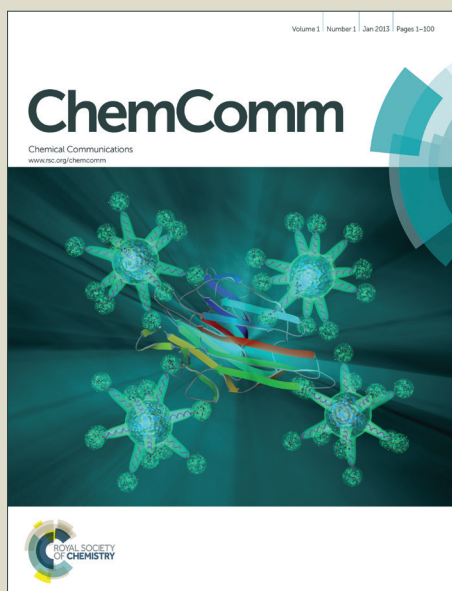


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Bond-Shift Isomers: The Co-existence of Allenic and Propargylic Phenylnitrile Imines

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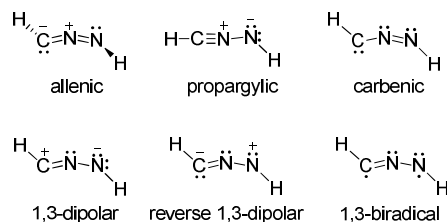
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We discovered a 1,3-dipolar species co-existing in two different structures. Photolysis of matrix-isolated 5-phenyltetrazole generates two forms of phenylnitrile imine: propargylic and allenic. They are not resonance structures but different energy minima, representing bond-shift isomers. These distinct species were characterized spectroscopically and confirmed by calculations up to CASSCF(14,12) theory level.

1,3-Dipolar cycloadditions are used in almost all areas of chemistry such as drug discovery, biological chemistry, synthetic chemistry or materials chemistry.¹ In developing the theory of 1,3-dipolar cycloadditions, Huisgen classified 1,3-dipoles in two categories: allylic type ($X=Y^+-Z^- \leftrightarrow X^+-Y-Z^-$) and propargylic type ($X \equiv Y^+-Z^- \leftrightarrow X^+=Y-Z^-$).² Generally, it has been accepted that 1,3-dipoles correspond to a single-minimum on the potential energy surface – which is better described by resonance structures rather than one Lewis structural formula.³

Nitrile imines ($R'-CNN-R''$) are a class of 1,3-dipoles with versatile reactivity as well as ongoing importance in mechanistic and theoretical chemistry.^{1a,1b,4} Six canonical structures with different weights have been considered for the description of nitrile imines (Scheme 1). However, the bonding and geometry of each



Scheme 1. Six different structures for parent nitrile imine.

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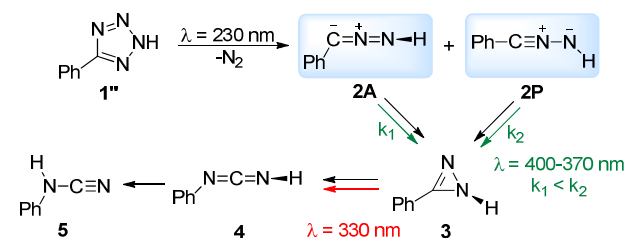
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nitrile imine may be closer to only one of these six structures. For the parent nitrile imine (HCNNH), high-level ab initio calculations with configuration interaction and large basis-sets show that this species has a non-planar, allenic geometry. The propargylic structure with a CN triple bond and a linearized HCN moiety is a transition state for inversion of the allenic form.^{5,6}

Due to the characteristically elusive nature of nitrile imines, IR spectroscopy and matrix-isolation have been used as important tools for the investigation of these species. In synergy with theoretical methods, it has been shown that several nitrile imines have essentially allenic structures characterized by IR absorptions at 2000–2100 cm^{-1} , whereas others are largely propargylic with absorptions in the nitrile region around 2200 cm^{-1} .^{4c,4g,5c,7} In all cases, these species exist in single-minimum potential energy wells characterized by largely allenic or propargylic structures, depending on the substituents.⁸ In this paper, we provide experimental and theoretical data showing the co-existence of two distinct forms of the same nitrile imine. More specifically, we discovered that the phenylnitrile imine (PhCNNH) has a double-minimum potential with an allenic and a propargylic form, which can be described as bond-shift isomers⁹ (Scheme 2). To the best of our knowledge, the co-existence of two different structures for a 1,3-dipolar species has never been observed before.



