Electronic Supplementary Information

Bond-Shift Isomers: The Co-existence of Allenic and Propargylic Phenylnitrile Imines

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I. EXPERIMENTAL SECTION

Sample. A commercial sample of 5-phenyltetrazole (purity >98%) was used.

Matrix Isolation FTIR Spectroscopy. The sample 5-phenyltetrazole was put in a miniature glass oven placed in the vacuum chamber of the cryostat. Matrices were then prepared by co-deposition of sample vapors, from the sublimation of 5-phenyltetrazole at ∼330 K, with a large excess of argon (N60) or krypton (N48) onto a CsI window cooled to 15–20 K. The temperature was measured directly at the sample holder window by a silicon diode sensor connected to a digital controller providing stabilization accuracy of 0.1 K. A closed-cycle helium cryostat system was used in the experiments. The mid-IR spectra were recorded with a resolution of 0.5 cm^{-1}, using an FTIR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector and a Ge/KBr beam splitter. The NIR spectra were recorded with a resolution of 1 cm^{-1}, using the same spectrometer and a mercury cadmium telluride (MCT-B) detector with a CaF_2 beam splitter. Modifications of the sample compartment of the spectrometer were done to accommodate the cryostat head and allow purging of the instrument by a stream of dry air to avoid interference from atmospheric H_2O and CO_2.

UV-Laser Irradiation Experiments. The matrixes were irradiated through an outer quartz window of the cryostat, using tunable narrow-band light (full width at half-maximum (fwhm) ~0.2 cm^{-1}) provided by a frequency-doubled signal beam from an optical parametric oscillator (OPO) pumped with a pulsed Nd:YAG laser (repetition rate = 10 Hz, pulse energy ~1-3 mJ, duration = 10 ns).

Calculations. All calculations were carried out using GAUSSIAN 09.[1] The geometries of the local minima were optimized using the TIGHT convergence criteria, and their harmonic vibrational frequencies were calculated at the same level of theory (DFT/B3LYP, MP2 and CASSCF with the use of both augmented triple-ξ and quadruple-ξ Pople or Dunning basis sets). The nature of stationary points was confirmed by the analysis of the corresponding Hessian matrices. To correct for the vibrational anharmonicity, basis set truncation and the neglected part of electron correlation, the harmonic vibrational frequencies calculated at the B3LYP/6-311++G(d,p) level were scaled by factors of 0.980 and 0.950, in the ranges below and above 2000 cm^{-1}, respectively.[2]

It has been reported that B3LYP calculated vibrational frequencies describe well the experimental IR spectra of several unstable nitrile imines, in particular the stretching vibrations of (CNN) fragment that is usually used to identify these species.[3] The data presented in Table S5 show that ν(CNN) harmonic vibrational frequencies calculated at the B3LYP/6-311++G(d,p) level, scaled by 0.950, have a good match with the experimental data of several nitrile imines isolated in argon matrixes in previous studies and support the choice of the scaling factor in the present work.

The calculated frequencies, together with infrared intensities, were then used to simulate the spectra by convoluting each peak with a Lorentzian function with fwhm equal to 2 cm^{-1}. The SYNSPEC software was used for this purpose.[10] In these simulations, the integrated band intensities were kept equal to the theoretically predicted absolute intensities. As a result of the broadening (fwhm = 2 cm^{-1}), the peak intensities in the simulated spectra were automatically reduced by factor of 0.3183 when compared to the absolute calculated infrared intensities (in km mol^{-1}).

Vertical excitation energies of the low-energy electronic excited states were calculated using the time-dependent density functional theory (TD-DFT).[4,5]

A complete active space (CAS) SCF method[6] was carried out to confirm the mono-determinantal nature of both **2A** and **2P** nitrile imine forms and then to justify the use of the mono-determinantal DFT (B3LYP) and MP2 approaches. The CASSCF wavefunction developed in this work is formed from a complete distribution of n active electrons in a set of m active orbitals. The results obtained both indicate that the choice of the active space may be of a decisive importance for the convergence properties of the CASSCF calculations and that the two **2A** and **2P** states are, in all cases, monodeterminantal. In particular, in the largest (n=14, m=12) case, an analysis reveals that none of the excited configurations contributes by more than 1.7% to the wavefunction (for a total that does not exceed 14% in the case of the **2P** form, and 16% for the **2A** form).

II. IR SPECTRA

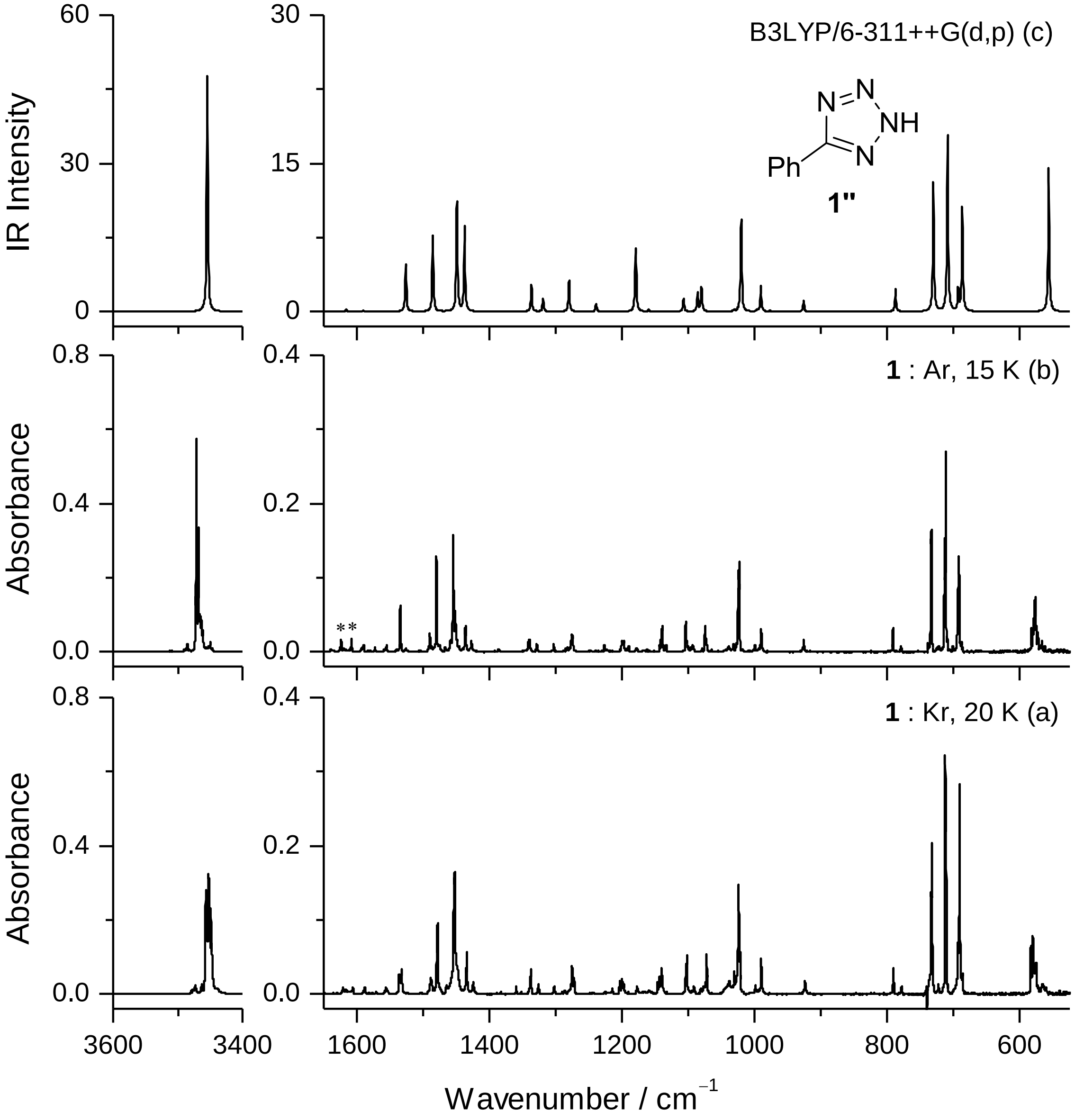

Figure S1. Experimental FTIR spectrum of 5-phenyltetrazole **1** isolated in (a) a krypton matrix at 20 K and (b) an argon matrix at 15 K. Asterisks designate bands due to matrix-isolated water monomer. (c) Simulated IR spectrum of 5-phenyl-2*H*-tetrazole **1''** using B3LYP/6-311++G(d,p) calculated scaled harmonic frequencies (see experimental section for details of simulations).

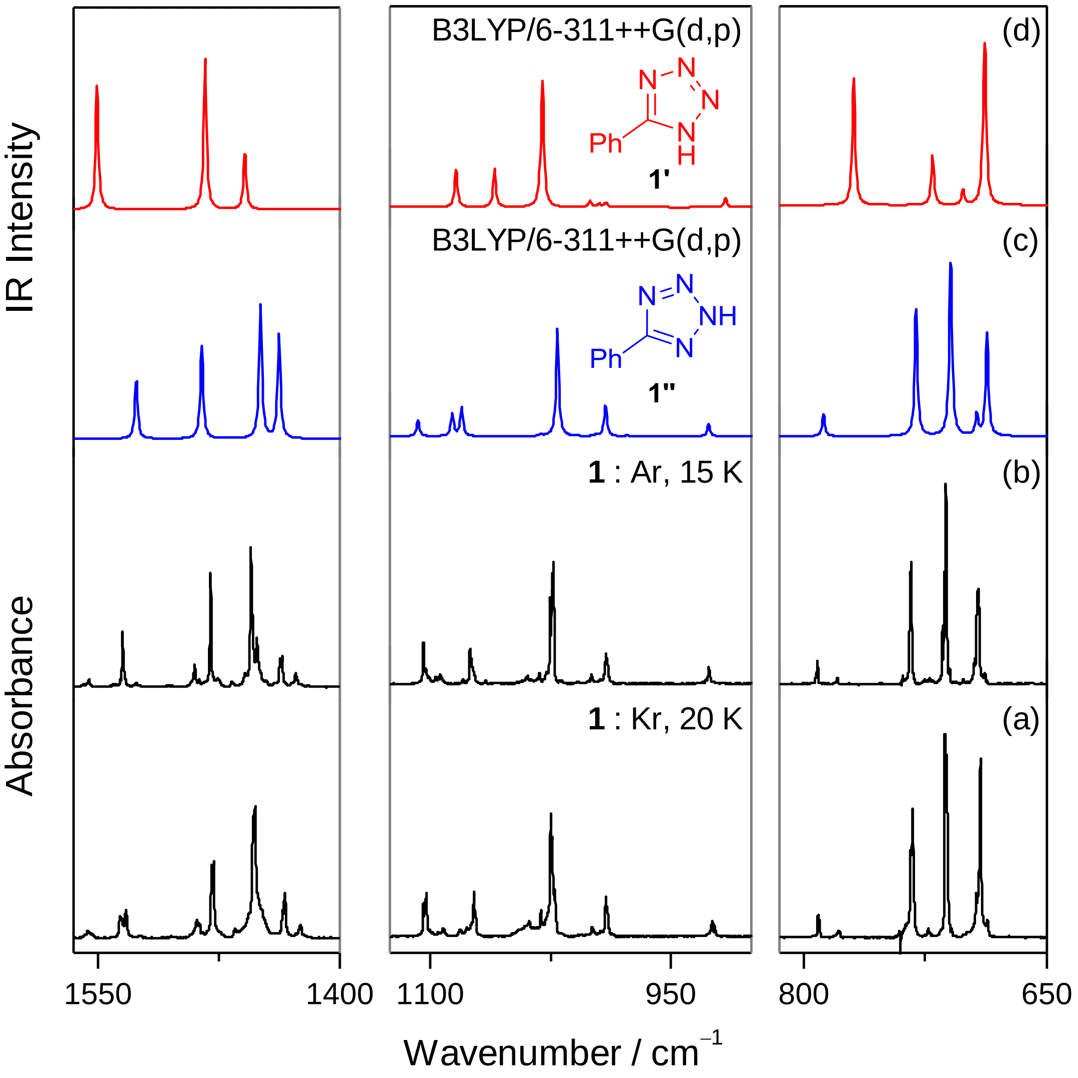

Figure S2. Selected regions of the IR spectrum of 5-phenyltetrazole **1** isolated in (a) a krypton matrix at 20 K and (b) an argon matrix at 15 K, compared with (c) the simulated IR spectrum of 5-phenyl-2*H*-tetrazole **1''** (blue) and (d) 5-phenyl-1*H*-tetrazole **1'** (red) using calculated harmonic frequencies at B3LYP/6-311++G(d,p) level. The 2*H*:1*H* tautomer ratio (same as **1'':1'**) estimated from the B3LYP/6-311++G(d,p) calculated Gibbs energies was found to be 98:2. This ratio is in concordance with a very good agreement between the experimental IR spectrum and the calculated IR spectrum for 5-phenyl-2*H*-tetrazole **1''** (See Figure S1 for other spectral ranges).

