7.65E+01
125	3.32E+03	3.30E+03	7.25E+03	8.36E+03
150	1.37E+05	1.37E+05	2.23E+05	2.43E+05
175	2.04E+06	2.03E+06	2.83E+06	2.99E+06
200	1.59E+07	1.58E+07	2.00E+07	2.09E+07
225	8.02E+07	8.00E+07	9.49E+07	9.80E+07
250	2.98E+08	2.98E+08	3.39E+08	3.47E+08
273.15	8.23E+08	8.22E+08	9.09E+08	9.28E+08
275	8.86E+08	8.85E+08	9.77E+08	9.97E+08
298.15	2.09E+09	2.08E+09	2.25E+09	2.29E+09
300	2.22E+09	2.22E+09	2.40E+09	2.44E+09
325	4.89E+09	4.88E+09	5.19E+09	5.26E+09
350	9.68E+09	9.67E+09	1.01E+10	1.03E+10
375	1.76E+10	1.76E+10	1.83E+10	1.85E+10
400	3.00E+10	2.99E+10	3.09E+10	3.11E+10

^{13}C3

T(K)	TST	CVT	CVT/ZCT	CVT/SCT
6	2.62E-178	2.35E-178	1.85E-08	1.85E-05
8	5.20E-131	4.80E-131	1.85E-08	1.85E-05
10	1.31E-102	1.23E-102	1.85E-08	1.85E-05
20	1.06E-45	1.02E-45	1.99E-08	1.90E-05
30	1.18E-26	1.15E-26	4.15E-08	2.55E-05
40	4.32E-17	4.25E-17	2.61E-07	5.93E-05
50	2.52E-11	2.49E-11	4.73E-06	2.71E-04
75	1.43E-03	1.42E-03	3.59E-02	1.06E-01
100	1.23E+01	1.22E+01	4.79E+01	6.40E+01
125	3.06E+03	3.04E+03	6.45E+03	7.38E+03
150	1.28E+05	1.28E+05	2.03E+05	2.21E+05
175	1.92E+06	1.91E+06	2.61E+06	2.76E+06
200	1.51E+07	1.50E+07	1.87E+07	1.95E+07
225	7.65E+07	7.64E+07	8.95E+07	9.23E+07
250	2.86E+08	2.86E+08	3.21E+08	3.29E+08
273.15	7.92E+08	7.91E+08	8.66E+08	8.84E+08
275	8.53E+08	8.52E+08	9.31E+08	9.50E+08
298.15	2.01E+09	2.01E+09	2.16E+09	2.19E+09
300	2.15E+09	2.14E+09	2.29E+09	2.33E+09
325	4.73E+09	4.73E+09	4.98E+09	5.05E+09
350	9.39E+09	9.38E+09	9.77E+09	9.89E+09
375	1.71E+10	1.71E+10	1.77E+10	1.78E+10
400	2.91E+10	2.91E+10	2.98E+10	3.01E+10

$^{13}C2$

T(K)	TST	CVT	CVT/ZCT	CVT/SCT
6	8.41E-178	7.61E-178	2.96E-08	2.83E-05
8	1.25E-130	1.16E-130	2.96E-08	2.83E-05
10	2.63E-102	2.48E-102	2.96E-08	2.83E-05
20	1.50E-45	1.46E-45	3.19E-08	2.90E-05
30	1.49E-26	1.46E-26	6.58E-08	3.87E-05
40	5.14E-17	5.06E-17	3.98E-07	8.90E-05
50	2.89E-11	2.86E-11	6.72E-06	3.97E-04
75	1.57E-03	1.56E-03	4.28E-02	1.31E-01
100	1.32E+01	1.31E+01	5.30E+01	7.15E+01
125	3.24E+03	3.22E+03	6.91E+03	7.95E+03
150	1.34E+05	1.34E+05	2.14E+05	2.33E+05
175	2.00E+06	2.00E+06	2.73E+06	2.89E+06
200	1.56E+07	1.56E+07	1.94E+07	2.02E+07
225	7.91E+07	7.90E+07	9.24E+07	9.54E+07
250	2.95E+08	2.94E+08	3.31E+08	3.39E+08
273.15	8.14E+08	8.13E+08	8.89E+08	9.07E+08
275	8.77E+08	8.76E+08	9.56E+08	9.75E+08
298.15	2.07E+09	2.06E+09	2.21E+09	2.25E+09
300	2.20E+09	2.20E+09	2.35E+09	2.39E+09
325	4.84E+09	4.84E+09	5.09E+09	5.16E+09
350	9.60E+09	9.60E+09	9.98E+09	1.01E+10
375	1.75E+10	1.75E+10	1.80E+10	1.82E+10
400	2.97E+10	2.97E+10	3.04E+10	3.07E+10