Scheme 2. Allenic **2A** and propargylic **2P** phenylnitrile imines captured in the photochemistry of 5-phenyl-2H-tetrazole **1''**.

Monomers of 5-phenyltetrazole **1** were isolated in argon and krypton matrices at 15 and 20 K, respectively, and characterized by IR spectroscopy. Details of the experiment are given in the Electronic Supplementary Information (ESI). It was found that **1**

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adopts predominantly the 2*H*-tautomeric form (**1''**) (Figure S1). The estimated 2*H*:1*H* tautomer ratio from the B3LYP/6-311++G(d,p) calculated Gibbs free energies is 98:2 (Table S1). This ratio reflects the experimental data: 1*H*-tautomer (**1'**) was detected only in trace amounts (Figure S2).¹⁰

When the matrix-isolated 5-phenyl-2*H*-tetrazole **1''** was irradiated, using monochromatic UV-light of 230 nm,¹¹ five photoproducts were detected – labeled as **2A**, **2P**, **3**, **4** and **5** in Figure 1. Based on previous experimental data, the characteristic IR peaks observed at 2073/2068 cm⁻¹ (**2A**), 2167/2130 cm⁻¹ (**4**), and 2255 cm⁻¹ (**5**) were readily assigned to phenylnitrile imine **2A**, phenylcarbodiimide **4**, and phenylcyanamide **5**, respectively (Scheme 2).^{4g} Interestingly, the kinetics of formation of the unknown IR peak at 2242 cm⁻¹ (**2P**) is similar to the kinetics of formation of the IR peak at 2073/2068 cm⁻¹ assigned to phenylnitrile imine **2A** (Figure S3). Furthermore, these two peaks are formed in the first stage of irradiation as primary photoproducts of **1''**.¹² Therefore, we postulate that the **2P** peak corresponds to a new phenylnitrile imine structure. In fact, calculations indicate the existence of two minima for phenylnitrile imine (see below); one having an allenic-like structure (**2A**) and other having a propargylic-like structure (**2P**) as presented in Scheme 2.

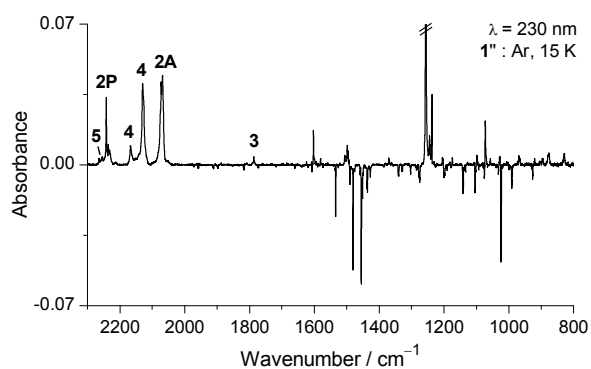


Figure 1. Experimental difference IR spectrum: spectrum after UV irradiation at $\lambda = 230$ nm (35 s, 5 mW) minus spectrum of 5-phenyl-2*H*-tetrazole **1''** before irradiation. The most characteristic bands of photoproducts in the 2300–1700 cm⁻¹ region are labeled as **2A**, **2P**, **3**, **4** and **5**.

To substantiate our hypothesis, we found that subsequent irradiations,¹³ using monochromatic UV-light in the 400–370 nm region, induce selective consumption of **2A** and **2P** to yield **3**, whereby the isomerization of **2A** (k_1) is slower than of **2P** (k_2). For example, it was observed that: (i) the irradiation of photoproducts of **1''** at 370 nm for 4 min consumed ~43% of **2A** and ~76% of **2P** (Figures 2b and S4); (ii) after a total of 8 min of irradiation at 370 nm, **2P** is totally consumed; (iii) subsequent irradiations (+20 min) consumed the remaining **2A** (Figures 2c and S4). These results demonstrate that **2A** and **2P** are distinct species and allowed us to obtain their individual IR signatures. The agreement between the experimental data (Figures 2b and 2c) and the calculated IR spectra at the B3LYP/6-311++G(d,p) level for the allenic **2A** and propargylic **2P** forms (Figure 2a) provides convincing evidence for the identification of these two structures of the phenylnitrile imine. Similar results were also obtained in krypton matrixes (Figures S5

and S6). The assignments of the most intense IR bands of allenic **2A** and propargylic **2P** phenylnitrile imine are given in Table 1.