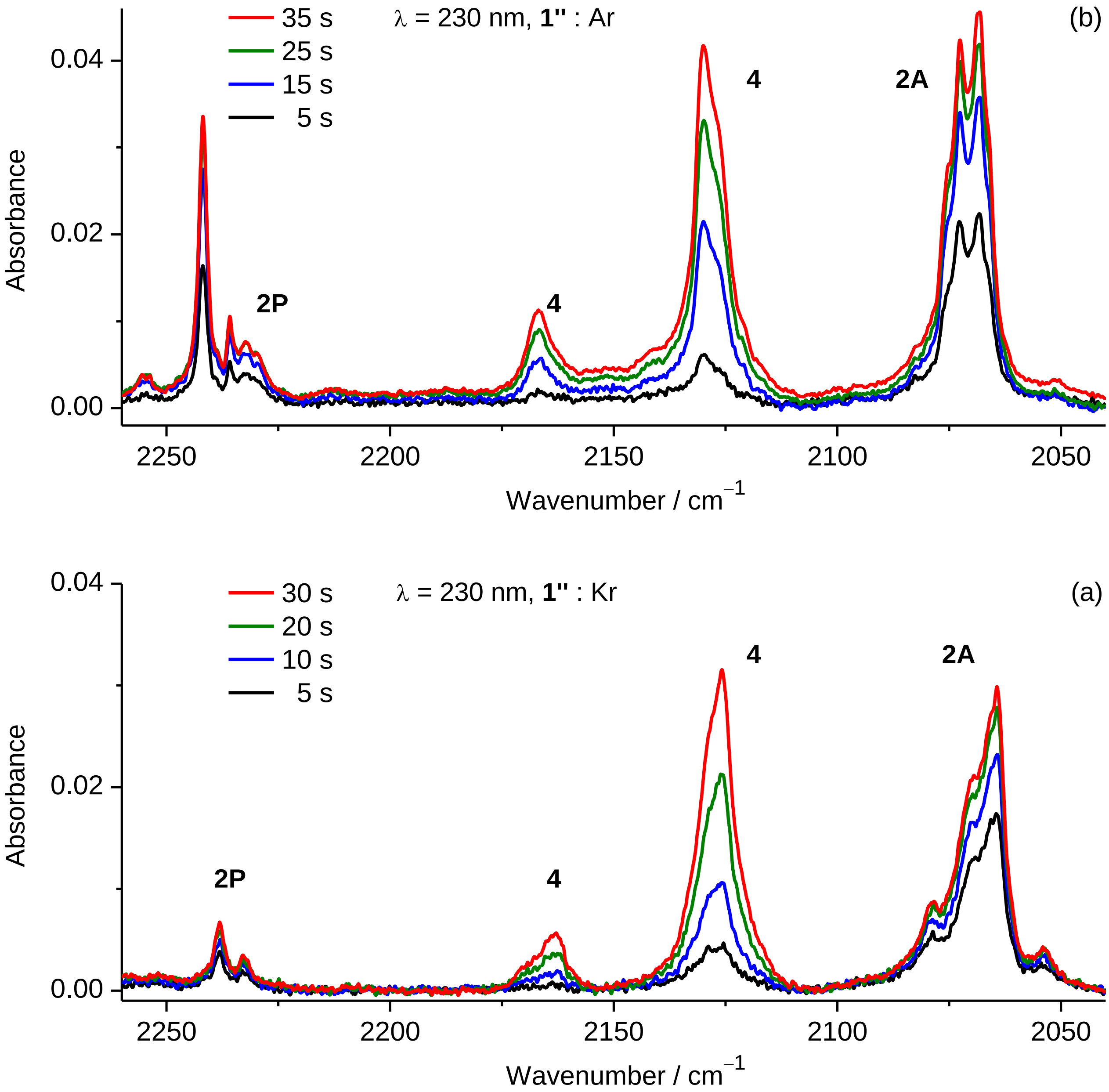

Figure S3. Experimental IR spectra obtained after a series of UV irradiations at 230 nm of 5-phenyl-2*H*-tetrazole **1''** isolated in (a) a krypton matrix at 20 K and (b) an argon matrix at 15 K. Labels **2A**, **2P**, and **4** indicate the most characteristic bands due three distinct photoproducts. From the kinetics of the photochemistry, **2A** and **2P** were characterized as primary photoproducts of **1''** and **4** as a secondary photoproduct (see the manuscript discussion for more details). See next page for frames (c) and (d) of this figure.

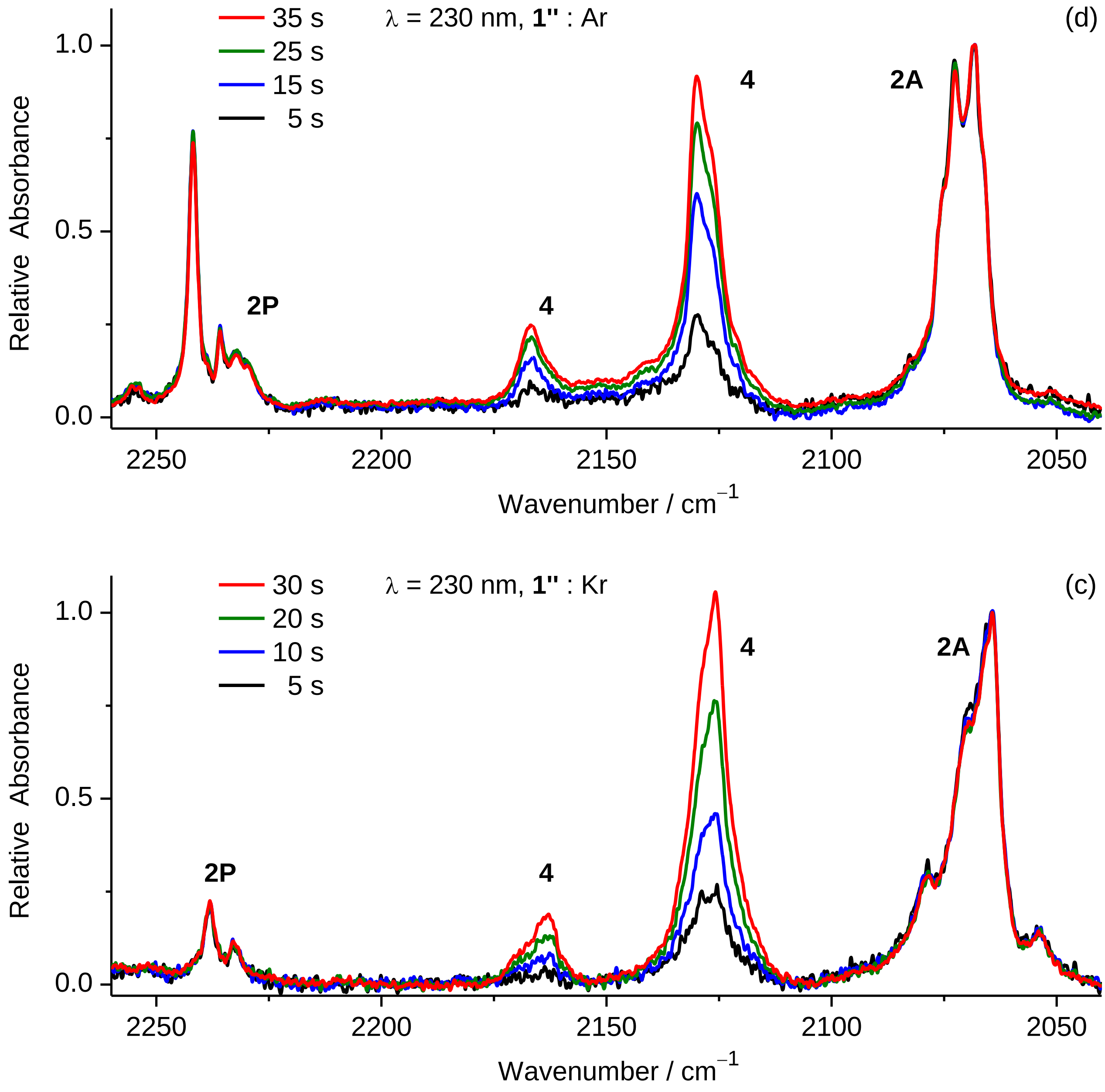

Figure S3 (continued).

Experimental IR spectra obtained after a series of UV irradiations at 230 nm of 5-phenyl-2*H*-tetrazole **1''** isolated in (c) a krypton matrix at 20 K and (d) an argon matrix at 15 K show the same results as those depicted in frames (a) and (b), respectively (see previous page for details). In frames (c) and (d) the peak value of the photoproduct **2A** has been normalized to unity at all irradiation stages. Note similarities in kinetics of formation of **2A** and **2P** and their difference from kinetics of **4**. See the caption to frames (a) and (b) for other details.

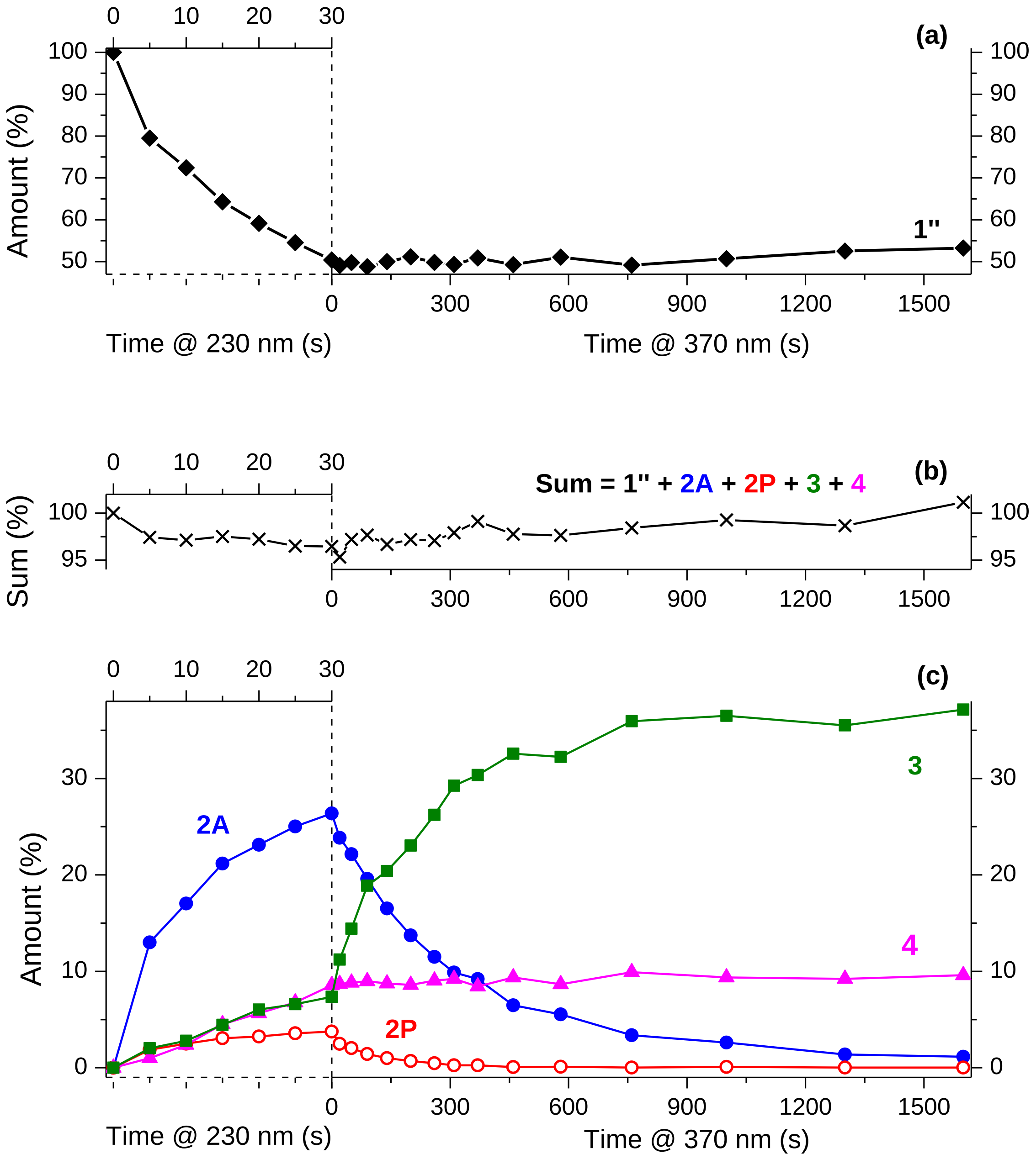

Figure S4. Normalized amounts of 5-phenyl-tetrazole (**1''**) and of its photoproducts generated in the course of UV irradiations of **1''** isolated in an Ar matrix, at 230 nm for 30 seconds (left frames) and at 370 nm for additional 1600 seconds (right frames). The change in wavelength is designated by the vertical dashed line. Note different linear abscissa scales for irradiation at different wavelengths. The normalization procedure is described on the next page.

(a) - amount of the reagent **1''**; (b) - sum of amounts of the reagent (**1''**) and of its photoproducts; (c) - individual amounts of photoproducts (**2A**, **2P**, **3**, and **4**); (d) - see next page.