$^{13}C6$

T(K)	TST	CVT	CVT/ZCT	CVT/SCT
6	1.77E-177	1.58E-177	3.26E-08	3.33E-05
8	2.17E-130	2.00E-130	3.27E-08	3.33E-05
10	4.10E-102	3.83E-102	3.27E-08	3.33E-05
20	1.87E-45	1.81E-45	3.51E-08	3.42E-05
30	1.72E-26	1.68E-26	7.36E-08	4.57E-05
40	5.74E-17	5.64E-17	4.55E-07	1.06E-04
50	3.16E-11	3.12E-11	7.67E-06	4.73E-04
75	1.66E-03	1.65E-03	4.75E-02	1.50E-01
100	1.37E+01	1.36E+01	5.75E+01	7.80E+01
125	3.34E+03	3.33E+03	7.43E+03	8.55E+03
150	1.38E+05	1.37E+05	2.29E+05	2.49E+05
175	2.04E+06	2.04E+06	2.89E+06	3.06E+06
200	1.59E+07	1.59E+07	2.04E+07	2.12E+07
225	8.02E+07	8.01E+07	9.66E+07	9.97E+07
250	2.98E+08	2.98E+08	3.44E+08	3.53E+08
273.15	8.23E+08	8.22E+08	9.21E+08	9.41E+08
275	8.87E+08	8.85E+08	9.91E+08	1.01E+09
298.15	2.09E+09	2.08E+09	2.28E+09	2.32E+09
300	2.22E+09	2.22E+09	2.43E+09	2.47E+09
325	4.89E+09	4.88E+09	5.25E+09	5.32E+09
350	9.68E+09	9.67E+09	1.03E+10	1.04E+10
375	1.76E+10	1.76E+10	1.85E+10	1.87E+10
400	2.99E+10	2.99E+10	3.11E+10	3.14E+10

$^{13}C7$

T(K)	TST	CVT	CVT/ZCT	CVT/SCT
6	1.90E-177	1.70E-177	2.67E-08	2.81E-05
8	2.29E-130	2.11E-130	2.67E-08	2.81E-05
10	4.28E-102	4.01E-102	2.67E-08	2.81E-05
20	1.91E-45	1.85E-45	2.89E-08	2.89E-05
30	1.75E-26	1.71E-26	6.20E-08	3.91E-05
40	5.80E-17	5.71E-17	3.99E-07	9.15E-05
50	3.19E-11	3.15E-11	7.06E-06	4.17E-04
75	1.67E-03	1.66E-03	4.66E-02	1.46E-01
100	1.38E+01	1.37E+01	5.66E+01	7.69E+01
125	3.36E+03	3.34E+03	7.30E+03	8.41E+03
150	1.38E+05	1.38E+05	2.25E+05	2.44E+05
175	2.05E+06	2.04E+06	2.84E+06	3.00E+06
200	1.60E+07	1.59E+07	2.01E+07	2.09E+07
225	8.05E+07	8.04E+07	9.52E+07	9.83E+07
250	2.99E+08	2.99E+08	3.39E+08	3.48E+08
273.15	8.26E+08	8.25E+08	9.11E+08	9.29E+08
275	8.89E+08	8.88E+08	9.79E+08	9.99E+08
298.15	2.09E+09	2.09E+09	2.26E+09	2.30E+09
300	2.23E+09	2.23E+09	2.40E+09	2.44E+09
325	4.90E+09	4.90E+09	5.19E+09	5.27E+09
350	9.70E+09	9.70E+09	1.02E+10	1.03E+10
375	1.77E+10	1.77E+10	1.83E+10	1.85E+10
400	3.00E+10	3.00E+10	3.09E+10	3.12E+10

