Ethynylogization of a Coarctate Fragmentation

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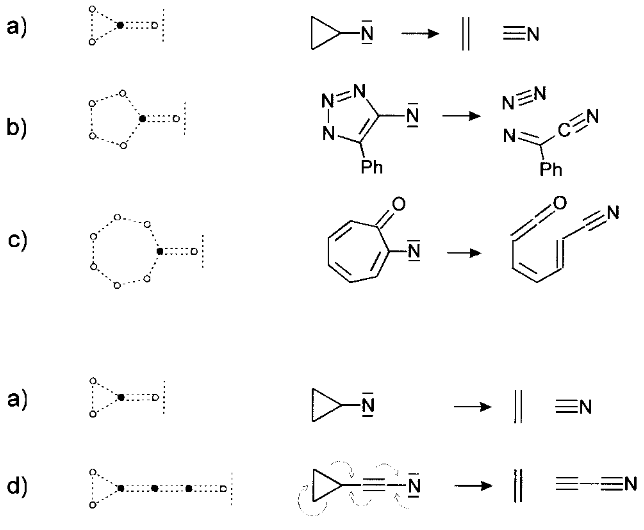
Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 70th birthday

Abstract: Coarctate reactions form a separate class of elementary closed-shell processes in addition to polar and pericyclic reactions. Hence, they also follow a different homology principle. Whereas vinylogous polar and pericyclic reactions differ in the length of the reacting system by a double bond, coarctate reactions can be homologized (ethynylogized) by extending a known system by a triple bond. The prediction, which is based on theoretical considerations, is confirmed experimentally by the fragmentation of cyclopropylethynyl nitrene to cyano acetylene and ethylene, a reaction that is "ethynyloguous" to the known fragmentation of cyclopropyl nitrene to ethylene and HCN.

Keywords: carbenes · coarctate reactions · matrix spectroscopy · nitrenes

Introduction

Coarctate[1] reactions are reactions that involve atoms at which two bonds are made and broken simultaneously. [2–4] The linear (coarctate) subsystem of making and breaking of two bonds is bound by terminators at both ends. Terminators are either atoms with a lone pair of electrons (e. g. carbene or nitrene centers) or two or more atoms, which complement the electron shift formally to a cyclic topology. Similar to polar reactions (e. g. S_N2, S_N2') and pericyclic reactions (e. g. 1,3-, 1,5-sigmatropic shift) there are also homology principles for coarctate reactions. In analogy to the pericyclic reactions, the ring size of the terminators in coarctate reactions can be varied by two atoms. Scheme 1 shows examples of three known coarctate reactions (a – c) with a coarctate center and a nitrene terminator combined with a three-,[5] five-,[6] and seven-membered ring terminator.[7] The reactions are not cheletropic. According to the original definition of pericyclic reactions, bond making and breaking has to take place in a cyclic array. This is not the case in coarctate reactions.[2] Reaction (a) is experimentally well investigated because of the biological importance of the formation of ethylene from the 1-amino-cyclopropane-1-carboxylic acid[8]. The reaction is known in the parent system[5a] as well as in a number of substituted systems.[5a–h] If the nitrene is generated by irradiation or thermolysis of the corresponding azide,[5a–c,e] oxaziridine,[5h] or isocyanate,[5e] the reaction is highly stereoselective.[9] Calculations also support a concerted mechanism.[10]



Scheme 1. Homology principle of coarctate reactions. Coarctate centers in the delocalized system of the transition state in the left column are marked with ● and terminator atoms are identified with o. Reactions a) – c) differ in the ring size of the terminator, a) and d) differ in the length of the linear (coarctate) subsystem.

In principle it should be possible to form a homologue of a coarctate reaction by extending the linear subsystem by two

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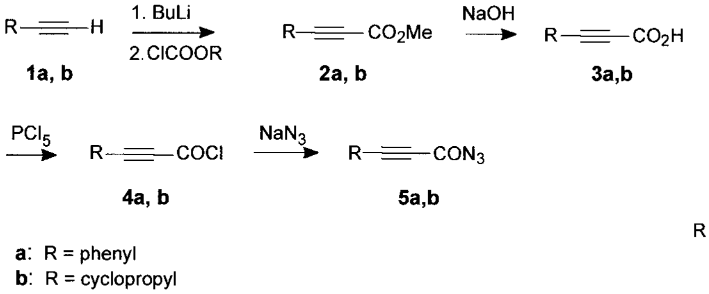
atoms. The most simple way to prove this hypothesis is to insert an ethynyl unit which allows the breakage of two π bonds.

