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# Methylcyanobutadiyne: Synthesis, X-ray Structure and Photochemistry; Towards an Explanation of Its Formation in the Interstellar Medium

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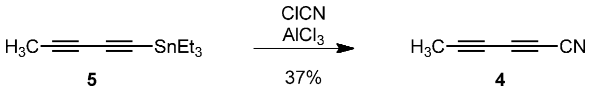
Cyanopolyynes, the formula of which is $H-(C\equiv C)_n-CN$, have been detected in the interstellar medium (ISM) with $n=2$ to 5.[1] Cyanoacetylene ($HC_3N$, **1**), which has been found in diverse environments from dark molecular clouds to the envelop of dying carbon stars,[2] has also been detected on Titan,[3] the largest moon of Saturn, and in comae,[4] and has been extensively studied during recent decades.[5] This compound could have played an important role in the prebiotic synthesis of amino acids and purines or pyrimidines,[6] and consequently, for the emergence of life on Earth. Cyanobutadiyne $HC_5N$ (**2**), the second member of this family, has been predicted to also be present on Titan by some models[7] but has not been detected there so far. Each cyanopolyyne seems to be formed by starting from acetylene or maybe polyynes and the corresponding smaller cyanopolyyne.[8]

Methylcyanopolyynes, the formula of which is $CH_3-(C\equiv C)_n-CN$, are the methylated derivatives of cyanopolyynes. Methylcyanoacetylene ($MeC_3N$, **3**) and methylcyanobutadiyne ($MeC_5N$, **4**), the first two members of this family, have been detected in the ISM. Even though the first compound (**3**) was detected long ago,[9] it has only been recently that **4** was observed in the ISM.[10] The superior counterparts ($n>2$) have never been detected. The very low number of studies on methylcyanobutadiyne reported in the literature[11] prompted us to investigate this compound in the context of space sciences. We report here a new and convenient synthesis of methylcyanobutadiyne and studies on its formation by photolysis in the gas phase for a better understanding of the ISM. Extension of the synthetic approach to the kinetically very unstable cyanobutadiyne is also reported.

To the best of our knowledge, the first and only synthesis of compound **4** was described by Kroto and co-workers in 1978.[12] It involves the reaction of stannylated compound **5** on aluminum chloride and cyanogen chloride (Figure 1). Given the high toxicity and difficult availability of the former, we investigated another pathway.



$$H_3C-C\equiv C-C\equiv C-SnEt_3 \xrightarrow[37\%]{ClCN,\ AlCl_3} H_3C-C\equiv C-C\equiv C-CN$$

Figure 1. Original synthesis of compound **4** by Kroto and co-workers.

Our approach starts with the synthesis of 1,3-pentadiyne (**6**) from commercially available 1,4-dichlorobut-2-yne and methyl iodide according to an adapted procedure described by Verkruijsse and Brandsma.[13] Compound **6** was then treated with *n*BuLi and cannulated to a solution of methylchloroformate to afford ester **7** in 86 % yield. Aqueous ammonia was then added to the latter compound **7** to give the corresponding amide **8** in 89 % yield. This amide was finally heated between 110 and 150 °C under vacuum in a mixture of sand and $P_4O_{10}$ to give the target methylcyanobutadiyne **4** in 36 % yield. During this last step the desired compound was distilled off from the reaction mixture as soon as it was formed and trapped in a cell cooled at −50 °C (Figure 2). Such an approach involving the dehydration of an amide was used by Moureu and Bongrand[17] at the beginning of the 20th century for the preparation of several alkynylnitriles, and remains the best synthesis of cyanoacetylene.

X-ray quality crystals of compounds **8** and **4** were obtained and confirmed the structure of both molecules (Figure 3). Crystals of the amide **8** were obtained by slow diffusion of cyclohexane into an acetone solution. The packing revealed an important hydrogen bonding pattern as expected for such an amide, which involves all oxygen atoms and all hydrogen atoms borne by the nitrogen atoms. π-Stacking is also involved between the diacetylenic parts. Crystals of methylcyanobutadiyne (**4**) were obtained by slow evaporation of *n*-pentane. Contrary to compound **8**, no hydrogen bond is involved, but the title compound exists as dimer in the unit cell. The two molecules are parallel to each other in a head-to-tail manner, probably for minimizing the global dipole moment. According to the distance between the two molecules (ca. 3.7 Å), π-stacking is likely to be the most important interaction at stake. Bond lengths of cyanopolyynes and methylcyanopolyynes have been calculated in the past in order to deduce the physical properties