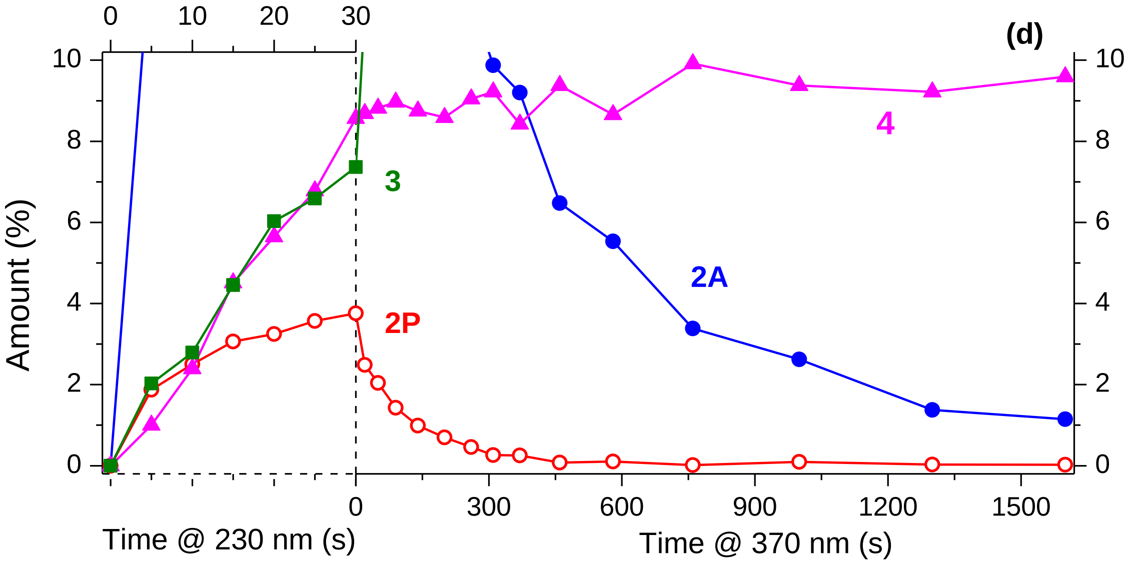

Figure S4 (continued).
(d) – the same as frame (c) with the ordinate axis expanded to show the 0-10% range.

Normalization procedure used in construction of Figure S4**.**

After we had established the spectral signatures of 5-phenyl-tetrazole **1''**, and its photoproducts **2A**, **2P**, **3** and **4**, their amounts were followed as functions of the irradiation time and wavelength, using the following procedure. Initially, the integrated absorption of selected bands (5-phenyl-tetrazole **1''**: 1534.5; 1480; 734; 714/712 cm^{-1}; propargylic nitrile imine **2P**: 2242, 1237 cm^{-1}; allenic nitrile imine **2A**: 2073/2068, 1256 cm^{-1}; 1*H*-diazirine **3**: 1787, 1205/1203, 1174, 1057, 969/966 cm^{-1}; phenylcarbodiimide **4**: 2167/2130 cm^{-1}), not overlapping with absorptions due to the other isomers, was measured. In the next step, the experimental intensities of these bands were divided by the corresponding calculated infrared intensities (i.e., were ‘‘reduced’’). After that, the results for each compound were averaged. As the final step, the amounts of every species (in ‘‘reduced’’ arbitrary units) were multiplied by a common unique scaling factor chosen so that the amount of **1''** prior to the irradiation would be equal to 100% (i.e., ‘‘normalized’’). Figure S4 includes reduced and normalized amounts of **1''** and its photoproducts **2-4**. Note: The amount of **1''**, with respect to its initial amount, besides the assessment using reduced intensities, was also measured directly (without resort to calculated infrared intensities) by comparison of experimental band intensities measured before any irradiation and at a certain stage of the monitored photochemical process.

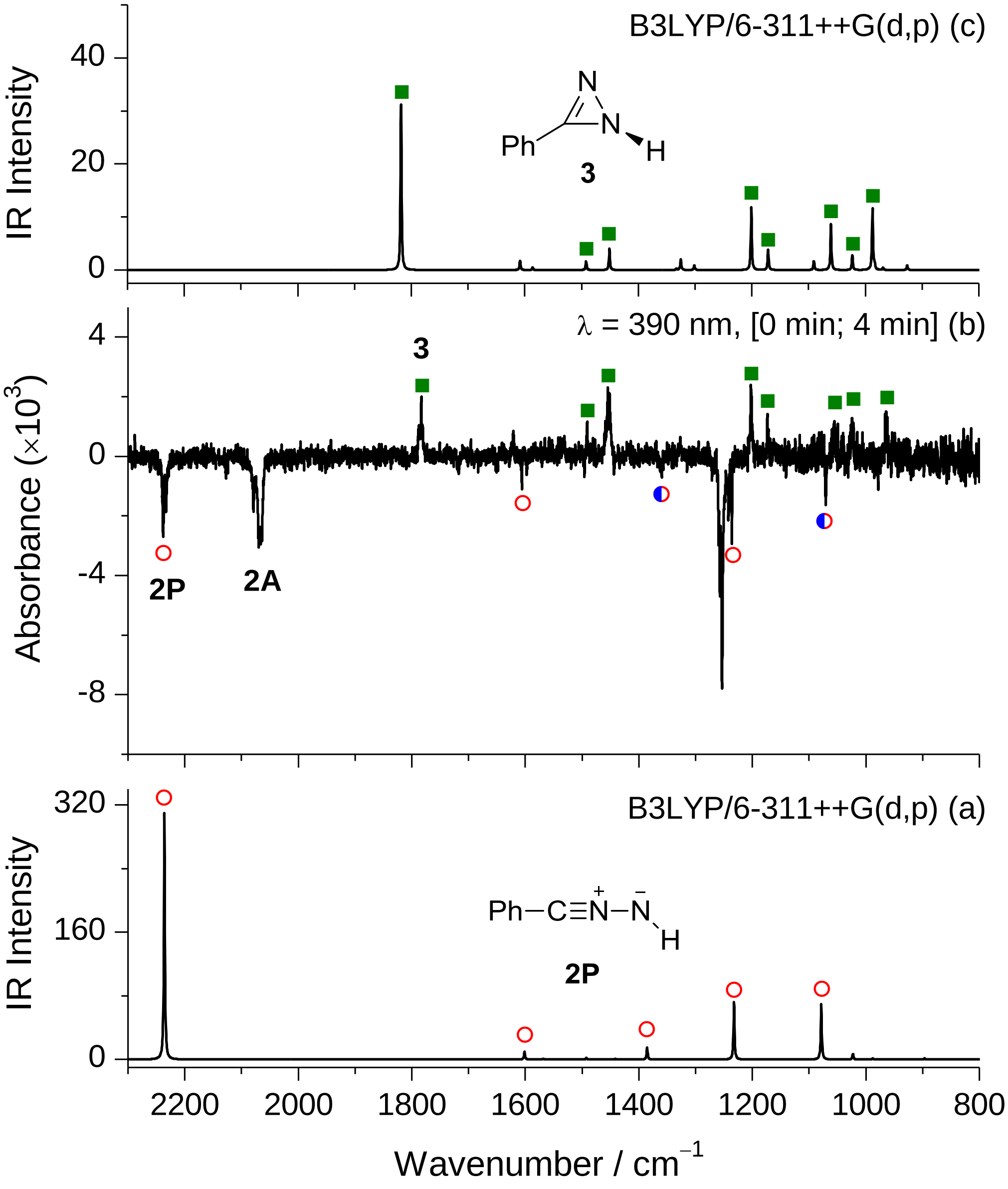

Figure S5. (a) Simulated IR spectrum of propargylic nitrile imine **2P** using data from B3LYP/6-311++G(d,p) harmonic calculation. (b) Experimental difference IR spectrum in a krypton matrix showing changes after irradiation at λ = 390 nm (4 min) (subsequent to the irradiation of 5-phenyl-2*H*-tetrazole **1''** at λ = 230 nm). The negative bands labeled with red open circles are due to the consumed photoproduct assigned to propargylic nitrile imine **2P**. The bands labeled with green squares are assigned to 1*H*-diazirine **3** growing at the expense of photoproducts **2P** and **2A**. The bands labelled in half with red open circles and in half with blue filled circles are assigned to both photoproducts **2P** and **2A**. (c) Simulated IR spectrum of 1*H*-diazirine **3** using data from B3LYP/6-311++G(d,p) harmonic calculation.

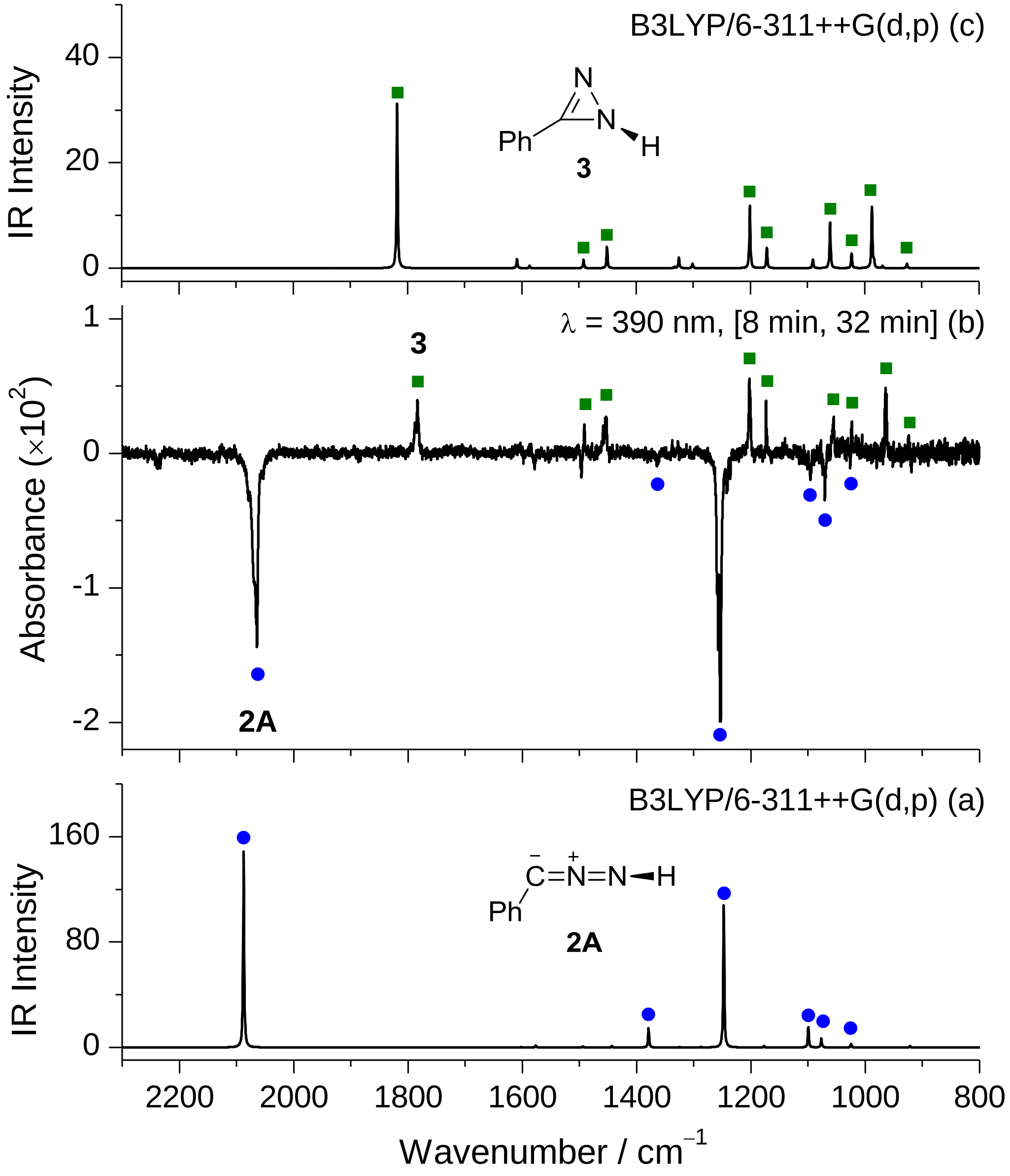

Figure S6. (a) Simulated IR spectrum of allenic nitrile imine **2A** using data from B3LYP/6-311++G(d,p) harmonic calculation. (b) Experimental difference IR spectrum in a krypton matrix showing changes after irradiation at λ = 390 nm for +24 min (subsequent to a set of 8 min irradiations at λ = 390 nm, which makes a total irradiation time of 32 min). The negative bands labeled with blue filled circles are due to the consumed photoproduct assigned to allenic nitrile imine **2A**. The bands labeled with green squares are assigned to 1*H*-diazirine **3** growing at the expense of photoproduct **2A**. (c) Simulated IR spectrum of 1*H*-diazirine **3** using data from B3LYP/6-311++G(d,p) harmonic calculation.