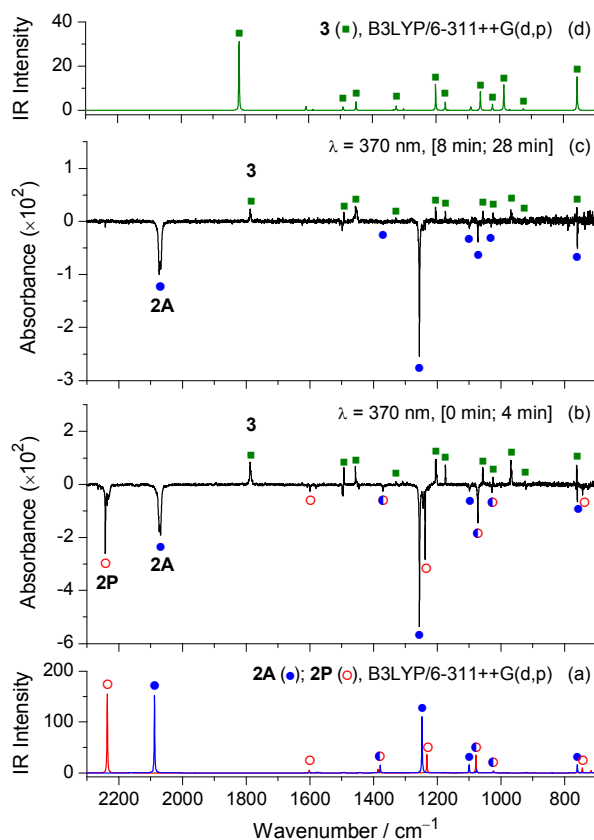


Figure 2. (a) Simulated IR spectra of allenic **2A** (blue) and propargylic **2P** (red) phenylnitrile imines assuming a ratio of 2:1. (b,c) Experimental difference IR spectra in argon matrix showing changes: (b) after 4 min irradiation at $\lambda = 370$ nm (15 mW) subsequent to the irradiation of **1''** at $\lambda = 230$ nm (see Figure 1); (c) after +20 min irradiation at $\lambda = 370$ nm (20 mW) subsequent to 8 min at the same conditions, making a total irradiation time of 28 min. The negative bands labeled with blue filled circles and red open circles are due to the consumed photoproducts assigned to allenic **2A** and propargylic **2P** phenylnitrile imine, respectively. The bands labeled with green squares are assigned to 1*H*-diazirine **3**, growing at the expense of photoproducts **2A** and **2P**. (d) Simulated IR spectrum of 1*H*-diazirine **3** (green). (See ESI for details of experiment and simulations).

The different rates of photoisomerization of **2A** and **2P** induced by irradiation at 370 nm are in agreement with predicted difference in UV-visible absorption of the two isomers (see Figure S8). It is important that photoisomerization of both **2A** and **2P** results in the same product **3** (see positive bands in Figure 2b and 2c), with a characteristic IR peak at 1789 cm⁻¹. This band also appeared during the irradiation of **1''** at 230 nm (Figure 1). We unambiguously identified **3** as the 3-phenyl-1*H*-diazirine (Scheme 2) based on an excellent match between the experimental data and the spectrum calculated at the B3LYP/6-311++G(d,p) level (Figures 2b-d). Noteworthy, the photogenerated **3** was photostable and accumulated in the sample (Figure S4) under irradiation at 370 nm.

The elusive and high energy 1*H*-diazirine **3** is one of just a few experimentally known 1*H*-diazirines,⁴ⁱ and its experimental IR spectrum is characterized in Table S2.¹⁴

Table 1. Experimental infrared spectra (argon matrix at 15 K), calculated B3LYP/6-311++G(d,p) vibrational frequencies ($\tilde{\nu}$, cm⁻¹) and absolute infrared intensities (A, km mol⁻¹), and approximate vibrational assignments of allenic **2A** and propargylic **2P** phenylnitrile imines.