Reaction (d) in Scheme 1 would be homologous (ethynylogous) to reaction (a). It is expected that in reaction (d) cyano acetylene should be eliminated instead of HCN, which is formed in reaction (a). To test this simple principle, we synthesized the nitrene precursor cyclopropyl-prop-2-ynoyl-azide (**5b**) and phenyl-prop-2-ynoyl-azide (**5a**) (which cannot undergo a coarctate reaction) as a reference compound from the corresponding alkyne and phenyl propyolic acid (Scheme 2). The nitrenes were generated from the azides photochemically as well as thermochemically by Curtius rearrangement and elimination of carbon monoxide.



Scheme 2. Synthesis of the nitrene precursors.

Results and Discussion

Photolysis of azides **5a** and **5b** in an argon matrix with light of the wavelength 335 and 305 nm generated the isocyanates **6a** and **6b**, which are identified by their typical IR absorptions at 2307.1, 2269.0 cm^{-1} (**6a**) and 2329.6, 2268.6 cm^{-1} (**6b**) (Figure 1). The same bands, in the case of **6a** shifted by about 11 and −5.6 cm^{-1}, are found upon flash vacuum pyrolysis of **5a** and **5b** at 400°C followed by isolation of the products in an argon matrix (**6a**: 2318.2, 2263.4 cm^{-1}). According to a calculation (B3LYP/6-31G*), the two bands are the two coupling modes of the isocyanate stretch with the triple bond. The calculated wave numbers are in agreement with the experimental absorption bands within the error limits of the method (**6a**: 2375.5, 2260.3, **6b**: 2390.3, 2271.8 cm^{-1}, B3LYP/6-31G*, scaled).[11] The discrepancy between the spectra of the isocyanate **6a** generated by photolysis and pyrolysis is attributed to a matrix effect. If the matrix with photochemically generated **6a** is warmed up to 38 K the bands shift and are in agreement with those of the pyrolytically generated species.[12] Ethynyl isocyanates have been postulated as intermediates formed upon thermolysis[13] and photolysis[14] of phenyl propyolyl azide. Chen et al. recently obtained isocyanates in solution by thermal decomposition of propyolyl azides.[15]

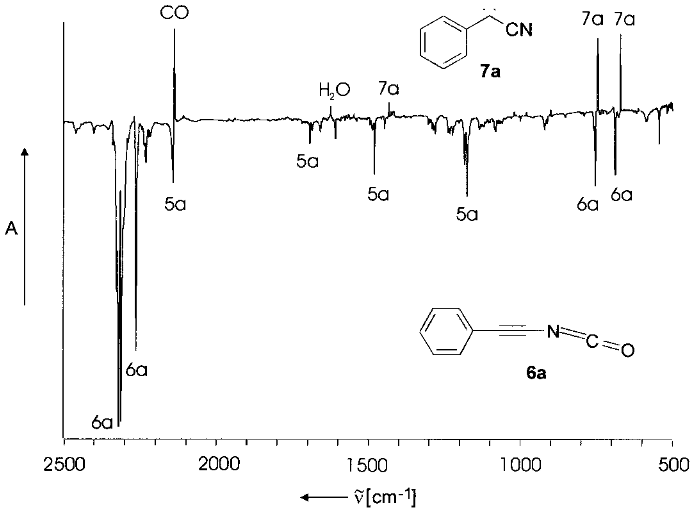
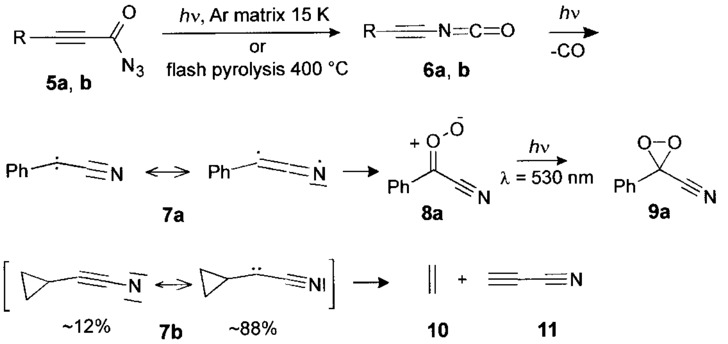