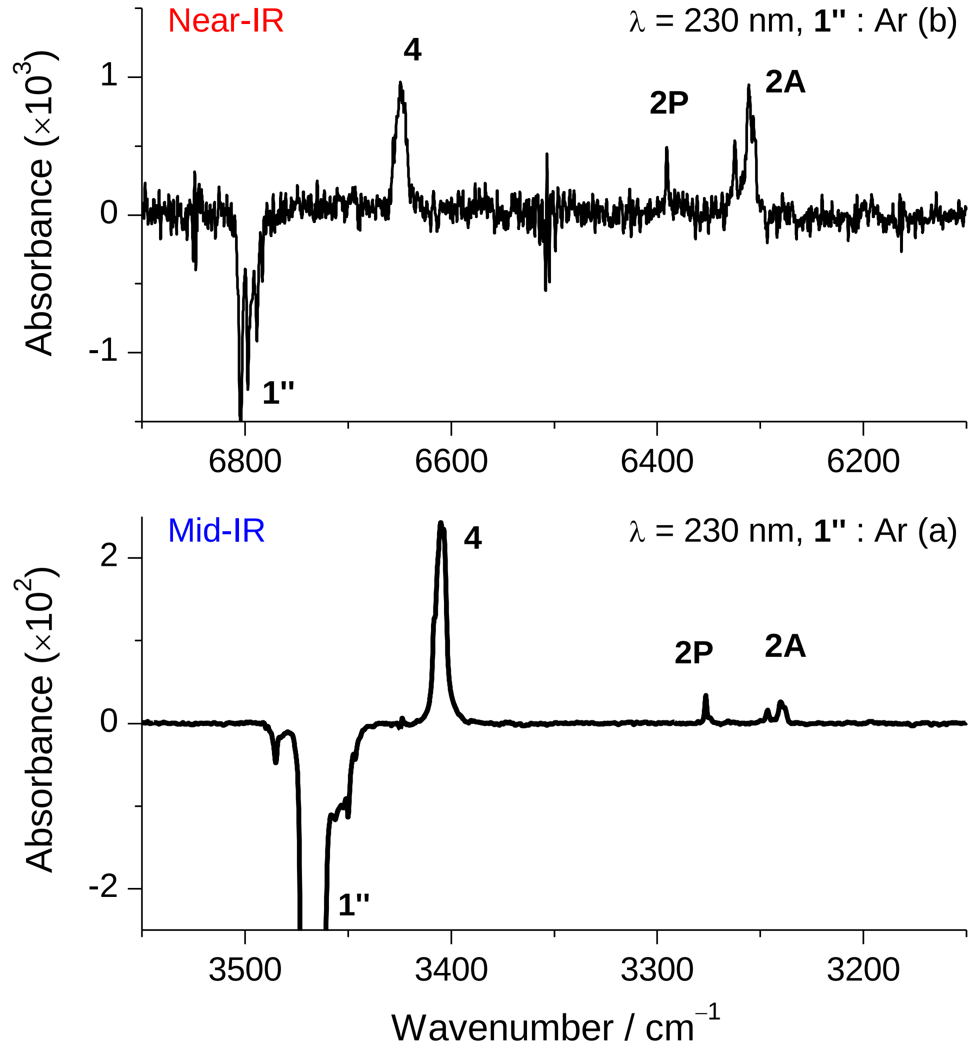

Figure S7. Experimental difference spectra, obtained as the spectrum after UV irradiation at λ = 230 nm of 5-phenyl-2*H*-tetrazole **1''** isolated in an argon matrix at 15 K “minus” the spectrum of the sample before irradiation. (a) The 3550-3150 cm^{-1} region (Mid-IR) showing the ν(N–H) fundamental bands of 5-phenyl-2*H*-tetrazole **1''** (negative band) and of photoproducts (labeled as **2P**, **2A** and **4**; See Scheme 2). (b) The 6900–6100 cm^{-1} region (Near-IR) showing the bands due to the 2ν(N–H) overtones of the same species.

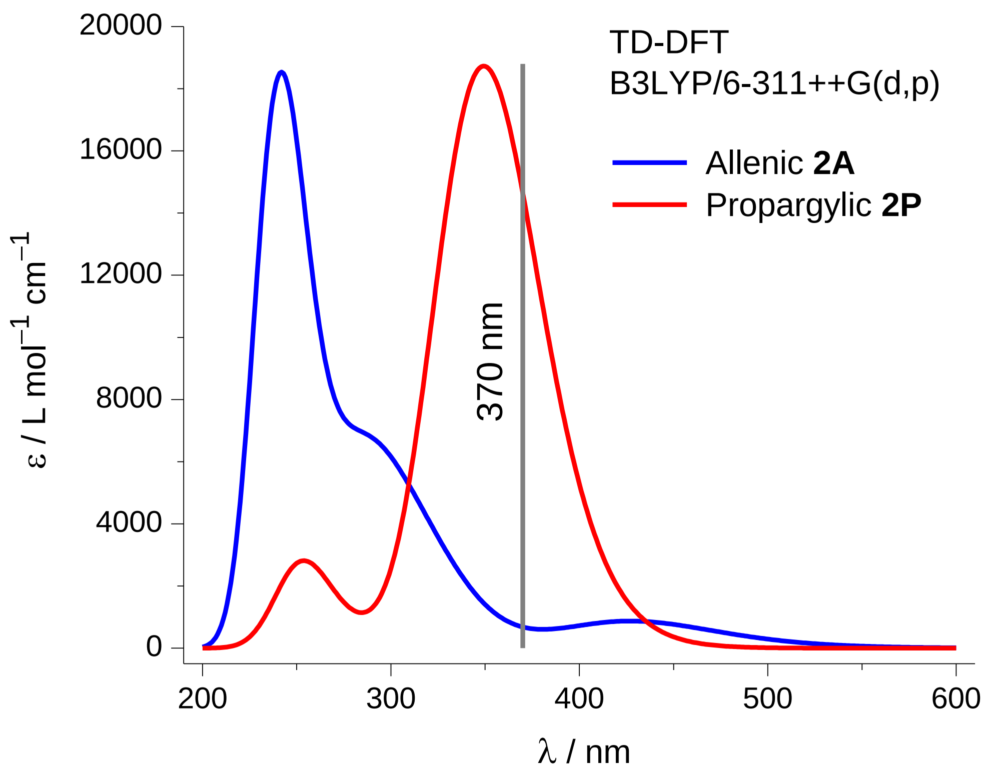

Figure S8. Simulated UV-vis spectra of allenic nitrile imine **2A** (blue) and propargylic nitrile imine **2P** (red) obtained in TD-DFT calculations, at the B3LYP/6-311++G(d,p) level, considering the twelve lowest singlet and twelve lowest triplet excited states. The calculated vertical transition wavelengths and oscillator strengths are given in Table S6. The simulated spectra were constructed from these data as described in Refs. 7 and 8. Vertical bar at 370 nm shows the position of narrow-band UV-irradiation implemented in this study.

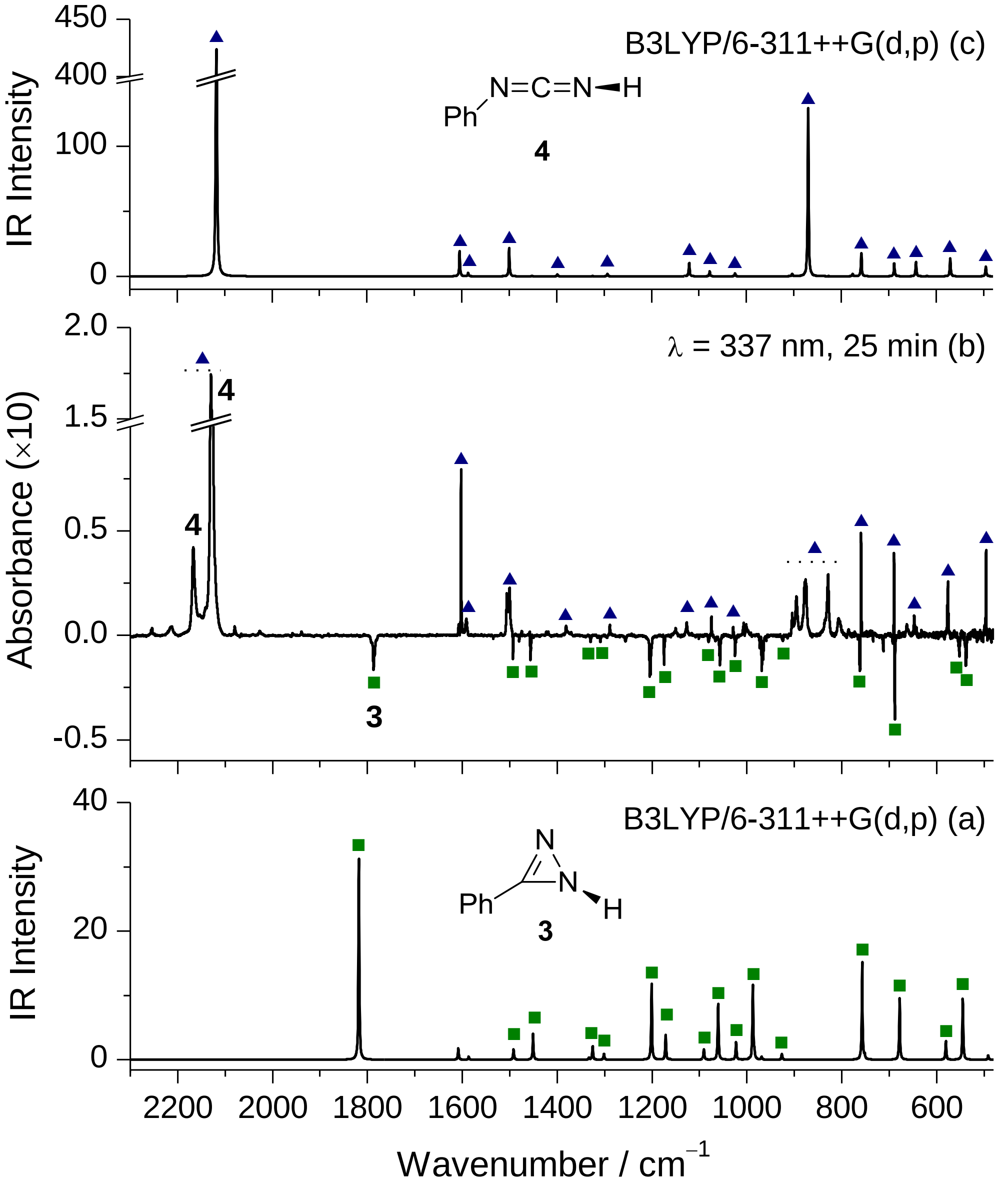

Figure S9. (a) Simulated IR spectrum of 1*H*-diazirine **3** using data from B3LYP/6-311++G(d,p) harmonic calculation. (b) Experimental difference IR spectrum showing changes in an argon matrix after irradiation at λ = 337 nm (25 min, 30 mW) (subsequent to the irradiation of photoproduct at λ = 370 nm; see Figure 2c in the main part). The negative bands labeled with green squares are assigned to the consumed photoproduct, 1*H*-diazirine **3**. The bands labeled with blue triangles are assigned to growing carbodiimide **4**, formed at the expense of 1*H*-diazirine **3**. (c) Simulated IR spectrum of carbodiimide **4** using data from B3LYP/6-311++G(d,p) harmonic calculation. The rectangle with gray background (in the 2300-1700 cm^{-1} range) indicates the most characteristic bands of photoproducts.

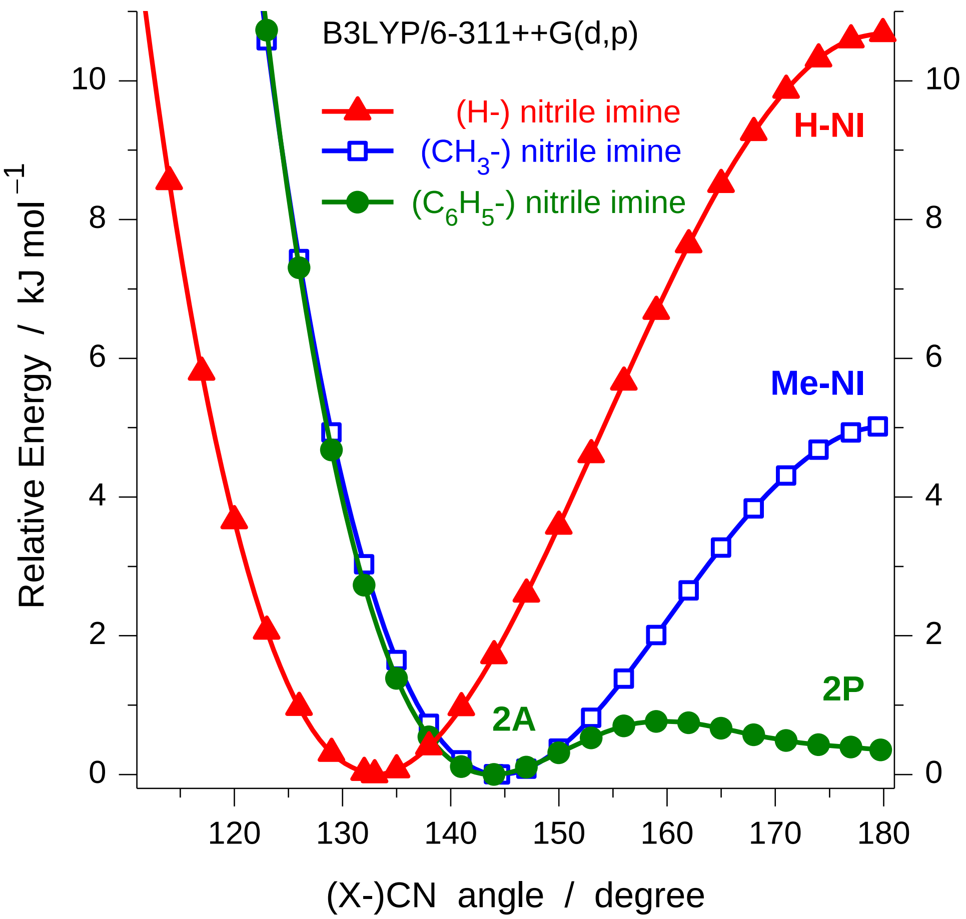

Figure S10. B3LYP/6-311++G(d,p) calculated relaxed potential energy scans, as functions of the (X-)CN angle of phenylnitrile imine (green circles, X=C), methylnitrile imine (blue squares, X=C), and parent nitrile imine (red triangles, X=H). Along the scans, the value of the CCN or the HCN angle was incrementally fixed in steps of 3 degrees, and all other geometrical parameters were fully optimized. Similar results are obtained at all other computational levels. Note a well-defined single (allenic-type) minimum for methylnitrile imine (Me-NI) and for the parent nitrile imine (H-NI), and a very shallow double-minimum potential for phenylnitrile imine. Table S4 shows relative electronic and relative zero-point corrected energies of **2A** and **2P** calculated at different theory levels. Note that the zero-point vibrational energy correction results in a lower energy of **2P** as compared to **2A** at all theory levels studied. Relative zero energy for each compound was selected at the allenic minimum.

