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Infrared-spectroscopic study of amino-substituted nitrilimines and their photochemical transformations in an argon matrix

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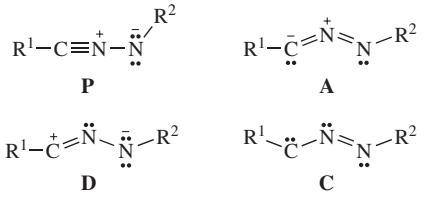
3-Amino- and 3-(dimethyl)amino-1-methylnitrilimines were obtained by the photolysis (λ = 254 nm) of the corresponding 5-amino- and 5-(dimethyl)amino-2-methyltetrazoles in an argon matrix at 10 K or in a gas phase at room temperature. They were characterized by IR spectroscopy and were found to be the primary products of the transformation; the prolonged UV irradiation of the matrix (λ = 254 nm) caused isomerization of the nitrilimines into diazirines.

Nitrilimines are the intermediates of many chemical processes, in particular, of practically important 1,3-dipolar cycloaddition.[1,2] The range of such reactions is continuously enlarged due to the appearance of new sources of nitrilimines, including *N*-cyclopropyl-substituted nitrilimines.[3,4] Bertrand and Wentrup[5] reported the studies of nitrilimines by physicochemical methods, including nitrilimine scavenging and the first experiments on their stabilization in organic matrices at lower temperatures. Stable nitrilimines containing bulky substituents form a special family, which was examined in detail by X-ray diffraction analysis.[6]

Maier *et al*.[7] prepared the simplest unsubstituted nitrilimine HCNNH in an argon matrix. Recent publications of debatable calculation data have aroused considerable interest in studying the nature, structure and reactivity of nitrilimines.[8–10] According to the calculations carried out by the PBE0 method using the 6-311++G (2df, pd) basis set in combination with the natural resonance theory (NRT),[8] nitrilimines can be considered as a combination of four resonance structures: propargylene (**P**), allene (**A**), 1,3-dipolar (**D**) and carbene (**C**).



P **A**

D **C**

The presence of BH_2 substituents at terminal C or N atoms leads to the domination of the 1,3-dipolar (**D**) and propargylene (**P**) structures,[8] whereas substituents such as F or NH_2 increase the contribution of a carbene component (**C**). A number of substituted nitrilimines was studied[11] by IR spectroscopy in an Ar matrix. In this case, the influence of substituents on the spectral characteristics was analyzed based on the quantum-chemical calculation of a vibrational spectrum with consideration for anharmonicity. Nitrilimines with IR absorptions above 2200 cm^{-1} predominantly have the propargylic structures ($PhCNNSiMe_3$, PhCNNPh, $R_2BCNNBR_2$), whereas those with below 2200 cm^{-1} are allenic (HCNNH, PhCNNH, HCNNPh, PhCNNMe and $Ph_3CCNNCPh_3$). Recently detected in an Ar matrix nitrilimines RCNNH with ν_{as}(CNN) at 2078 (R = CH_2CHCH_2),[12] 2138 cm^{-1} (R = Me),[13,14] possess a similar allene structure.

As follows from calculation data,[8,15] amino-substituted nitrilimines should have a more expressed carbene character; however, published experimental data on the spectral characteristics of amino-substituted nitrilimines are absent because they readily undergo isomerization or decomposition. They were not detected in the products of thermal decomposition of amino-substituted tetrazolium iodides with the use of time-of-flight mass spectrometry or IR spectroscopy.[16] We succeeded in stabilizing such molecules in an Ar matrix at 10 K.† Here, we report the main results obtained in a study of amino-substituted nitrilimines $R_2NCNNMe$ (R = H, Me), which were generated by the photolysis of 2,5-substituted tetrazoles (Schemes 1 and 2), by matrix IR spectroscopy.‡

Precursors **1**, **11** were evaporated at 60 °C and co-deposited with a large excess of argon at the molar ratio of *ca*. 1:1000 on the surface of the copper cube cooled to 10 K.