Figure 1. Matrix IR spectrum (Ar, 10 K): Difference spectrum of the reaction of the isocyanate **6a** to the carbene **7a** upon irradiation (90 min, 208 nm). The bands of the products which are formed during the photolysis point upwards, the bands of the isocyanate **6a** and of the azide **5a** point downwards.

Upon prolonged irradiation or photolysis at shorter wavelengths (>305 nm, **5a** and >280 nm, **5b**), carbon monoxide is eliminated (Scheme 3). The phenylethynyl isocyanate **6a** yields a species that is stable under matrix conditions and which according to the IR spectrum (experimental 746.2, 672.6 cm^{-1}, B3LYP/6-31+G*, 759.1, 684.0 cm^{-1}) is the triplet cyanophenyl carbene **7a** (Figure 1). This assignment is confirmed by trapping experiments with oxygen. Upon irradiation of **5a** (305 nm) in an oxygen-containing (0.5%) matrix and subsequent warming to 40 K, the IR bands of **7a** disappear and the typical absorptions of carbonyl oxide **8a** appear at 1373.0, 1353.2, 1213.9, 1059.7, 947.1, 944.5, 769.1, 680.8, and 678.0 cm^{-1}. The band at 947.1 cm^{-1} is shifted to 899.1 cm^{-1} upon isotopic labeling with ^{18}O, showing that this intense absorption is likely to be assigned to $\nu_{O\text{-}O}$ of the carbonyl oxide. Additional irradiation of the carbonyl oxide **8a** at 530 nm leads to the dioxirane **9a** (1332.4, 1298.7, 759.1, 691.4 cm^{-1}). Benzoyl cyanide was identified by its known IR spectrum as an additional product. Cyanophenyl carbene **7a** was characterized for the first time in matrix. Up to now it had only been generated from different precursors and was trapped with alkenes under formation of cyclopropanes.[16–18] A triplet ground state was postulated because of the non-stereospecific reaction with 2-butenes.[16, 19] The carbene structure (Scheme 3, **7a** left) does not accurately represent the true electronic structure. The high spin density value (0.85, B3LYP/6-31+G*) at the terminal nitrogen atom indicates that the diradical allene structure contributes substantially to



Scheme 3. Matrix photolysis and flash pyrolysis of nitrene precursors.

the overall wave function. The calcuated C-C-C angle at the carbene center (160.1°) is considerably larger than in the parent cyano carbene (140°).[20, 21]

Contrary to **7a**, the cyclopropyl derivative **7b** is not stable under matrix conditions. As expected, it fragments in a coarctate reaction to form ethylene[22] and cyano acetylene.[23] A carbene species could not be trapped with oxygen. A ring enlargement to 1-cyano cyclobutene analogous to the reaction of cyclopropyl carbenes[24] also was not observed.[25] The bands in the spectrum of the product after irradation (4h, 280 nm) of **5b** could be assigned to ethylene and cyano acetylene (Figure 2). According to calculations, the singlet–triplet splitting of **7b** is relatively small. Only after a systematic investigation with an increasing size of basis sets and an increasing level of correlation treatment was an unambiguous preference of the singlet state of about 3 kcal mol^{-1} established.[26] The electronic structure of the singlet ground state is well represented by a pair of resonance structures of the cyclopropylethynyl nitrene and cyanocyclopropyl carbene. The nitrene structure contributes about 12 % and the carbene structure 88 % to the overall wave function.[27] There are two possible conformations of **7b** because of the bent geometry at the carbene center. The carbene lone pair can be located *endo* or *exo* with respect to the three-membered ring. According to a calculation (B3LYP/6–31 + G*) the *endo* conformation is 1.44 kcal mol^{-1} more stable (Table 1).