Ar matrix ^a		Calculated ^b		Approx. Assignment ^c
$\tilde{\nu}$	I	$\tilde{\nu}$	A	
Nitrile imine 2A				
6325/6311	vw	6301	14.6	2v(N-H)
3246/3240	vw	3239	5.7	v(N-H)
2073/2068	s	2087	476.9	v(CNN)as
1580	vw	1577	5.4	v(ring) _b
1369 sb	m	1379	47.2	$\delta(\text{NH})+[v(\text{NN})-v(\text{CC}_\text{N})]$
1256	s	1248	346.4	$\delta(\text{NH})-[v(\text{NN})-v(\text{CC}_\text{N})]$
1099	m	1100	50.1	v(ring) _c + $[v(\text{NN})+v(\text{CC}_\text{N})]$
1072 sb	w	1077	22.4	v(ring) _a + $\delta(\text{CH})_b$
1028 sb	m	1025	9.4	v(ring) _d + $\delta(\text{CH})_e$
760	m	760	51.0	$\gamma(\text{CH})_a$
690 sb		685	36.2	$\gamma(\text{CH})_b$
619	w	622	16.1	$\delta(\text{ring})_b$
603/593	m	601	53.7	$\tau(\text{NH})$
Nitrile Imine 2P				
6391	vw	6367	12.6	2v(N-H)
3276	vw	3277	33.6	v(N-H)
2242/2236	s/m	2236	975.9	v(C≡N)- $[v(\text{NN})+v(\text{CC}_\text{N})]$
1600	vw	1601	31.9	v(ring) _b
1498/1496	vw	1492	6.5	$\delta(\text{CH})$
1369 sb	m	1385	49.1	$\delta(\text{NH})+[v(\text{NN})-v(\text{CC}_\text{N})]$
1244/1237	m/s	1232	232.5	$\delta(\text{NH})-[v(\text{NN})-v(\text{CC}_\text{N})]$
-	w	1080	5.4	v(ring) _a + $\delta(\text{CH})_b$
1072 sb	m	1078	218.2	v(ring) _c + $[v(\text{NN})+v(\text{CC}_\text{N})]$
1028 sb	m	1023	22.1	v(ring) _d + $\delta(\text{CH})_e$
744	w	745	62.5	$\gamma(\text{CH})_a$
ov	-	716	29.6	$\delta(\text{ring})_a-[v(\text{NN})+v(\text{CC}_\text{N})]$
690 sb	m	686	30.9	$\gamma(\text{CH})_b$

^aOnly bands in the 2300–600 cm⁻¹ region having calculated intensities above 5 km mol⁻¹, plus the v(N-H) and 2v(N-H) bands shown in Figure S6, are included. Bands of **2P** superimposed with bands of **2A** indicated by "sb", band of **2P** overlapped with **1'** indicated by "ov". ^bCalculated harmonic frequencies scaled by 0.980 and 0.950 below and above 2000 cm⁻¹, respectively. The 2v(N-H) frequencies (not scaled) and infrared intensities were obtained in anharmonic calculations. ^cAssignments made by inspection of Chemcraft animations. Abbreviations: v, bond stretching; δ , bending; γ , out-of-plane; τ , torsion; as, antisymmetric. Subscripts "a-d" indicate different normal vibrations of the same type. C_N = CNN carbon atom. Signs "+" and "-" designate combinations of vibrations occurring in "syn"-phase ("+") and in "anti"-phase ("-").

Calculations for phenylnitrile imine (PhCNNH) in vacuum were carried at the B3LYP and CASSCF levels in order to confirm the existence of two different forms. This was important, because it could be thought the existence of two isomers was due to a matrix effect, i.e. the stabilization of an unnatural structure by the solid matrix environment. The results at different levels of theory, up to CASSCF(14,12), agree unanimously that two forms, **2A** and **2P**, exist as separate energy minima with almost identical energies and with a small barrier between them (Table S4, Figure S10). In all cases, the

estimated energy difference between **2A** and **2P**, as well as the height of the barrier separating them (calculations for the vacuum), are below the chemical accuracy of the calculations (i.e. < 1 kcal mol⁻¹).¹⁵ To attempt mutual conversion of the two isomers, annealing experiments for **2A** and **2P** isolated in Ar or Kr matrixes were conducted. **2A** : **2P** ratios prior to annealing were chosen to be different (either at their maximum amounts or after **2P** was largely consumed by UV-irradiation at 370 nm). In both cases, annealing up to 35 K did not produce any noticeable changes in populations of **2A** and **2P**. For these reasons, we postulate that the matrix increases the barrier between the bond-shift isomers and prevents their interconversion.¹⁶ This situation is far from exceptional.¹⁷