The photolysis of 2,5-disubstituted tetrazoles **1**, **11** was accomplished by two methods. In the first case, the photolysis was carried out in a gas phase at room temperature; the compound was passed through a quartz tube (1.5×25 cm) connected to the cryostat with simultaneous irradiation with light from a Philips low-pressure mercury lamp (λ = 254 nm, 11 W). In the second case, the matrix-isolated tetrazoles were photolyzed using a low-

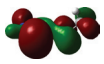
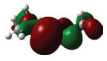
† Previously, the results of our studies were presented at the conferences.[17,18]

‡ The matrix isolation experiments were performed with the use of a Displex 208R closed-cycle cryogenic system (Air Products & Chemicals) as described previously.[19] IR spectra were recorded on a Bruker IFS-113v FTIR spectrometer with resolution 1–0.5 cm^{-1} in the range of 4000–400 cm^{-1} in the reflection mode. The quantum-chemical calculations were performed using the GAUSSIAN 09 program package[20] with the use of the B3LYP density functional[21] and 6-31G(d,p), 6-311G(d,p), cc-pVTZ basis sets and PBE0 density functional[22] and the 6-311++G (2df, pd) basis set.

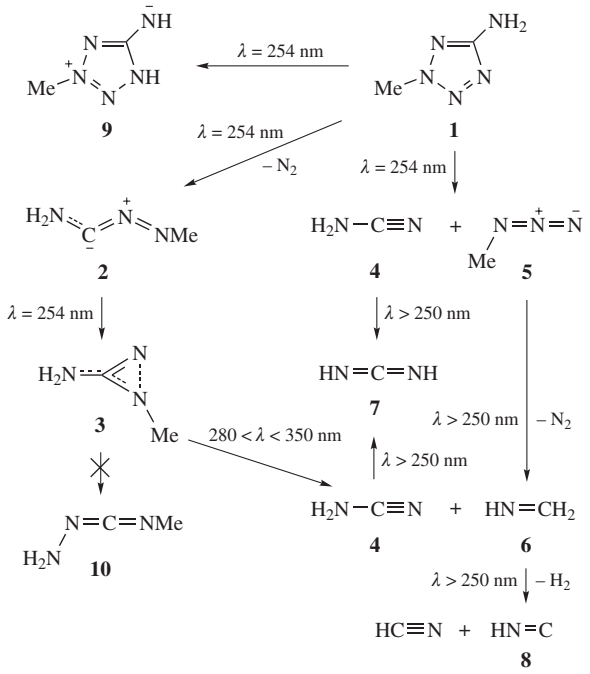
5-Amino-2-methyl-2*H*-tetrazole **1** of 99% purity from Chemical Block Ltd. was used in the experiments without further purification.

*5-(Dimethyl)amino-2-methyl-2*H*-tetrazole* **11**. A solution of 1.00 g (10 mmol) of 5-amino-2-methyl-2*H*-tetrazole and 0.67 g (22 mmol) of paraformaldehyde in 2.32 g (50 mmol) of formic acid was heated for 12 h at 100–110 °C. After cooling, the reaction mass was diluted with water (20 ml), extracted with ethyl acetate (2×20 ml) and dried with anhydrous $MgSO_4$. After the distillation of the solvent, the product was purified by chromatography on silica gel (eluent: $CHCl_3$–AcOEt, 1:1). Compound **11** was obtained as colourless oil (1.01 g, yield 78%). ^{1}H NMR ($CDCl_3$) δ: 2.98 (s, 6H, 2Me), 4.10 (s, 3H, Me). ^{13}C NMR ($CDCl_3$) δ: 38.6 (2Me), 39.1 (Me), 170.0 (C). MS, *m*/*z* (%): 127 (100) $[M]^+$, 99 (18), 56 (94). Found (%): C, 37.80; H, 7.12; N, 55.04. Calc. for $C_4H_9N_5$ (%): C, 37.79; H, 7.13; N, 55.08. For experimental details, see Online Supplementary Materials.

Table 1 Effect of substituents on the structure and spectral characteristics of nitrilimines R^1CNNR^2, B3LYP/cc-pVTZ calculation.

R^1	R^2	θ(CNN)/°	R(C–N)/Å	ω(CNN)[a]/cm^{-1}	HOMO
H	H	169.7	1.189	2130	
NH_2	Me	157.4	1.228	1955	
NMe_2	Me	144.2	1.259	1789	

[a] Frequencies calculated in the harmonic approximation.



Scheme 1

pressure mercury lamp (λ = 254 nm) and then a high-pressure mercury arc lamp DRSh-500 with a set of glass cut filters.