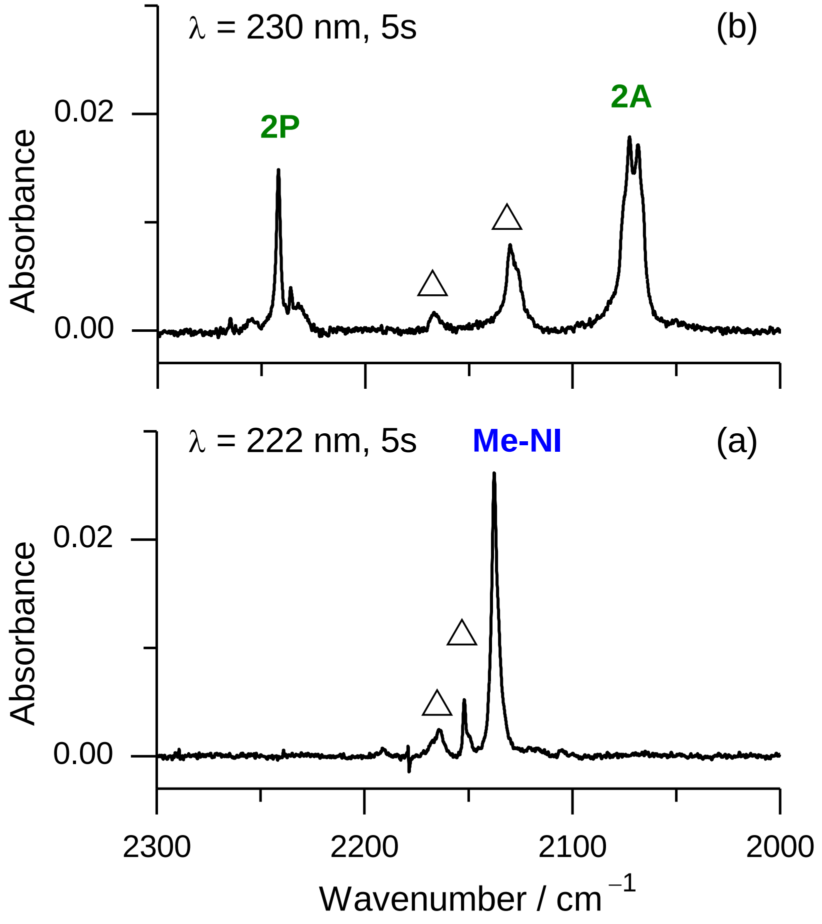

Figure S11. (a) Experimental IR spectrum of photoproducts formed after 5 seconds of UV irradiation at λ = 222 nm of 5-**methyl**-2*H*-tetrazole (5-Me-Tet) isolated in an argon matrix. (b) Experimental IR spectrum of photoproducts formed after 5 seconds of UV irradiation at λ = 230 nm of 5-**phenyl**-2*H*-tetrazole (5-Ph-Tet) isolated in an argon matrix. The band due to the main primary photoproduct of 5-Me-Tet is designated **Me-NI** (methylnitrile-imine); the bands due to main primary photoproducts of 5-Ph-Tet are designated **2P** and **2A**. The doublet bands due to one of the secondary photoproducts (carbodiimide) are designated with triangles (△). Compare with the calculated potential energy profiles of the two nitrile imines shown in Figure S10. Note: experimental spectrum of the parent nitrile imine HCNNH isolated in an argon matrix at 12 K can be found in Reference 11 (same as reference 5c of the main part). In the spectral range shown in Figure S11, HCNNH exhibits only one, very well-defined band centered at 2032.7 cm^{-1}.[11]

III. TABLES

Table S1. Relative zero-point energies ($\Delta E_{ZPE,}$ kJ mol^{-1}) and relative Gibbs free energies at 298 K ($\Delta G_{298K,}$ kJ mol^{-1}), calculated at the B3LYP/6-311++G(d,p), MP2/6-311++G(d,p) and CBS-QB3 levels, and the equilibrium populations of 5-phenyl-2*H*-tetrazole **1’’** and 5-phenyl-1*H*-tetrazole **1’** tautomers estimated from the relative Gibbs free energies at 298 K (P_{298}, %).

Structure	B3LYP			MP2			CBS-QB3		
	ΔE_{ZPE}	ΔG_{298K}	P_{298}	ΔE	ΔG_{298K}	P_{298}	ΔE	ΔG_{298K}	P_{298}
1’’	0.0	0.0	98	0.0	0.0	100	0.0	0.0	90
1’	11.1	10.3	2	17.0	17.3	0	10.2	5.4	10

Table S2. Experimental IR spectrum (argon matrix at 15 K), and calculated B3LYP/6-311++G(d,p) vibrational frequencies ($\tilde{\nu}$, cm^{-1}) and infrared intensities (A, km mol^{-1}) of 3-phenyl-1*H*-diazirine **3**.[a]

Ar matrix[b]		Calculated[c]	
$\tilde{\nu}$	I	$\tilde{\nu}$	A
1787	s	1818	101.8
1602	w	1608	5.8
1587	w	1586	1.5
1493	m	1492	5.2
1456	m	1451	13.1
-		1333	1.0
1330	w	1325	6.9
1309	w	1301	3.0
1257	w	-	-
1205/1203	s/s	1201	38.0
1174	m	1171	12.6
-	-	1163	0.3
1081	w	1091	5.6
1057	m	1061	28.6
1025	m	1023	8.9
-	-	995	0.4
973/969/966	w/m/m	987	37.1
		984	3.4
960	vw	969	1.5
924	vw	926	3.0
-	-	842	0.03
762/761	m/m	757	48.6
-	-	751	1.7
712	w	-	-
688	s	678	30.9
-	-	618	0.1
552	m	581	9.3
539/537	m	545	31.1

[a] The table includes only bands in the 2300–500 cm^{-1} region. [b] Experimental intensities (I) are presented in qualitative terms: s = strong, m = medium, w = weak, vw = very weak. [c] B3LYP/6-311++G(d.p) calculated harmonic frequencies scaled by a factor of 0.980.

Table S3. Experimental IR spectrum (argon matrix at 15 K), and calculated B3LYP/6-311++G(d,p) vibrational frequencies ($\tilde{\nu}$, cm^{-1}) and infrared intensities (A, km mol^{-1}) of phenylcarbodiimide **4**.[a]

Ar matrix[b]		Calculated[c]	
$\tilde{\nu}$	I	$\tilde{\nu}$	A
2167/2130	m/s	2117	1379.1
1603	s	1605	60.6
1591	w	1587	8.8
1506/1500	m/m	1500	67.9
-	-	1452	1.2
1381	w	1398	4.3
-	-	1325	0.6
1281	w	1293	6.2
-	-	1173	0.1
1150 (?)	vw	1158	0.0
1127	w	1121	33.5
1075	w	1077	11.6
1029	vw	1024	6.9
1006/1001 (?)	vw	996	0.3
-	-	977	0.1
-	-	961	0.1
904	w	903	6.4
896/877/829/807	m/m/m/w	870	428.5
-	-	827	0.1
786	vw	776	6.3
760	m	758	59.2
690	m	688	32.7
663	vw	-	-
647	w	643	34.9
-		619	0.6
576	m	570	44.4
500	m	495	24.4

[a] The table includes only bands in the 2300–500 cm^{-1} region. [b] Experimental intensities (I) are presented in qualitative terms: s = strong, m = medium, w = weak and very weak = vw. [c] B3LYP/6-311++G(d.p) calculated harmonic frequencies were scaled by factors of 0.980 and 0.950, in the ranges below and above 2000 cm^{-1}, respectively.

Table S4. Absolute (E_{el}) and relative (ΔE_{el}) electronic energies for phenylnitrile imines **2A** and **2P** calculated at various levels of theory.[a]

Method	Basis set	E_{el} (Hartree) **2A**	E_{el} (Hartree) **2P**	ΔE_{el} (kJ mol^{-1})
B3LYP	6-311++G(d,p)	-379.8676315	-379.8674861	-0.38
	6-311++G(3df,3pd)	-379.8978588	-379.8980148	0.41
	cc-pVTZ	-379.9016496	-379.9013769	-0.72
	aug-cc-pVTZ	-379.9072417	-379.9073388	0.25
	cc-pVQZ	-379.9303431	-379.9302185	-0.33
	aug-cc-pVQZ	-379.9328071	-379.9328560	0.13
CASSCF(14,12)	cc-pVTZ	-377.6443552	-377.6455027	3.01

[a] $\Delta E_{el} = E_{el}$ (**2A**) – E_{el} **(2P)**

Table S4 (continued). Absolute (E_{ZPE}) and relative (ΔE_{ZPE}) zero-point corrected energies for phenylnitrile imines **2A** and **2P** calculated at various levels of theory.[b]

Method	Basis set	E_{ZPE} (Hartree) **2A**	E_{ZPE} (Hartree) **2P**	ΔE_{ZPE} (kJ mol^{-1})
B3LYP	6-311++G(d,p)	-379.753804	-379.754147	0.90
	6-311++G(3df,3pd)	-379.783807	-379.784470	1.74
	cc-pVTZ	-379.787355	-379.787746	1.03
	aug-cc-pVTZ	-379.793103	-379.793696	1.56
	cc-pVQZ	-379.816142	-379.816685	1.43
CASSCF(14,12)	cc-pVTZ	-377.522755	-377.524438	4.42

[b] $\Delta E_{ZPE} = E_{ZPE}$ (**2A**) – E_{ZPE} **(2P)**

Table S5. Calculated B3LYP/6-311++G(d,p) harmonic frequencies and experimental infrared wavenumbers (cm^{-1}) of the CNN moiety of nitrile imines R'−CNN−R'' in the 2400-2000 cm^{-1} range.[a]

Substituents		Structure	B3LYP/6-311++G(d,p)[b]		Argon matrix[c]	Δ
R'	R''	type [a]	ω_{unscaled}(CNN)	ω_{scaled}(CNN)	ν_{exp}(CNN)	($\omega_{\text{scaled}} - \nu_{\text{exp}}$)
H	H	A	2128	2021	2033	-12
Me	H	A	2228	2117	2138	-21
Ph	H	2A	2197	2087	2073/2068	14/19
Ph	Me	A	2140	2033	2032	1
Ph	H	2P	2354	2236	2242/2236	-6/0
Ph	$Si(CH_3)_3$	P	2352	2234	2245	-11
Ph	Ph	P	2341	2224	2242	-18

[a] The canonic structures that describe better the type of structure of the nitrile imine are denoted by A for the allenic type and P for the propargylic type.

[b] Calculated harmonic frequencies were scaled by a factor of 0.950. The least-squares linear fit of the experimental versus calculated ν(CNN) frequencies gives a value of 0.953; thus supporting the choice of the scale factor used in this work.

[c] Experimental values were taken from ref. 3.

Table S6. TD-DFT calculated, at the B3LYP/6-311++G(d,p) level, vertical transition wavelengths (λ/nm) and oscillator strengths (*f*) for the lowest twelve excited singlet states and lowest twelve excited triplet states of phenylnitrile imines **2A** and **2P**.