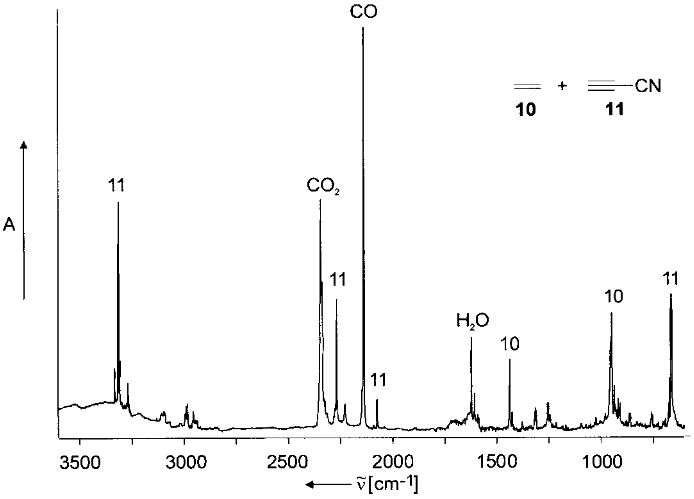


Figure 2. Matrix IR spectrum of the products after irradiation of the azide **5b** (16 h, 335 nm).

Both conformations can undergo a coarctate fragmentation to ethylene and cyano acetylene via two different transition states. Calculations predict an activation barrier of 11.1 kcal mol^{-1} for the energetically most favorable fragmentation process, namely the conformational change from *endo*- to *exo*-**7b** and a subsequent concerted coarctate fragmentation via the *exo* transition state. Provided that during the photochemical generation **7b** is formed in a vibrationally excited state, the calculated value is in agreement with the experimentally observed fragmentation in matrix. An alternative explanation would be that **7b** is indeed formed in matrix, but under the conditions of the irradiation ($\lambda >$ 280 nm) it might react with a higher quantum yield than it is formed. Compound **7b** therefore could be present in a photostationary concentration too low for spectroscopic detection.

Table 1. Calculated (B3LYP/6–31 + G* + ZPE) relative energies of the stationary points on the reaction hypersurface of the fragmentation of *exo*- and *endo*-**7b** in kcal mol^{-1} relative to *endo*-**7b**.

	7b	**[7b → 10 + 11]**‡	**10 + 11**
endo	0.0	16.6	– 21.2
exo	1.4	11.1	– 21.2

Conclusion

We have demonstrated a new homology principle in coarctate reactions by experimental verification of the predicted reaction of **7b** to give ethylene and cyano acetylene. In polar and pericyclic reactions the next higher homologue (vinylogue) is defined by extending the reacting system by a double bond. The next higher homologue (ethynylogue) of coarctate reactions, however, is formally generated by introducing a triple bond which reacts with *both* π bonds.

Experimental Section

2b: A solution of 1.6 M *n*-butyllithium in hexane (13.9 mL, 22.3 mmol) was slowly added to a solution of cyclopropyl acetylene (**1b**)[28] (1.47 g, 22.3 mmol) in dry THF at – 80 °C. After an hour methyl chloroformate (5.27 g, 55.7 mmol) was added at – 80° C. The reaction mixture was slowly allowed to warm up and lithium chloride precipitated. Additional lithium chloride precipitated by addition of diethyl ether. The product was obtained by distillation (88 °C, 23 mbar), yield 2.26 g (82 %); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88–1.00 (m, 4H; CH_2CH_2), 1.32–1.48 (m, 1H), 3.74 (s, 3H; OCH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ = -0.8 (cyclopr. CH), 9.1 (CH_2CH_2), 52.3 (OCH_3), 68.1 ($C{\equiv}\mathit{C}$-CO), 93.4 ($\mathit{C}{\equiv}C$-CO), 154.1 ($\mathit{C}{=}O$).