The calculation of amino-substituted nitrilimines $H_2NCNNMe$ **2** and $Me_2NCNNMe$ **12** indicates a considerable change in the structural parameters, as compared with those of the simplest nitrilimine HCNNH, and a pronounced localization of the HOMO, which has the nature of a lone pair of electrons on the carbon atom (Table 1). The CN bond length in such nitrilimines increased, as compared with that in the simplest nitrilimine, and the CNN angle considerably decreased to affect spectral characteristics, primarily, the CNN antisymmetrical stretch.

As follows from published data,[1,7,11–14] nitrilimines are formed in good yields upon the photolysis of 2,5-substituted tetrazoles. The photolysis of 5-amino-2-methyl-2*H*-tetrazole **1** (λ > 235 nm) was studied previously.[23] Under these conditions, the entire set of products was formed immediately (see Scheme 1), but 3-amino-1-methylnitrilimine **2** was not identified. The cyclic isomer 3-amino-1-methyl-1*H*-diazirine **3**, to which some bands of nitrilimine **2** were erroneously assigned, was considered as the main primary product.

However, we successfully separated the resulting products upon the stepwise photolysis of **1**. The photolysis was carried out in a flow reactor using a low-pressure lamp (λ = 254 nm) at room temperature (under these conditions, the conversion was about 15%) or in Ar matrices at 10 K. A number of new absorptions [3543.5 (m), 3536.8 (m), 3405.7 (w), 3398.9 (w), 2953.5 (m), 2919.9 (m), 2868.8 (m), 1963.3 (w), 1937.3 (w), 1901.5 (w), 1880.2 (w), 1605.4 (m), 1456.0 (m), 1449.1 (w), 1406.4 (s), 1375.8 (vs), 1371.1 (vs), 1160.9 (m), 1133.8 (sh, m), 1067.4 (w), 1036.6 (w), 865.6 (vw), 552.6 (m), 540.2 (vs), 489.7 (w) cm^{-1}] (see Figure S2, Online Supplementary Materials), assigned to nitrilimine **2** as the primary product of dediazotization, were observed in the IR spectrum of gas-phase photolysis products isolated in an Ar matrix. According to these data, compound **2** has an allene structure.

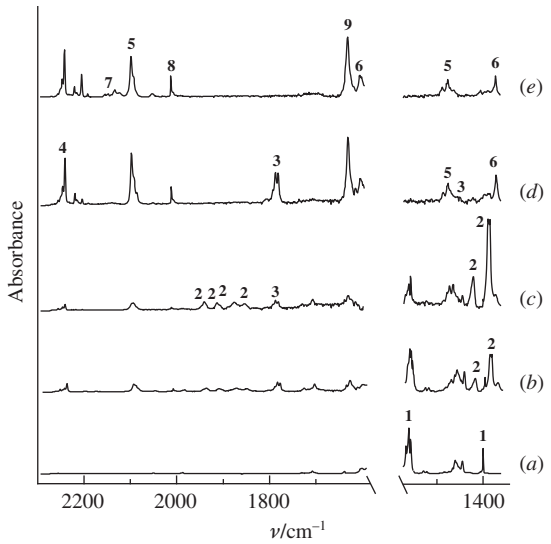


Figure 1 IR spectra of tetrazole **1** and its photolysis products: (*a*) **1** in an Ar matrix at 10 K, (*b*) after photolysis (λ = 254 nm) for 10 min, (*c*) after photolysis (λ = 254 nm) for 40 min, (*d*) after additional photolysis (280 < λ < 350 nm) for 30 min and (*e*) after additional photolysis without a filter for 20 min.

The same bands appeared in the first minutes of the photolysis (λ = 254 nm) of tetrazole **1** isolated in an Ar matrix [Figures 1(*b*) and 2]. The above bands synchronously increased within the following 40 min [Figure 1(*c*)], and the appearance of secondary products was observed simultaneously. More prolonged photolysis (λ = 254 nm) for 70 min led to the complete disappearance of the initial product and an increase in the bands of cyclic isomerization product **3** [3564.7 (w), 2994.8 (m), 2950.6 (m), 2895.5 (w), 1821.4 (sh, m), 1815.7 (vs), 1810.8 (vs), 1584.3 (m), 1457.8 (m), 1434.8 (w), 1358.6 (s), 976.8 (m), 836.9 (w), 658.8 (w), 511.0 (br., w) cm^{-1}] [Figures 1(*d*), 2, Table S4].