Allenic phenylnitrile imine **2A**				Propargylic phenylnitrile imine **2P**			
Mult.[a]	λ_{calc}	λ_{sc} [b]	*f*	Mult.[a]	λ_{calc}	λ_{sc} [b]	*f*
T	447.36	540.70	0	T	511.94	624.33	0
T	402.29	482.34	0	T	335.40	395.71	0
T	364.05	432.81	0	T	332.51	391.97	0
S	360.34	428.01	0.0214	S	306.11	357.78	0.0002
T	296.10	344.82	0	S	299.68	349.46	0.4287
T	287.67	333.90	0	S	298.18	347.51	0.0333
T	278.11	321.52	0	T	297.33	346.41	0
S	276.83	319.86	0.0546	T	274.61	316.99	0
T	273.09	315.02	0	S	270.88	312.16	0.0012
S	273.05	314.97	0.0058	T	269.89	310.88	0
T	255.22	291.88	0	T	261.06	299.44	0
S	253.60	289.78	0.1022	T	259.39	297.28	0
T	252.05	287.77	0	T	252.56	288.44	0
S	249.42	284.37	0.0137	T	250.06	285.20	0
T	241.52	274.14	0	S	247.18	281.47	0.0075
S	236.65	267.83	0.0495	S	243.28	276.42	0.0017
T	227.10	255.46	0	T	233.70	264.01	0
S	225.56	253.47	0.0033	S	233.32	263.52	0.0003
S	219.32	245.39	0.2332	S	225.48	253.37	0.0652
T	216.47	241.70	0	T	223.69	251.05	0
S	213.31	237.61	0.1891	S	221.40	248.08	0.0000
S	211.29	234.99	0.0345	S	211.85	235.72	0.0040
S	208.77	231.73	0.0073	S	205.77	227.84	0.0002
S	205.76	227.83	0.0061	S	204.24	225.86	0.0000

[a] Mult. – Multitplicity: T, triplet; S, singlet.

[b] Calculated wavelengths were scaled according to Ref. 9, using the equation $\lambda_{sc} = 1.295 \times \lambda_{calc} - 38.63$. Parameters λ_{sc} and *f* were used to construct the simulated spectra shown in Figure S7.

IV. CALCULATIONS

Data from harmonic calculations at the B3LYP/6-311++G(d,p) level (Reference [1]), except specified otherwise.

5-Phenyl-1*H*-tetrazole **1’**
Energy = -489.4424995

N	1.87325100	1.00904800	0.15380600
N	3.15203600	0.57517400	0.09332800
N	3.08534300	-0.69604000	-0.10210500
N	1.79809800	-1.11652100	-0.17211800
C	1.03999700	-0.04428700	-0.01127700
H	1.68096500	1.98304000	0.32969700
C	-0.42269600	-0.00662200	-0.00740700
C	-1.13190500	-1.21244200	0.08197300
C	-1.12894000	1.20018700	-0.09634700
C	-2.52192100	-1.20456400	0.09014900
H	-0.58018900	-2.14178000	0.14558300
C	-2.52043800	1.20228600	-0.08521700
H	-0.60252100	2.14395100	-0.19166400
C	-3.22007700	0.00049800	0.00898100
H	-3.06240800	-2.14127100	0.16172600
H	-3.05710600	2.14107100	-0.15720400
H	-4.30395400	0.00303200	0.01635700

$\tilde{\nu}$	A	$\tilde{\nu}$	A
35	8.2	1053	3.1
112	1.2	1082	12.1
152	5.8	1106	11.9
293	1.5	1167	1.5
350	0.1	1186	0.1
409	0.2	1207	1.2
441	4.4	1265	8.3
501	0.8	1318	2.4
560	84.1	1354	2.1
632	0.1	1376	3.7
702	42.1	1403	8.5
704	7.0	1489	18.0
716	4.0	1514	47.1
735	13.3	1582	39.0
785	34.4	1623	1.9
852	0.2	1648	2.5
935	2.8	3162	7.9
989	0.3	3173	1.3
1011	1.2	3184	15.2
1012	0.4	3194	10.3
1015	1.1	3206	2.3
1021	2.0	3654	76.3
1051	39.0		

5-Phenyl-2*H*-tetrazole **1’’**
Energy = -489.4472896

N	-1.14517400	-1.76798100	0.00000000
N	-0.64858000	-2.99699300	0.00000000
N	0.67550400	-3.05841900	0.00000000
N	1.08373300	-1.82137700	0.00000000
C	-0.03223400	-1.03407800	0.00000000
H	-1.22865800	-3.82437600	0.00000000
C	0.00000000	0.43146900	0.00000000
C	1.22940000	1.10272300	0.00000000
C	-1.19004400	1.17086700	0.00000000
C	1.26430000	2.49382400	0.00000000
H	2.14704200	0.52788300	0.00000000
C	-1.14800600	2.56110000	0.00000000
H	-2.14046900	0.65129600	0.00000000
C	0.07807900	3.22665600	0.00000000
H	2.21953400	3.00638800	0.00000000
H	-2.07302600	3.12643400	0.00000000
H	0.10822300	4.31039700	0.00000000

$\tilde{\nu}$	A	$\tilde{\nu}$	A
47	2.6	1102	7.9
115	2.2	1108	6.2
156	2.4	1130	4.3
298	1.8	1184	0.6
352	0.4	1203	3.9
411	0.0	1204	18.8
456	3.5	1265	2.7
507	3.7	1306	10.3
568	46.7	1346	4.2
633	0.0	1364	8.5
701	33.0	1467	27.1
707	7.0	1479	35.8
724	58.5	1516	24.2
746	42.2	1557	15.7
804	7.1	1623	0.3
861	0.0	1649	0.6
945	3.4	3166	0.0
989	0.0	3176	10.8
997	0.3	3187	16.0
1011	8.5	3197	5.8
1017	0.4	3201	3.3
1041	30.0	3636	150.6
1052	0.4		

Harmonic calculations (Reference [1])

Phenylnitrile imine **2A**

Energy = -379.8676315

C	-1.45278400	-0.56772800	-0.11967300
N	-2.54058000	-0.11806000	0.02501000
N	-3.71834200	0.30018300	-0.04246200
C	-0.04728100	-0.25844800	-0.05284200
H	-4.17847900	0.16191200	0.86125100
C	0.89866900	-1.29407100	-0.01437600
C	2.25725800	-1.00072600	0.04645100
C	2.68766500	0.32543300	0.05119800
C	1.75408300	1.36212600	0.00101400
C	0.39463600	1.07768000	-0.04538700
H	-0.33279000	1.88017100	-0.08033000
H	2.08726900	2.39376400	0.00253400
H	3.74702400	0.55199000	0.09122400
H	2.98070000	-1.80707400	0.08186900
H	0.55525200	-2.32121800	-0.03270500

$\tilde{\nu}$	A	$\tilde{\nu}$	A
45	12.0	1099	22.4
83	5.0	1122	50.1
206	43.4	1184	0.1
338	44.9	1201	3.4
367	26.5	1273	346.4
415	3.2	1314	1.4
439	3.4	1352	0.7
461	8.6	1407	47.2
563	42.8	1473	3.6
614	53.7	1525	3.2
635	16.1	1609	5.4
699	36.2	1634	1.0
763	2.0	2197	476.9
776	51.1	3167	0.3
856	0.1	3176	4.1
940	3.8	3185	10.5
986	0.0	3192	12.3
1002	0.1	3198	6.5
1015	0.2	3410	5.7
1046	9.4		

Phenylnitrile imine **2P**

Energy = -379.8674863

C	-1.45359300	0.03112600	-0.00009100
N	-2.62144000	0.03193500	-0.00000300
N	-3.87172800	-0.15361400	0.00006900
C	-0.03912100	0.01802200	-0.00004500
H	-4.33873400	0.75452800	0.00010800
C	0.69070000	1.22317200	-0.00002500
C	2.07961600	1.19469000	0.00002100
C	2.76502100	-0.02047100	0.00004300
C	2.04632800	-1.21631400	0.00001800
C	0.65718900	-1.20729400	-0.00002500
H	0.10229100	-2.13741400	-0.00004400
H	2.57077300	-2.16508000	0.00003400
H	3.84845300	-0.03541100	0.00007700
H	2.63000400	2.12865800	0.00003900
H	0.16255300	2.16888200	-0.00004500

$\tilde{\nu}$	A	$\tilde{\nu}$	A
36	0.7	1101	217.2
89	1.8	1103	6.3
163	116.4	1184	0.2
235	0.1	1204	0.3
381	7.6	1257	232.5
408	1.2	1308	1.6
411	0.0	1356	0.1
491	8.2	1414	49.1
495	2.5	1471	3.1
546	1.6	1523	6.5
636	0.2	1600	3.1
700	30.8	1634	31.9
731	29.5	2354	975.4
760	63.0	3169	2.4
843	0.0	3176	3.7
915	4.4	3187	9.9
980	0.0	3193	14.1
998	0.2	3198	5.4
1008	4.1	3449	33.6
1044	22.5		

Phenylnitrile imine **2A**
Anharmonic calculation (Reference [12])
(vibrational energies, E / cm^{-1})
(infrared intensities, I / km mol^{-1})

Fundamental bands

Mode (quanta)	E (harm)	E (anharm)	I (harm)	I (anharm)
1(1)	3409.9	3231.8	5.7	2.4
2(1)	3197.8	3057.1	6.5	12.3
3(1)	3192.1	3064.5	12.3	22.7
4(1)	3185.3	3043.7	10.5	29.3
5(1)	3176.0	3042.4	4.1	4.0
6(1)	3166.9	3022.4	0.3	0.5
7(1)	2197.4	2153.5	476.7	266.6
8(1)	1634.4	1589.4	1.0	1.3
9(1)	1608.8	1567.6	5.4	2.8
10(1)	1524.9	1492.1	3.2	3.3
11(1)	1472.7	1447.0	3.6	1.8
12(1)	1407.2	1381.1	47.2	30.7
13(1)	1351.7	1318.3	0.7	0.3
14(1)	1313.8	1280.3	1.4	0.7
15(1)	1273.0	1241.3	346.4	307.0
16(1)	1201.1	1184.4	3.4	3.9
17(1)	1184.5	1169.0	0.1	0.1
18(1)	1122.1	1100.8	50.1	53.4
19(1)	1098.8	1078.4	22.4	21.4
20(1)	1045.7	1028.4	9.4	7.5
21(1)	1014.9	999.5	0.2	0.2
22(1)	1001.7	1043.2	0.1	0.3
23(1)	986.3	999.1	0.0	0.3
24(1)	940.5	926.7	3.8	3.2
25(1)	855.9	842.3	0.1	0.1
26(1)	775.8	766.7	51.0	20.8
27(1)	762.7	747.8	2.0	1.2
28(1)	698.6	715.7	36.2	33.9
29(1)	634.6	626.6	16.1	3.4
30(1)	613.6	595.0	53.7	48.0
31(1)	563.2	549.4	42.8	29.8
32(1)	461.1	463.0	8.6	6.3
33(1)	438.7	432.6	3.4	2.9
34(1)	414.6	409.0	3.2	1.4
35(1)	366.8	365.3	26.5	21.7
36(1)	337.8	312.6	44.9	39.9
37(1)	205.7	191.4	43.4	48.4
38(1)	82.6	79.9	5.0	4.1
39(1)	45.2	32.4	12.0	14.5

Phenylnitrile imine **2A**
Anharmonic calculation (Reference [12])
(vibrational energies, E / cm^{-1})
(infrared intensities, I / km mol^{-1})

Overtones

Mode (quanta)	E (harm)	E (anharm)	I (anharm)
1(2)	6819.8	6300.8	14.58
2(2)	6395.5	6076.7	0.14
3(2)	6384.3	6100.3	0.03
4(2)	6370.5	6062.5	0.09
5(2)	6352.1	6050.3	0.19
6(2)	6333.7	6030.6	0.98
7(2)	4394.8	4242.6	1.56
8(2)	3268.9	3179.8	0.02
9(2)	3217.5	3142.6	2.70
10(2)	3049.7	2977.6	0.07
11(2)	2945.5	2889.2	0.06
12(2)	2814.4	2757.1	2.21
13(2)	2703.5	2646.2	0.003
14(2)	2627.7	2563.7	0.09
15(2)	2546.0	2462.0	8.73
16(2)	2402.2	2369.0	0.01
17(2)	2369.0	2340.6	0.29
18(2)	2244.2	2196.8	32.47
19(2)	2197.6	2162.8	49.44
20(2)	2091.4	2055.8	0.01
21(2)	2029.8	1998.2	0.02
22(2)	2003.4	2114.5	6.31
23(2)	1972.5	2009.4	0.53
24(2)	1881.0	1852.0	0.67
25(2)	1711.9	1684.2	0.03
26(2)	1551.6	1531.5	0.58
27(2)	1525.4	1493.8	0.81
28(2)	1397.2	1438.0	0.12
29(2)	1269.3	1253.4	0.63
30(2)	1227.2	1181.6	0.21
31(2)	1126.5	1072.7	0.05
32(2)	922.2	925.6	0.23
33(2)	877.4	864.4	0.04
34(2)	829.2	817.8	0.004
35(2)	733.6	723.8	0.05
36(2)	675.7	621.9	2.66
37(2)	411.4	376.6	2.06
38(2)	165.2	143.3	0.01
39(2)	90.5	58.2	0.70

Phenylnitrile imine **2P**
Anharmonic calculation (Reference [12])
(vibrational energies, E / cm^{-1})
(infrared intensities, I / km mol^{-1})