The calculated geometrical parameters of **2A** and **2P** reveal features close to what is expected for allenic and propargylic types. For example, **2A** is non-planar with the CCNH dihedral angle = 97°, and the CCN fragment is bent (bond angle = 137°); whereas **2P** is planar with the CCNH dihedral angle = 180°, and the CCN fragment is linear (Figure 3). Additionally, the estimated CN bond length for **2P** is = 1.159 Å, which is comparable to the experimental C≡N triple bond of acetonitrile (1.157 Å).¹⁸ By contrast, the estimated CN bond length for **2A** is = 1.188 Å, which agrees with the experimental C=N double bond of ethyl isocyanate (1.188 Å).¹⁹ Finally, the differences in geometrical and electronic properties of **2A** and **2P** correlate with the vibrational frequency differences of their CNN moieties. For the allenic form **2A**, the v(CNN) band is observed at ~2070 cm⁻¹, in good agreement with the estimated frequency of 2087 cm⁻¹ corresponding to the antisymmetric stretching of the CNN moiety (Table 1, Figure S11). For the propargylic form **2P**, the v(CNN) band is observed at ~2239 cm⁻¹, close to the estimated frequency of 2236 cm⁻¹, corresponding to the C≡N stretching mode (Table 1, Figure S11), also in agreement with the typical values of the v(C≡N) modes of nitriles.²⁰

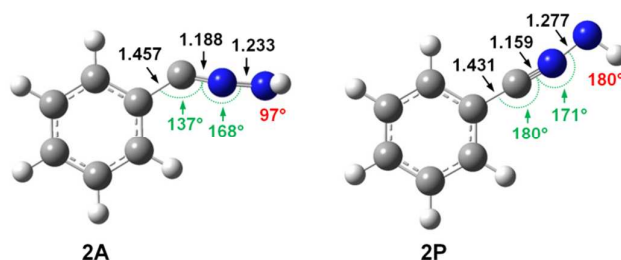


Figure 3. Structures and selected geometric parameters for phenylnitrile imines **2A** and **2P** calculated at the CASSCF(14,12)/cc-pVTZ level. Bond lengths (black) in Å, bond angles (green) and the CCNH dihedral angle (red) in degrees. H, white; C, gray; N, blue.

In summary, we have found two bond-shift isomers of a 1,3-dipole, phenylnitrile imine (PhCNNH). Phenylnitrile imine was generated by photolysis of 5-phenyltetrazole in Ar and Kr matrixes and both the allenic and the propargylic bond-shift isomers were observed. They were identified by means of their experimental IR signatures, and they were found to react photochemically, with different rates, to 1*H*-diazirine. The existence of two distinct energy minima of PhCNNH, was confirmed by calculations at several levels of theory up to CASSCF(14,12). Our findings give a new view on the

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structural nature of 1,3-dipolar species. Further studies are underway in order to expand our understanding of the factors that allow the observation of bond-shift isomers of nitrile imines.

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- After the irradiation of **1** at 230 nm, subsequent irradiations were performed at longer wavelengths under conditions where **1** is unreactive. Starting at 440 nm and gradually decreasing the wavelength of the tunable UV-light revealed that at ~400 nm the bands of photoproducts of **1** start to be affected. In the range from 400–370 nm, **2A** and **2P** were selectively consumed as discussed.
- Subsequent irradiation at 337 nm leads to the photoisomerization of 1*H*-diazirine **3** to phenylcarbodiimide **4** (Figure S9 and Table S3). This constitutes strong proof that the photoisomerization of nitrile imines to carbodiimides occurs via intermediacy of 1*H*-diazirines. As proposed previously, the rearrangement of **3** to **4** proceeds by ring opening (via the NN bond cleavage) followed by a 1,2-phenyl shift. See refs. 4g and 4i, and also: R. N. Veedu, D. Kvaskoff and C. Wentrup, *Aust. J. Chem.*, 2014, **67**, 457–468.
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