Photolysis with a light within 280 < λ < 350 nm [Figure 1(*e*)] results in the decrease of bands of diazirine **3** and the growth of bands of the following products: cyanamide **4** (3445.7, 3433.6, 2265.7, 2256.3, 2251.5 and 1062.5 cm^{-1}), methyl azide **5** (2114.5, 1469.4, 1416.5, 1277.8 and 891.9 cm^{-1}), complex of methylenimine **6** with compound **4** (1649.7 and 1359.6 cm^{-1}) and iminocarbene HNC **8** (3579.3 and 2031.2 cm^{-1}). The same transformations were observed earlier.[23] Upon additional photolysis with unfiltered light [Figure 1(*e*)], carbodiimide **7** (2167.8, 2160.9, 2147.2, 1042.2 and 882.9 cm^{-1}) was formed[24] and the subsequent degradation of intermediates with the formation of HCN (3303 and 721 cm^{-1}) and its complexes (3260 and 780 cm^{-1}) also occurred. The spectrum also contained bands due to 5-aminido-3-methyl-1*H*-tetrazol-3-ium **9**, a tautomer of the initial tetrazole (1664.1 and 802.1 cm^{-1}), which appeared already at the early stage of irradiation and did not disappear even upon prolonged photolysis. Note that, unlike the previously studied nitrilimines with other substituents,[11–14] which isomerized into carbodiimide **10** as the end product, this isomerization was not observed in the case of amino-substituted nitrilimines.

Good agreement between the experimental bands in the IR spectrum and calculation data (Table S2) and an analogy with the generation conditions of other substituted nitrilimines[11–14] made it possible to assign the bands observed in the initial period

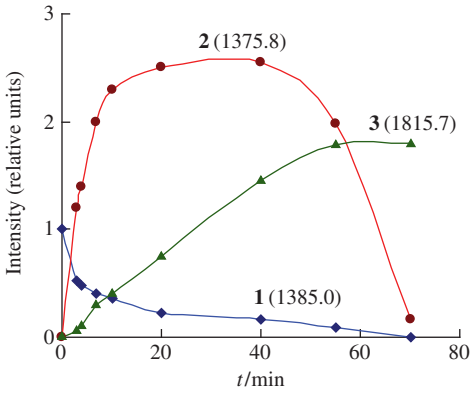


Figure 2 Intensities of IR absorption bands of initial tetrazole **1** (1385.0 cm^{-1}), nitrilimine **2** (1375.8 cm^{-1}) and diazirine **3** (1815.7 cm^{-1}) under photolysis at λ = 254 nm in an Ar matrix *vs.* irradiation time.

of photolysis to nitrilimine **2**. Four weak bands (1963.3, 1937.3, 1901.5 and 1880.2 cm^{-1}), which changed synchronously with the other bands of nitrilimine **2**, were detected in a region at 1900 cm^{-1}, where the ν_{as}(CNN) mode should appear according to calculations. One of these bands, a weak band at 1880.2 cm^{-1}, can be assigned to the CNN antisymmetrical stretch (Table S4). It is likely that the presence of several bands in this region is related to the resonance of the fundamental vibration frequency and the composite vibration frequencies δ(Me) (1375.8) + δ(CNN) (540.2), δ(Me) (1375.8) + τ(NH_2) (552.6) and ν_{as}(CNN) (1406.4) + δ(NCN) (540.2). The low intensity and a considerable shift of this band to the low-frequency region in amino-substituted nitrilimines, as compared with alkyl- or phenyl-substituted ones, are consistent with published predictions[8,11,15] and the results of our calculations (Table 1). The intensities of bands due to ν_s(CNN) stretch (1406.4 cm^{-1}), δ(Me) symmetrical deformation (1375.8 and 1371.1 cm^{-1}) and δ(NCN) deformation (540.2 cm^{-1}) of nitrilimine **2** were much higher (Table S2, Figure S2).