Fundamental bands

Mode (quanta)	E (harm)	E (anharm)	I (harm)	I (anharm)
1(1)	3449.4	3262.0	33.6	25.0
2(1)	3198.0	3053.5	5.4	7.5
3(1)	3192.9	3065.6	14.0	31.8
4(1)	3186.9	3047.8	9.9	19.8
5(1)	3175.3	3045.5	3.7	0.9
6(1)	3168.3	3017.6	2.5	1.6
7(1)	2353.7	2277.1	975.9	711.0
8(1)	1633.7	1594.0	31.9	23.5
9(1)	1600.4	1563.4	3.0	1.7
10(1)	1522.6	1494.0	6.5	7.6
11(1)	1470.8	1442.5	3.0	2.1
12(1)	1413.6	1384.9	49.1	40.8
13(1)	1355.3	1336.6	0.061	0.005
14(1)	1307.7	1275.3	1.6	0.8
15(1)	1257.4	1232.6	232.5	136.6
16(1)	1203.3	1188.7	0.4	1.3
17(1)	1183.9	1171.6	0.2	0.2
18(1)	1102.4	1098.0	5.4	56.5
19(1)	1100.3	1093.8	218.2	213.9
20(1)	1043.4	1027.2	22.1	19.8
21(1)	1008.2	996.8	4.0	2.2
22(1)	998.3	988.7	0.14	0.01
23(1)	981.4	968.7	0.0	0.1
24(1)	915.2	899.7	4.8	3.4
25(1)	844.7	830.5	0.03	0.03
26(1)	759.8	736.0	62.5	61.5
27(1)	731.0	724.1	29.6	19.2
28(1)	700.2	684.0	30.9	22.4
29(1)	635.9	627.2	0.2	0.3
30(1)	546.1	538.7	1.6	0.3
31(1)	495.6	477.2	2.5	0.1
32(1)	491.6	495.8	8.0	21.4
33(1)	410.6	407.2	0.0	0.0
34(1)	408.5	400.7	1.2	0.3
35(1)	381.1	378.6	7.6	8.1
36(1)	234.4	221.7	0.1	0.2
37(1)	162.1	106.4	116.3	101.1
38(1)	88.2	61.3	1.8	0.4
39(1)	35.7	18.6	0.7	2.6

Phenylnitrile imine **2P**
Anharmonic calculation (Reference [12])
(vibrational energies, E / cm^{-1})
(infrared intensities, I / km mol^{-1})

Overtones

Mode (quanta)	E (harm)	E (anharm)	I (anharm)
1(2)	6898.9	6366.7	12.63
2(2)	6396.0	6081.4	0.08
3(2)	6385.8	6105.7	0.003
4(2)	6373.9	6062.0	0.19
5(2)	6350.6	6060.1	0.18
6(2)	6336.7	6022.8	0.84
7(2)	4707.4	4550.9	0.57
8(2)	3267.3	3189.3	0.17
9(2)	3200.8	3134.6	5.04
10(2)	3045.2	2981.6	0.001
11(2)	2941.5	2880.2	0.07
12(2)	2827.2	2762.9	5.71
13(2)	2710.6	2663.5	0.00
14(2)	2615.5	2547.5	0.79
15(2)	2514.8	2448.0	13.02
16(2)	2406.7	2376.4	0.13
17(2)	2367.8	2345.8	0.005
18(2)	2204.8	2171.6	0.19
19(2)	2200.7	2157.6	3.30
20(2)	2086.9	2053.5	0.01
21(2)	2016.4	1992.8	0.01
22(2)	1996.6	1982.8	4.27
23(2)	1962.9	1939.1	0.75
24(2)	1830.4	1798.2	2.24
25(2)	1689.4	1660.6	0.13
26(2)	1519.7	1467.9	0.01
27(2)	1462.1	1446.4	0.27
28(2)	1400.3	1366.6	0.01
29(2)	1271.7	1254.7	0.01
30(2)	1092.2	1067.7	0.09
31(2)	991.3	952.2	2.97
32(2)	983.3	958.8	0.02
33(2)	821.2	814.2	0.02
34(2)	817.1	801.6	0.36
35(2)	762.1	757.7	1.65
36(2)	468.8	435.8	0.70
37(2)	324.2	95.3	11.26
38(2)	176.4	122.5	0.02
39(2)	71.3	33.0	0.21

Harmonic calculation (Reference [1])

3-Phenyl-1*H*-diazirine **3**

Energy = -379.8566308

N	2.64061400	-0.88638100	-0.04580900
C	1.65771000	-0.11977200	-0.01506600
H	3.00731600	1.01869600	0.89336800
N	2.75574900	0.76949000	-0.06935800
C	0.21339500	-0.06022900	-0.00792900
C	-0.42212200	1.18689600	-0.02297600
C	-0.54568200	-1.23981000	0.01391600
C	-1.81218700	1.25415500	-0.01458100
H	0.17788200	2.08916200	-0.05139600
C	-1.93209600	-1.16428500	0.02281100
H	-0.04237800	-2.19967200	0.02321100
C	-2.56557800	0.08130300	0.00945100
H	-2.30704200	2.21813700	-0.02879500
H	-2.52262900	-2.07284500	0.03988700
H	-3.64833200	0.13520900	0.01613900

$\tilde{\nu}$	A	$\tilde{\nu}$	A
83	4.0	1082	28.0
135	3.0	1113	5.4
151	2.3	1186	0.3
364	0.6	1195	12.4
384	8.1	1225	37.2
409	0.1	1328	2.9
501	2.2	1352	6.8
556	30.4	1360	0.9
592	9.1	1481	12.8
631	0.1	1522	5.1
692	30.3	1619	1.5
767	1.7	1641	5.6
772	47.6	1855	99.7
860	0.0	3169	0.0
945	3.0	3178	2.4
989	1.5	3184	5.3
1004	3.3	3192	9.3
1008	36.3	3197	7.9
1016	0.4	3370	3.9
1044	8.7		

Phenylcarbodiimide **4**

Energy = -379.9393949

H	4.12412600	0.55990100	0.75739900
N	3.57119100	0.38562000	-0.07324100
N	1.42541300	-0.76013800	-0.05330400
C	2.47152400	-0.14287600	0.01635700
C	0.08803500	-0.32336900	-0.02195500
C	-0.91404100	-1.29739800	0.00401500
C	-0.26162300	1.03334900	-0.02819300
C	-2.25308700	-0.91812500	0.02836900
H	-0.62698300	-2.34179600	0.00384000
C	-1.60263200	1.40293200	-0.00547900
H	0.51519500	1.78964700	-0.05635100
C	-2.60339200	0.43123700	0.02395100
H	-3.02424000	-1.67979900	0.04906700
H	-1.86648900	2.45458400	-0.01224200
H	-3.64654800	0.72459200	0.04171500

$\tilde{\nu}$	A	$\tilde{\nu}$	A
48	5.6	1045	6.9
107	1.8	1099	11.6
225	14.6	1144	33.5
383	6.5	1181	0.0
416	72.4	1197	0.1
421	12.7	1319	6.2
470	1.0	1352	0.6
505	24.4	1427	4.3
582	44.4	1482	1.2
632	0.6	1531	67.9
656	34.9	1619	8.8
702	32.7	1637	60.6
773	59.2	2229	1379.1
792	6.3	3164	2.3
843	0.1	3172	2.6
888	428.5	3180	14.0
922	6.4	3189	16.0
980	0.1	3198	5.3
997	0.1	3582	85.3
1016	0.3		

Harmonic calculations (Reference [1])

Phenylcyanamide **5**

Energy = -379.9390032

N	-3.47121500	0.62655200	0.00002600
C	-2.53843400	-0.06195700	0.00000600
N	-1.46090400	-0.84248400	-0.00002700
H	-1.61076700	-1.84062200	-0.00000200
C	-0.12648900	-0.36597600	-0.00001100
C	0.91698100	-1.29529900	0.00000300
C	0.15049000	1.00223400	-0.00001700
C	2.23561900	-0.85195800	0.00001300
H	0.69898800	-2.35850000	0.00000400
C	1.47539500	1.43081700	-0.00000500
H	-0.66075900	1.72068600	-0.00003400
C	2.52334000	0.51216900	0.00001000
H	3.03981200	-1.57873900	0.00002200
H	1.68497600	2.49430000	-0.00000700
H	3.55117500	0.85422300	0.00002100

$\tilde{\nu}$	A	$\tilde{\nu}$	A
59	2.8	1099	2.3
132	8.1	1133	7.6
220	17.2	1183	1.1
270	80.7	1203	9.7
355	0.9	1264	76.3
417	0.5	1329	31.4
456	0.6	1359	1.6
506	13.7	1453	46.5
514	0.0	1520	1.5
632	0.2	1533	140.5
661	6.2	1638	5.2
702	28.7	1644	103.2
763	65.8	2337	250.4
833	0.0	3159	9.8
834	4.3	3172	0.0
903	5.8	3181	12.9
977	0.0	3190	8.0
998	0.1	3198	7.2
1013	0.5	3614	63.1
1047	3.3		

Transition State between **2A** and **2P**

Energy = -379.867339213

C	-1.456971000	-0.207420000	-0.228884000
N	-2.596757000	-0.061738000	0.009061000
N	-3.821449000	0.215665000	0.107182000
C	-0.042483000	-0.100126000	-0.109189000
H	-4.295504000	-0.544047000	0.599311000
C	0.761847000	-1.252832000	-0.055979000
C	2.141544000	-1.134477000	0.063261000
C	2.742437000	0.123713000	0.103773000
C	1.950494000	1.270300000	0.033145000
C	0.568190000	1.168361000	-0.065703000
H	-0.046332000	2.059197000	-0.111267000
H	2.411039000	2.251254000	0.062614000
H	3.819502000	0.210455000	0.186180000
H	2.751095000	-2.029443000	0.114013000
H	0.297303000	-2.230017000	-0.107095000

$\tilde{\nu}$	A	$\tilde{\nu}$	A
43 i	16.7		
72	4.1	1101	24.7
218	109.2	1108	143.8
253	23.5	1184	0.0
379	22.0	1202	1.2
408	0.7	1261	268.1
420	0.9	1310	0.7
485	6.7	1354	0.0
515	16.6	1412	46.7
575	18.3	1471	3.5
636	2.7	1523	6.0
699	28.7	1603	2.8
740	13.1	1634	19.6
760	68.0	2304	802.5
847	0.4	3168	1.5
921	5.3	3175	4.0
982	0.0	3186	10.5
999	0.1	3193	13.5
1010	1.4	3197	5.5
1044	16.5	3439	23.6

Data from harmonic calculations at the B3LYP/aug-cc-pVTZ level (Reference [1])

Phenylnitrile imine **2A**
Energy = -379.907241706

C	-1.450504000	-0.565542000	-0.113411000
N	-2.535258000	-0.115963000	0.021927000
N	-3.711086000	0.295848000	-0.045254000
C	-0.046686000	-0.258192000	-0.049928000
H	-4.170876000	0.174227000	0.858243000
C	0.897330000	-1.290576000	-0.013037000
C	2.252557000	-0.997933000	0.044214000
C	2.681809000	0.324670000	0.048557000
C	1.750283000	1.358386000	0.000925000
C	0.394465000	1.074369000	-0.043355000
H	-0.331331000	1.875010000	-0.076281000
H	2.082522000	2.387673000	0.002267000
H	3.738715000	0.550847000	0.086566000
H	2.974403000	-1.802381000	0.078187000
H	0.555449000	-2.315670000	-0.029484000

$\tilde{\nu}$	A	$\tilde{\nu}$	A
39	11.1	1100	21.7
84	5.3	1125	54.2
203	38.1	1184	0.2
339	36.1	1202	3.5
369	26.6	1278	356.3
417	2.4	1313	0.7
441	3.7	1357	0.7
466	6.7	1409	41.8
573	44.8	1478	3.3
615	49.2	1529	3.0
636	15.9	1610	5.3
708	34.4	1635	1.1
766	1.7	2197	497.5
783	43.2	3169	0.4
864	0.1	3178	3.7
952	3.2	3187	9.3
1002	0.0	3193	11.5
1020	0.1	3199	6.5
1021	0.0	3409	7.7
1049	8.1		

Phenylnitrile imine **2P**
Energy = -379.907338763

C	-0.506395000	1.360854000	0.000000000
N	-0.928353000	2.446205000	0.000000000
N	-1.550256000	3.542368000	0.000000000
C	0.000000000	0.041153000	0.000000000
H	-0.878031000	4.307928000	0.000000000
C	1.385426000	-0.194565000	0.000000000
C	1.868014000	-1.493362000	0.000000000
C	0.992041000	-2.574515000	0.000000000
C	-0.380582000	-2.345939000	0.000000000
C	-0.881211000	-1.053985000	0.000000000
H	-1.947779000	-0.880561000	0.000000000
H	-1.068585000	-3.180431000	0.000000000
H	1.375222000	-3.585304000	0.000000000
H	2.936366000	-1.661708000	0.000000000
H	2.069314000	0.642204000	0.000000000

$\tilde{\nu}$	A	$\tilde{\nu}$	A
37	0.1	1102	229.0
87	1.5	1104	4.5
182	91.7	1184	0.2
235	0.2	1205	0.1
383	6.4	1263	237.2
411	0.9	1307	1.7
411	0.0	1361	0.1
492	10.2	1415	42.1
500	0.0	1476	2.9
548	1.7	1527	7.4
637	0.1	1602	2.9
706	26.3	1634	33.3
732	29.4	2349	996.9
765	56.8	3170	2.4
854	0.0	3177	3.6
926	3.8	3189	8.5
994	0.0	3194	12.7
1013	5.7	3200	5.4
1014	0.1	3448	37.0
1046	18.5		