$^{13}C5$

T(K)	TST	CVT	CVT/ZCT	CVT/SCT
6	1.79E-177	1.59E-177	2.80E-08	2.97E-05
8	2.19E-130	2.01E-130	2.80E-08	2.97E-05
10	4.13E-102	3.86E-102	2.80E-08	2.97E-05
20	1.88E-45	1.82E-45	3.03E-08	3.05E-05
30	1.73E-26	1.69E-26	6.47E-08	4.14E-05
40	5.75E-17	5.65E-17	4.10E-07	9.86E-05
50	3.17E-11	3.12E-11	7.17E-06	4.51E-04
75	1.66E-03	1.65E-03	4.66E-02	1.48E-01
100	1.38E+01	1.37E+01	5.64E+01	7.70E+01
125	3.35E+03	3.33E+03	7.26E+03	8.38E+03
150	1.38E+05	1.38E+05	2.23E+05	2.43E+05
175	2.05E+06	2.04E+06	2.82E+06	2.99E+06
200	1.59E+07	1.59E+07	2.00E+07	2.08E+07
225	8.05E+07	8.03E+07	9.48E+07	9.79E+07
250	2.99E+08	2.99E+08	3.38E+08	3.47E+08
273.15	8.26E+08	8.25E+08	9.07E+08	9.27E+08
275	8.89E+08	8.88E+08	9.75E+08	9.96E+08
298.15	2.09E+09	2.09E+09	2.25E+09	2.29E+09
300	2.23E+09	2.23E+09	2.39E+09	2.44E+09
325	4.90E+09	4.90E+09	5.18E+09	5.26E+09
350	9.71E+09	9.70E+09	1.01E+10	1.03E+10
375	1.77E+10	1.77E+10	1.83E+10	1.85E+10
400	3.00E+10	3.00E+10	3.08E+10	3.11E+10

$^{13}C1$

T(K)	TST	CVT	CVT/ZCT	CVT/SCT
6	2.01E-177	2.01E-177	1.25E-07	1.03E-04
8	2.40E-130	2.40E-130	1.25E-07	1.03E-04
10	4.44E-102	4.44E-102	1.25E-07	1.03E-04
20	1.95E-45	1.95E-45	1.32E-07	1.05E-04
30	1.77E-26	1.77E-26	2.37E-07	1.31E-04
40	5.86E-17	5.86E-17	1.15E-06	2.62E-04
50	3.22E-11	3.22E-11	1.65E-05	1.00E-03
75	1.69E-03	1.68E-03	8.26E-02	2.60E-01
100	1.39E+01	1.39E+01	8.53E+01	1.17E+02
125	3.39E+03	3.39E+03	9.70E+03	1.13E+04
150	1.40E+05	1.40E+05	2.74E+05	3.01E+05
175	2.07E+06	2.07E+06	3.27E+06	3.50E+06
200	1.61E+07	1.61E+07	2.23E+07	2.34E+07
225	8.13E+07	8.13E+07	1.03E+08	1.07E+08
250	3.02E+08	3.02E+08	3.61E+08	3.72E+08
273.15	8.34E+08	8.34E+08	9.56E+08	9.80E+08
275	8.98E+08	8.98E+08	1.03E+09	1.05E+09
298.15	2.11E+09	2.11E+09	2.35E+09	2.40E+09
300	2.25E+09	2.25E+09	2.49E+09	2.55E+09
325	4.95E+09	4.95E+09	5.35E+09	5.45E+09
350	9.80E+09	9.80E+09	1.04E+10	1.06E+10
375	1.78E+10	1.78E+10	1.87E+10	1.89E+10
400	3.03E+10	3.03E+10	3.14E+10	3.18E+10

^{15}N

T(K)	TST	CVT	CVT/ZCT	CVT/SCT
6	3.02E-177	2.73E-177	3.07E-08	3.31E-05
8	3.25E-130	3.02E-130	3.07E-08	3.31E-05
10	5.66E-102	5.33E-102	3.07E-08	3.31E-05
20	2.20E-45	2.13E-45	3.31E-08	3.40E-05
30	1.92E-26	1.88E-26	6.97E-08	4.51E-05
40	6.21E-17	6.12E-17	4.34E-07	1.02E-04
50	3.37E-11	3.33E-11	7.43E-06	4.48E-04
75	1.73E-03	1.72E-03	4.78E-02	1.49E-01
100	1.42E+01	1.41E+01	5.86E+01	7.90E+01
125	3.42E+03	3.41E+03	7.56E+03	8.69E+03
150	1.40E+05	1.40E+05	2.32E+05	2.52E+05
175	2.08E+06	2.07E+06	2.93E+06	3.10E+06
200	1.61E+07	1.61E+07	2.06E+07	2.15E+07
225	8.13E+07	8.11E+07	9.76E+07	1.01E+08
250	3.02E+08	3.01E+08	3.47E+08	3.56E+08
273.15	8.31E+08	8.30E+08	9.29E+08	9.48E+08
275	8.95E+08	8.94E+08	9.98E+08	1.02E+09
298.15	2.10E+09	2.10E+09	2.30E+09	2.34E+09
300	2.24E+09	2.24E+09	2.44E+09	2.49E+09
325	4.92E+09	4.92E+09	5.28E+09	5.35E+09
350	9.74E+09	9.73E+09	1.03E+10	1.04E+10
375	1.77E+10	1.77E+10	1.86E+10	1.88E+10
400	3.01E+10	3.01E+10	3.13E+10	3.15E+10