Based on a comparison with calculation data, we assigned the bands of isomeric cyclic product **3** to normal vibration modes

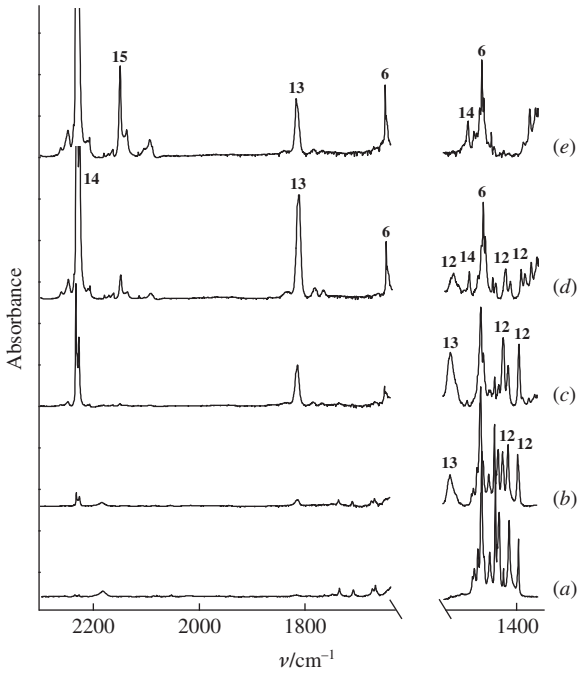


Figure 3 IR spectra of tetrazole **11** and the products of photolysis: (*a*) **11** in an Ar matrix at 10 K, (*b*) after photolysis (λ = 254 nm) for 5 min, (*c*) after photolysis (λ = 254 nm) for 20 min, (*d*) after photolysis (λ = 254 nm) for 60 min and (*e*) after additional photolysis (280 < λ < 350 nm) for 20 min.

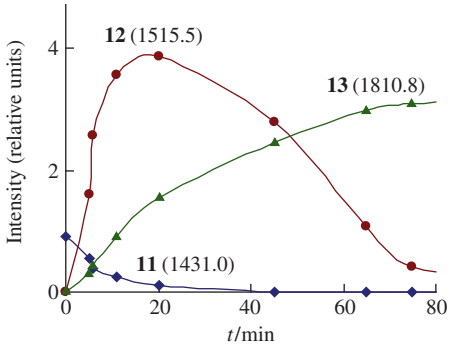
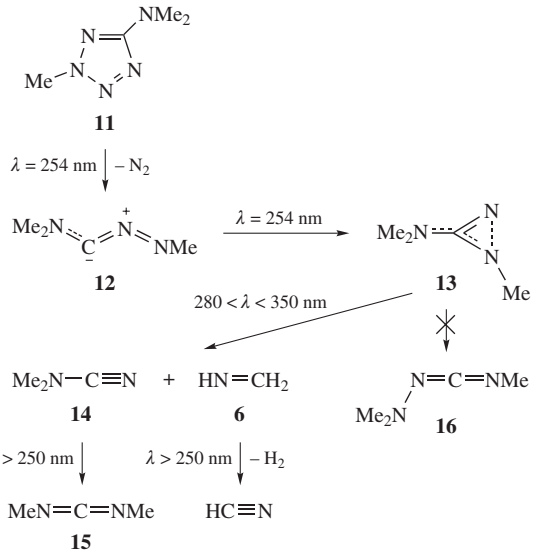


Figure 4 Intensities of IR absorption bands of initial tetrazole **11** (1431.0 cm^{-1}), nitrilimine **12** (1515.5 cm^{-1}) and diazirine **13** (1810.8 cm^{-1}) under photolysis at λ = 254 nm in an Ar matrix *vs.* irradiation time.

(Table S4). The experimental results are partially consistent with published data.[23] Thus, the most intense split band (1815.7 and 1810.8 cm^{-1}) was attributed to the characteristic antisymmetrical stretch of the NCN fragment; at the same time, we assigned some bands, which were earlier ascribed to diazirine **3**, to nitrilimine **2**.

A number of new bands [2987.3 (w), 2954.3 (m), 2937.2 (m), 2902.3 (w), 2872.0 (w), 2854.6 (w), 1725 (vw), 1515.5 (vs), 1460.9 (m), 1457.8 (s), 1452.2 (m), 1448.3 (m), 1415.6 (s), 1405.6 (m), 1384.6 (s), 1236.8 (m), 1140.2 (w), 1065.4 (w), 1058.8 (s), 1038.5 (m), 913.0 (w), 799.4 (m), 639.5 (vs), 631.6 (vs), 621.2 (vs) and 470 (br.) cm^{-1}] were detected in the spectrum of the products of gas-phase photolysis (λ = 254 nm) of 5-(dimethyl)amino-2-methyltetrazole **11** (Figure S5, Table S6). As in the case of nitrilimine **2**, the same bands appeared in the first minutes of photolysis [Figure 3(*b*)] in an Ar matrix and synchronously increased on the irradiation of compound **11** for 20 min [Figures 3(*c*), 4]. By analogy with compound **2**, we assigned these bands to nitrilimine **12**.