Data from harmonic B3LYP/aug-cc-pVTZ calculation
(Reference [1])

Transition state between **2A** and **2P**
Energy = -379.907089394

C	-1.455372000	-0.277910000	-0.247577000
N	-2.580257000	-0.071270000	0.010082000
N	-3.791875000	0.236578000	0.107430000
C	-0.043332000	-0.132278000	-0.116575000
H	-4.267410000	-0.440447000	0.703512000
C	0.787978000	-1.259620000	-0.054615000
C	2.160017000	-1.106293000	0.073627000
C	2.725990000	0.163911000	0.111479000
C	1.907779000	1.286712000	0.029828000
C	0.532822000	1.148125000	-0.076345000
H	-0.102884000	2.020543000	-0.129602000
H	2.342042000	2.276899000	0.056659000
H	3.797434000	0.278645000	0.200119000
H	2.791016000	-1.982606000	0.132652000
H	0.349430000	-2.246068000	-0.104858000

$\tilde{\nu}$	A	$\tilde{\nu}$	A
40 i	13.1		
75	3.8	1103	21.9
225	77.1	1113	130.3
272	38.6	1184	0.0
381	25.5	1203	1.2
412	1.0	1270	289.1
425	1.4	1310	1.2
486	7.4	1359	0.1
529	20.7	1413	39.3
588	30.2	1477	3.3
638	5.3	1528	5.9
707	28.8	1605	2.8
746	6.7	1635	15.7
771	58.1	2279	753.3
858	0.5	3169	1.3
935	4.7	3177	3.8
995	0.0	3188	9.4
1016	0.4	3194	12.3
1016	1.0	3199	5.5
1048	12.5	3433	22.7

Data from harmonic calculation at the CASSCF(14/12)/cc-pVTZ level (Reference [1])

Phenylnitrile imine **2A**
Energy = -377.6443552

C	0.926264	-1.297509	-0.004389
C	2.274352	-0.956604	0.027750
C	-0.050070	-0.301296	-0.029579
C	2.655956	0.380729	0.028136
C	1.685287	1.379854	-0.002304
C	0.338585	1.043377	-0.029410
C	-1.457385	-0.678318	-0.067310
N	-2.505236	-0.127278	0.034339
N	-3.645575	0.325799	-0.088460
H	-4.090039	0.376941	0.810268
H	-0.409373	1.811892	-0.053865
H	1.976111	2.412668	-0.004152
H	3.696092	0.643320	0.050288
H	3.018679	-1.728992	0.049167
H	0.626273	-2.326874	-0.010226

$\tilde{\nu}$	A	$\tilde{\nu}$	A
131	4.3	1149	5.3
135	4.6	1180	21.4
282	13.8	1199	11.0
390	19.4	1275	0.2
418	21.6	1313	18.0
465	3.4	1393	345.0
486	0.5	1453	1.5
529	15.2	1483	2.9
622	81.7	1577	4.0
668	2.4	1637	7.7
698	57.7	1707	12.5
770	21.5	1736	2.2
812	11.4	2243	519.2
895	85.8	3322	0.0
965	0.2	3331	4.5
1034	3.6	3340	20.5
1060	0.5	3349	23.3
1080	0.1	3354	9.2
1096	0.1	3694	23.5
1103	4.3		

Phenylnitrile imine **2P**
Energy = -377.6455027

C	-2.050104	-1.202526	-0.000109
C	-0.665504	-1.199167	0.000231
C	0.026149	0.012291	0.000253
C	-0.688647	1.213915	0.000144
C	-2.073136	1.191402	-0.000046
C	-2.754714	-0.019605	-0.000217
C	1.457527	0.022532	0.000106
N	2.616551	0.030844	-0.000008
N	3.880473	-0.150284	-0.000247
H	4.313580	0.753756	-0.000123
H	-0.121949	-2.123296	0.000331
H	-2.572931	-2.139609	-0.000229
H	-3.827457	-0.031482	-0.000427
H	-2.617775	2.115637	-0.000111
H	-0.162057	2.148019	0.000169

$\tilde{\nu}$	A	$\tilde{\nu}$	A
26	0.0	1132	182.1
102	2.1	1165	4.1
268	6.1	1230	1.9
301	105.7	1283	1.7
407	7.1	1336	224.1
428	0.1	1351	9.7
494	0.0	1459	18.6
506	6.4	1463	13.0
554	2.7	1582	7.1
569	2.0	1641	25.1
675	0.1	1721	3.9
763	41.9	1750	29.6
776	3.0	2412	1225.0
898	102.2	3328	0.9
969	0.8	3336	3.0
1038	3.2	3346	21.1
1068	39.0	3352	27.8
1093	0.1	3357	14.3
1108	66.7	3720	20.9
1132	2.5		

Other nitrile imines (R’−CNN−R’’). All subsequent data obtained in harmonic calculations (Reference [1])

Data from calculations at the B3LYP/6-311++G(d,p) level

Nitrile imine (R’ = R’’ = H)

H	-1.63632800	0.77455100	0.01335500
N	0.05575000	0.01798800	0.01518100
C	1.23601300	0.00905900	-0.13310300
N	-1.17600400	-0.13950700	0.01751900
H	2.06202500	0.02172400	0.55636800

$\tilde{\nu}$	A
465	10.2
524	114.9
621	285.9
836	47.0
1241	128.8
1309	44.3
2128	415.7
3295	54.2
3419	11.8

Nitrile imine (R’ = Me; R’’ = H)

H	2.35640200	0.17877900	0.77740800
N	0.67846300	-0.07331800	0.02309700
C	-0.46335500	-0.37415100	0.00172500
N	1.90712900	0.13086600	-0.14022300
C	-1.84154700	0.14535500	0.00391000
H	-1.87200200	1.24027100	0.00192100
H	-2.37592600	-0.22507600	-0.87412700
H	-2.37820000	-0.22403100	0.88087100

$\tilde{\nu}$	A	$\tilde{\nu}$	A
51	12.6	1381	7.8
165	39.7	1410	0.9
377	38.6	1475	9.9
526	41.5	1483	13.1
569	44.0	2228	421.5
839	5.1	3015	39.9
1037	51.7	3086	8.8
1054	4.3	3098	4.0
1267	253.1	3421	6.0

Nitrile imine (R’ = Ph; R’’ = Me)

C	-0.89251200	-0.67508100	-0.38372100
N	-1.97470400	-0.16713200	-0.36266100
N	-3.12954000	0.25609200	-0.50765600
C	0.48749300	-0.30034700	-0.16647300
C	1.45905300	-1.29719500	0.00759000
C	2.79198300	-0.95243700	0.20938000
C	3.17457000	0.38814400	0.21972200
C	2.21705700	1.38718600	0.03404900
C	0.88169500	1.05057900	-0.15207700
H	0.13661800	1.82507800	-0.29322100
H	2.51272900	2.43031900	0.03916200
H	4.21461800	0.65523600	0.36868000
H	3.53380500	-1.73034400	0.34933600
H	1.15461400	-2.33649300	-0.01802600
C	-3.98319200	0.11424100	0.68310900
H	-3.59161900	0.67971700	1.53690400
H	-4.96712600	0.50235900	0.42538200
H	-4.08080600	-0.93913300	0.97452300

$\tilde{\nu}$	A	$\tilde{\nu}$	A
28	3.8	1099	17.6
69	1.6	1126	1.9
83	1.7	1176	50.5
138	14.4	1183	0.1
185	1.4	1201	7.6
323	11.3	1312	30.9
365	11.2	1351	0.7
414	1.3	1404	238.3
450	6.6	1447	4.9
525	7.2	1472	3.2
570	91.0	1486	30.7
606	17.6	1492	12.4
633	6.2	1526	6.2
700	31.9	1609	5.7
761	2.3	1634	2.1
770	57.1	2140	579.2
854	0.3	2990	87.0
935	14.5	3043	38.7
937	4.2	3132	21.4
989	0.0	3165	0.8
1005	0.0	3173	3.8
1015	0.5	3183	9.7
1046	5.7	3190	15.3
1091	5.7	3196	8.2

Nitrile imine (R’ = Ph; R’’ = Si(Me)$_3$)

C	-0.72450200	-0.40555200	-0.01147300
N	0.41633000	-0.66792100	-0.01911300
N	1.60533400	-1.03680500	-0.03229000
C	-2.12282600	-0.17571300	-0.00490900
C	-2.63673100	1.13609800	-0.00604700
C	-4.00971000	1.34947500	-0.00023500
C	-4.89402200	0.27049200	0.00658000
C	-4.39267900	-1.03163100	0.00781700
C	-3.02237300	-1.26100700	0.00241000
H	-2.63542400	-2.27268100	0.00371600
H	-5.07343600	-1.87541200	0.01324400
H	-5.96395700	0.44247200	0.01083600
H	-4.39110200	2.36431000	-0.00144700
H	-1.95226100	1.97565200	-0.01198700
C	2.92438400	1.24595200	-1.45582700
C	3.02183300	1.02601800	1.61678700
C	4.48238100	-1.08535600	-0.12412000
H	2.91523400	0.70648100	-2.40723300
H	2.02738600	1.87220400	-1.41865200
H	3.79136500	1.91495500	-1.45737900
H	3.06409300	0.35643500	2.48054200
H	3.89370200	1.68723200	1.66098400
H	2.12977300	1.65130900	1.72295200
H	5.41679200	-0.51594100	-0.10717800
H	4.50319300	-1.79415700	0.70830900
H	4.45444700	-1.66260200	-1.05235300
Si	2.99385900	0.04787000	0.00211200

A	$\tilde{\nu}$
15	0
21	1
30	0.4
66	0.2
88	0.6
133	0
152	0
162	0.1
176	0
190	0.1
220	3.8
241	1.6
260	18.1
273	11.8
371	9.2
409	0
450	0.7
494	12.2
500	1.5
530	20.4
595	15.6
635	1.8
675	30.5
681	14.3
693	0
698	5.2
700	29
761	63.5
765	23.8
767	58.1
785	75.1
846	0.1
870	89.2
872	79.1
879	479
919	4.2
980	0
996	0.1
1010	4.4
1045	19
1101	5.9
1138	334.9
1184	0
1203	1.4
1291	40.2
1294	45.1
1304	21.9
1306	0.4
1354	0
1449	644.9
1452	0.2
1458	0
1459	2.2
1464	4.6
1467	4.1
1470	3
1476	9.3
1531	46.7
1600	3.1
1634	19
2352	1705.6
3017	8
3019	9.8
3026	8.2
3082	0.1
3085	36.8
3094	7.8
3094	7.6
3096	27.9
3102	13.3
3167	3
3174	4.4
3186	12.5
3193	14.6
3197	6.4

Nitrile imine (R’ = R’’ = Ph)

C	-0.95526400	-0.54101700	-0.00001100
N	0.16015000	-0.88837000	-0.00001000
N	1.30767800	-1.40889100	-0.00001100
C	-2.32046300	-0.17631900	-0.00000500
C	-2.70294600	1.18020900	-0.00000800
C	-4.04932600	1.52013800	-0.00000200
C	-5.03214400	0.52944800	0.00000900
C	-4.65753400	-0.81475900	0.00001200
C	-3.31634300	-1.17480600	0.00000600
H	-3.02772400	-2.21867500	0.00001000
H	-5.41525000	-1.58989700	0.00001900
H	-6.08063500	0.80263300	0.00001300
H	-4.33303600	2.56632500	-0.00000400
H	-1.94291300	1.95173100	-0.00001600
C	2.40924700	-0.53989300	-0.00000200
C	2.32533400	0.86236300	-0.00000300
C	3.67703000	-1.14566300	0.00000300
C	3.48596400	1.63188200	0.00000200
H	1.35749300	1.35042600	-0.00000800
C	4.82636300	-0.36715800	0.00000800
H	3.73271500	-2.22776000	0.00000400
C	4.74189700	1.02745600	0.00000900
H	3.40539500	2.71368000	0.00000200
H	5.79705400	-0.85090700	0.00001300
H	5.64121500	1.63197500	0.00001400

A	$\tilde{\nu}$	A	$\tilde{\nu}$
22	0.2	1042	3.8
32	0.2	1045	13.3
39	0.1	1098	44.7
85	0.4	1104	8.4
126	0.2	1105	59
222	0	1178	7.4
252	0.3	1185	0.1
284	0.9	1191	52.6
373	1.4	1204	2.6
405	0.1	1242	212.4
417	0.4	1309	0.9
436	3.2	1324	23
492	8.9	1353	7.6
501	8	1356	0.1
506	6.7	1408	485.9
521	0.5	1471	3.7
630	0.4	1481	0.8
634	0.6	1515	182.5
659	19	1520	3.9
694	0	1599	3.5
696	54	1610	9.4
750	59.4	1631	30.7
757	19.9	1633	169.2
758	105.8	2341	1621.3
828	0.2	3159	8
830	4.6	3167	7.6
843	0	3170	4.2
892	5.4	3177	3.7
916	3.9	3179	15.5
967	0.2	3187	19.6
978	0	3188	8.8
982	0	3193	14
994	0.1	3194	11.5
1008	3.9	3199	6.6
1009	7.5		

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