3b: Sodium hydroxide (4.27 g, 106.4 mmol) in water (450 mL) was added to a solution of **2b** (11.9 g, 95.9 mmol) in ethanol (800 mL) over a period of 45 min. After the mixture had been stirred for an additional 90 min, water (600 mL) was added. The solution was extracted with dichloromethane (2 × 300 mL). The organic phase was discarded, the water phase was treated with hydrochloric acid (50 mL) and immediately extracted with dichloromethane (4 × 300 mL). The combined extracts were concentrated and dried under high vacuum. Yield: 9.10 g (86 %), m.p. 55° C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88–1.08 (m, 4H, CH_2CH_2), 1.31–1.51 (m, 1H), 11.55 (s, 1H, CO_2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = – 0.5 (cyclopr. *C*H), 9.5 (CH_2CH_2), 68.0 ($C{\equiv}\mathit{C}$-CO), 96.7 ($\mathit{C}{\equiv}C$-CO), 158.6 ($C{=}O$); IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1} (br.), 2350 (w), 2225 (s), 1685 (s), 1413 (m), 1285 (m), 1186 (m), 1135 (w), 1000 (w), 863 (m), 605 (w); MS (EI, 70 eV): *m*/*z* (%): 110 (100) [M^+], 93 (40) [M^+ – OH], 92 (18), 82 (21), 81 (22), 66 (62) [M^+ – CO_2], 65 (84) [M^+ – CO_2H], 63 (20), 53 (36).

4b: Under an atmosphere of nitrogen, phosphorus pentachloride (6.25 g, 30 mmol) was added to a solution of **3b** (3.3 g, 30 mmol) in dry tetrachloromethane (95 mL). The mixture was stirred until the gas evolution stopped and the phosphorous pentachloride was consumed. The product was obtained by distillation in vacuo (b.p. 56.5 °C, 9.2 mbar); yield 2.92 g (76 %). The product is thermolabile, therefore the temperature should not rise above 70 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.02–1.16 (m, 4H, CH_2CH_2), 1.51 (tt, *J* = 8.3 and 5 Hz, 1H; cyclopr. CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 0.0 (cyclopr. CH), 10.7 (CH_2CH_2), 72.7 ($C{\equiv}\mathit{C}$-CO), 103.5 ($\mathit{C}{\equiv}C$-CO), 148.7 ($C{=}O$); IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1} (w), 2261 (w), 2222 (s), 2202 (s), 1744 (s), 1454 (w), 1356 (w), 1211 (m), 1166 (m), 1052 (m), 880 (s), 804 (m), 758 (m), 648 (m); MS (EI, 70 eV): *m*/*z* (%): 129 (17) [M^++H], 128 (3) [M^+], 102 (8), 100 (20), 93 (100) [$M^+ - \mathrm{Cl}$], 89 (10), 76 (84) [$M^+ - \mathrm{COCl}$].

5b: Sodium azide (0.52 g, 8.0 mmol) was suspended in a mixture of dry diethyl ether (10 mL) and dry acetonitrile (10 mL). The mixture was cooled to −10 °C and **4b** (0.77 g, 6.0 mmol) dissolved in acetonitrile (2 mL) was added over a preiod of about 30 min. After stirring for 2 h at −10 °C, the reaction mixture was allowed to warm up to 20 °C and stirred for an additional 3 h. For workup diethyl ether (20 mL) was added and the organic phase was subsequently washed with water, a solution of sodium bicarbonate, and water again. The organic phase was dried over sodium sulfate and concentrated in vacuo at about 35 °C. The prdoduct was obtained by vacuum distillation at 50 °C (4.6×10^{-2} mbar); yield: 0.53 g (65 %). Compound **5b** starts to decompose at a temperature of about 70 °C. Above 100 °C violent explosions are observed. ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$): $\delta = 0.90-1.08$ (m, 4H, $\mathrm{CH_2CH_2}$), 1.35–1.51 (m, 1H; cyclopr. CH); ^{13}C NMR (50 MHz, $\mathrm{CDCl_3}$): $\delta = -0.3$ (cyclopr. CH), 9.8 ($\mathrm{CH_2CH_2}$), 70.0 ($\mathrm{C}\equiv C$-CO), 99.6 ($C\equiv\mathrm{C}$-CO), 158.0 ($\mathrm{C=O}$); IR (KBr): $\tilde{\nu} = 3020\ \mathrm{cm^{-1}}$ (w), 2305 (w), 2228 (s), 2145 (azide, s), 1676 (s), 1455 (w), 1429 (w), 1359 (m), 1235 (s), 1178 (s), 1125 (m), 1084 (m), 1035 (w), 945 (s), 882 (m), 813 (w), 713 (m); MS (EI, 70 eV): m/z (%): 135 (14) [M^+], 107 (3) [$M^+ - \mathrm{N_2}$], 93 (100) [$M^+ - \mathrm{N_3}$], 65 (28) [$M^+ - \mathrm{CON_3}$], 63 (5), 53 (9), 52 (8), 51 (10 %); HR-MS: calcd $\mathrm{C_6H_5N_3O}$: 135.0433; found 135.0432 (0.0003)