Photolysis with the same light for 60 min results in the decrease of bands of primary product **12** [Figure 3(*d*)]. Simultaneously, the bands of the secondary product [2924.8 (m), 2913.0 (w), 1810.8 (vs), 1466.6 (w), 1433.0 (w), 1377.8 (s), 1281.2 (s), 1140.1 (w), 1129.8 (w), 1062.0 (m), 1030.8 (m) and 934.6 (w) cm^{-1}] raised. Based on a comparison with calculation data (Table S8), these bands can be assigned to cyclic diazirine isomer **13** with a characteristic intense band at 1810.8 cm^{-1} in the matrix, which is close to the absorption (1815.7 cm^{-1}) of analogous diazirine **3**. Furthermore, bands due to the products of the subsequent decomposition appeared in the spectrum (Scheme 2).



Scheme 2

On photolysis with a high-pressure Hg lamp with a filter ($280 < \lambda < 380$ cm^{-1}), the intensity of these bands increased synchronously with a decrease in the intensity of bands due to diazirine **13**. One of the degradation products was methylenimine CH_2=NH **6** (3030.4, 2925.2, 1641.2, 1453.3, 1350.8, 1121.6 and 1063.0 cm^{-1}), whose bands were consistent with published data[25] for an individual molecule of **6** in a matrix of Ar. Another group of bands (3012.7, 2886.9, 2231.2, 2226, 1483.9, 1337.1, 1208.3, 1156.0, 1081.9, 1067.4 and 525.5 cm^{-1}) can be assigned to dimethylcyanamide **14** (2233 cm^{-1} in a gas phase[26] and 2228 cm^{-1} in an Ar matrix[27]). Furthermore, the isomerization of **14** into dimethylcarbodiimide **15** (2948.0, 2147.4, 1472.3, 1393.0, 1104.0, 970.2 and 946.9 cm^{-1}) was observed,[28] and the bands of the latter increased on the subsequent irradiation of the matrix with unfiltered light. As in the case of compound **2**, the final product **16** of the isomerization of nitrilimine **12** was not detected.

The bands formed in the initial period of irradiation were due to an unstable species, as evidenced by the absence of these bands upon the deposition of photolysis products onto the surface cooled to 10 K but without an Ar matrix. This special feature is characteristic of unstable nitrilimines, which are converted into a dimer, bis(azo)ethylene,[29] in the absence of an insulating substrate. The conditions of generation and the behavior of the unstable species, which is similar to that of previously described nitrilimines,[5,7,11–14] and also an analogy with nitrilimine **2**, allowed us to assign the initially observed bands to nitrilimine **12**. The calculation of the structure and vibrational spectrum of **12** with the use of B3LYP or PBE0 density functional with different basis sets gave similar results and indicated an electron density redistribution, bent geometry and considerable elongation of C–N bonds (Table 1). This redistribution was especially strongly manifested in a reduction of the frequency of the antisymmetric CNN vibration, which reflects the nature of the nitrilimine structure. According to the calculation data, the contribution of a carbene component in nitrilimine **12** increases and, as a result, the vibration band ν_{as}(CNN) should be shifted to a region of 1700–1800 cm^{-1} with a several times decrease in its relative intensity as compared with that of other nitrilimines. It is likely that, for this reason, we failed to detect bands noticeably different from background noise and having a similar behavior with other bands due to the primary product in the test region. A very weak band at 1725 cm^{-1} can be tentatively related to this vibration. At the same time, good agreement of other bands observed in the IR spectrum with calculation data (Table S6) allowed us to conclude that they belonged to nitrilimine **12**. This species is characterized by a high value and intensity of the $\nu(CNMe_2)$ vibration (1515.5 cm^{-1}). Other intense bands were attributed to the deformation vibrations of methyl groups δ(Me) and $\delta(Me_2)$ (1457.8, 1415.6 and 1384.6 cm^{-1}), *r*(Me) (1058.8), skeletal ν_s(CNN) (1236.8) and δ(NCN) (621.2 cm^{-1}).

In conclusion, we were the first to detect amino-substituted nitrilimines using direct matrix isolation and to obtain their IR spectra. The experimentally observed low values and low intensities of the IR band ν_{as}(CNN) suggest an increase in the carbene component in the structure of amino-substituted nitrilimines.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2014.06.002.

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