^{17}O

T(K)	TST	CVT	CVT/ZCT	CVT/SCT
6	2.02E-177	1.80E-177	3.14E-08	3.12E-05
8	2.40E-130	2.21E-130	3.14E-08	3.12E-05
10	4.45E-102	4.15E-102	3.14E-08	3.12E-05
20	1.95E-45	1.88E-45	3.39E-08	3.21E-05
30	1.77E-26	1.73E-26	7.15E-08	4.36E-05
40	5.86E-17	5.76E-17	4.42E-07	1.04E-04
50	3.22E-11	3.18E-11	7.51E-06	4.67E-04
75	1.68E-03	1.67E-03	4.65E-02	1.48E-01
100	1.39E+01	1.38E+01	5.55E+01	7.60E+01
125	3.38E+03	3.37E+03	7.06E+03	8.19E+03
150	1.40E+05	1.39E+05	2.17E+05	2.37E+05
175	2.07E+06	2.06E+06	2.74E+06	2.91E+06
200	1.61E+07	1.61E+07	1.94E+07	2.03E+07
225	8.13E+07	8.11E+07	9.26E+07	9.57E+07
250	3.02E+08	3.02E+08	3.31E+08	3.40E+08
273.15	8.34E+08	8.33E+08	8.90E+08	9.09E+08
275	8.98E+08	8.97E+08	9.57E+08	9.78E+08
298.15	2.11E+09	2.11E+09	2.21E+09	2.25E+09
300	2.25E+09	2.25E+09	2.35E+09	2.40E+09
325	4.95E+09	4.94E+09	5.10E+09	5.18E+09
350	9.80E+09	9.79E+09	1.00E+10	1.01E+10
375	1.78E+10	1.78E+10	1.81E+10	1.83E+10
400	3.03E+10	3.03E+10	3.05E+10	3.08E+10

Optimized Cartesian coordinates computed at the M06-2X/6-311+G(2d,p) level for benzazirine **5**, cyclic ketenimine **6** and the respective transition state **TS**.

5

C	1.746477	-0.856670	-0.639318
C	0.499136	-1.135978	0.007469
C	-0.604684	-0.162972	0.258702
C	-0.047328	1.151797	0.542414
C	1.259364	1.383081	0.271207
C	2.108664	0.426669	-0.417777
N	-0.103189	-1.411261	1.057470
C	-1.952855	-0.322061	-0.311493
O	-2.677493	0.603531	-0.564404
H	2.319229	-1.577631	-1.202374
H	3.067173	0.773645	-0.784339
H	1.673693	2.365685	0.456531
H	-0.705778	1.958592	0.841617
H	-2.264691	-1.372910	-0.465718

TS

C	1.811099	-0.824650	-0.677907
C	0.712350	-1.227123	0.023033
C	-0.688238	-0.130454	0.303807
C	-0.099865	1.120612	0.386884
C	1.276112	1.363937	0.308447
C	2.163813	0.475637	-0.302034
N	-0.053898	-1.324842	0.973952
C	-2.050476	-0.350052	-0.215355
O	-2.787705	0.543735	-0.539874
H	2.305066	-1.416332	-1.431192
H	3.140798	0.845487	-0.591941
H	1.624068	2.372099	0.488573
H	-0.779396	1.965626	0.337026
H	-2.360382	-1.410307	-0.262384

6

C	-2.112682	-0.743251	0.551520
C	-1.046822	-1.275887	0.002792
C	0.783307	-0.179037	-0.154717
C	0.205861	1.034500	-0.026701
C	-1.193789	1.386292	-0.239865
C	-2.274747	0.613860	0.002383
N	0.021990	-1.305864	-0.613506
C	2.245503	-0.387812	0.005547
O	3.005321	0.470222	0.366293
H	-2.686274	-1.160673	1.363231
H	-3.267473	1.007042	-0.191721
H	-1.365821	2.398128	-0.590124
H	0.891858	1.848978	0.182999
H	2.591441	-1.406192	-0.245944

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