5a: At −10 °C a solution of propyolyl chloride **4a**[29] (3.54 g, 21.5 mmol) in dry acetonitrile (7 mL) was added to a suspension of sodium azide (1.87 g, 28.7 mmol) in a mixture of dry diethyl ether (35 mL) and dry acetonitrile (35 mL). After 2 h the mixture was allowed to warm to room temperature and the solution was stirred for an additional 3 h. After addition of diethyl ether (70 mL) the organic phase was washed with water and aqueous sodium bicarbonate and dried over sodium sulfate. The solvent was removed in vacuo at about 35 °C and the solid residue was purified by chromatography over silica gel using a 1:1 mixture of diethyl ether and hexane; yield: 2.94 g (80 %); m.p. 51–52 °C, b.p. 65 °C (1.5×10^{-2} mbar), the decomposition starts at about 80 °C, above about 100 °C vigorous decomposition is observed. ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$): $\delta = 7.30-7.68$ (m, 5H, phenyl); ^{13}C NMR (50 MHz, $\mathrm{CDCl_3}$): $\delta = 81.9$ ($\mathrm{C}\equiv C$-CO), 91.5 ($C\equiv\mathrm{C}$-CO), 118.9 (*ipso*) 128.7 (*meta*), 131.3 (*para*), 133.3 (*ortho*), 158.4 ($\mathrm{C=O}$); IR (KBr): $\tilde{\nu} = 2927\ \mathrm{cm^{-1}}$ (w), 2854 (w), 2222 (s), 2160 (m), 2137 (azide, m) 1668 (s), 1488 (w), 1444 (w), 1281 (s), 1180 (m), 1164 (s), 1154 (s), 1117 (m), 1076 (m), 1071 (m), 996 (w), 904 (w), 792 (w), 776 (m).

Matrix investigations: At a sample temperature of 20 °C (**5a**) and −5 °C (**5b**) the azides were sublimed onto the spectroscopic window (CsI). The deposition was performed at a temperature of 30 K, the subsequent irradiations were carried out at a temperature of 10 K. During the pyrolysis experiments the deposition temperature was maintained at 10 K. The setup for matrix isolation has been described previously.[30] The irradiations were performed using a 500-W Hg high-pressure lamp, whose light was filtered using dichroitic mirrors or cut-off filters to select the appropriate wavelength range.

Acknowledgement

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[26] We performed density functional theory calculations using the B3LYP functional and the basis sets 6–31G*, 6–31+G*, 6–311+G**, and MP2, MP4SDTQ, QCISD, QCISD(T) and CCSD(T) correlation methods using the 6–31+G* basis set. The systematic increase of the size of the basis set and the systematical improvement of the correlation treatment leads to a relative stabilization of the singlet state. At the QCISD(T)/6–31G* +ZPE level the singlet state is $2.6\ \mathrm{kcal\,mol^{-1}}$ lower in energy than the triplet state.

[27] The contribution of the mesomeric structures of **7b** to the overall wave function was estimated using a NBO analysis (B3LYP/6–31+G*). The NBO bond orders of the $\mathrm{C{\equiv}C\text{-}N}$ and $\mathrm{C\text{-}C{\equiv}N}$ fragment of **7b** were compared with the NBO bond orders of acetylene, acetonitrile, methylnitrene, and methylcarbene. The contribution of the nitrene-type mesomeric structure is additionally confirmed by the fact that the angle at the formal carbene center (119.7°) is much larger than the corresponding angle in cyclopropyl carbene (108.1°). The formal C–N triple bond in **7b** (1.179 Å) is longer than in acetonitrile (1.158 Å) and the formal single bond between the carbene center and the cyano

group (1.392 Å) is shorter than a "normal" C–CN bond (1.461 Å in acetonitrile).

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