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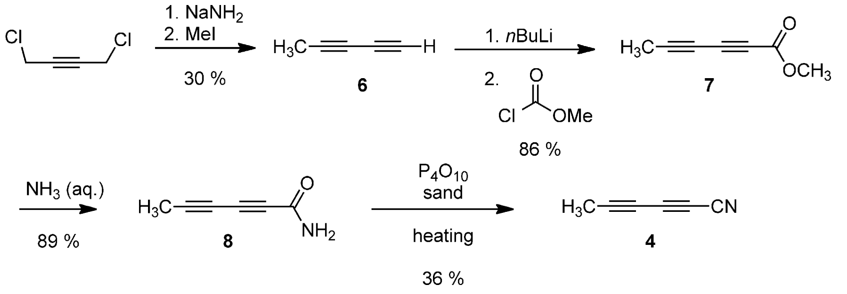


Figure 2. New synthesis of methylcyanobutadiyne (**4**).

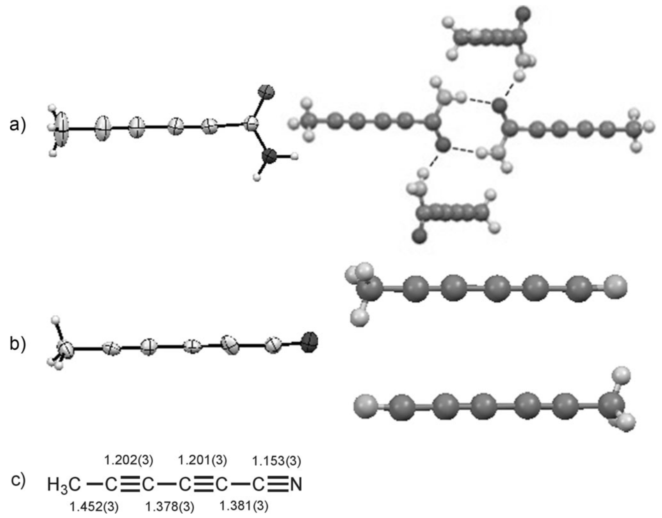


Figure 3. X-ray structure and crystal packing of: a) the amide **8**, and b) methylcyanobutadiyne (**4**), and c) bond lengths [Å] of methylcyanobutadiyne (**4**) according to the X-ray structure. The dotted lines represent H bonds.

of these compounds. These lengths (Figure 3c) are in good agreement with what has recently been published.[14] However, these values might serve as standards for future evaluations of the properties of this product and could be extrapolated to cyanopolyynes and derivatives.

Several attempts for the synthesis of cyanobutadiyne (**2**) have been reported in the literature before the first isolation of this compound by our group,[15] but the amide approach has never been described. Our approach was limited on the preparative scale by a yield of only 15% for the last step and was performed starting from 1,3-butadiynetributylstannane, a compound that can only be kept at −20°C.[16] Its synthesis could be simplified by having the corresponding amide precursor in hand. Starting from commercially available 1,4-bis(trimethylsilyl)butadiyne, the corresponding ester **9** was obtained in 55% yield by a first addition of MeLi·LiBr to form the corresponding monolithiated acetylide, which was then treated with an excess of methylchloroformate. The resulting compound **9** was turned into the amide **10** by addition of aqueous ammonia in 53% yield. It is important to note that the TMS function does not survive these conditions. The latter compound was then heated from 120 up to 180°C under vacuum in a mixture of sand and $P_4O_{10}$ to give cyanobutadiyne in 14% yield by trapping it in a cell cooled at −100°C (Figure 4).

This last strategy does not really improve the one we reported earlier[15] if one considers the yield of the last step. However, it allows a more stable amide precursor that can be easily purified by column chromatography.

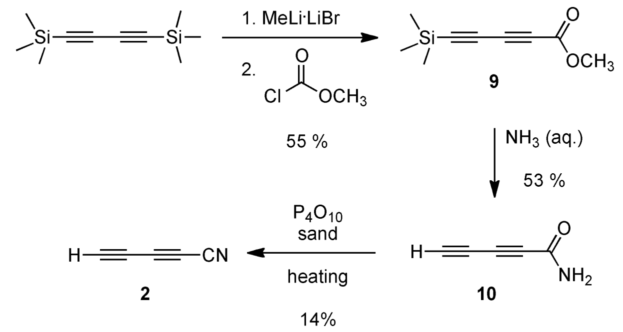


Figure 4. Synthesis of cyanobutadiyne.

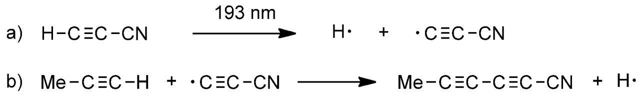
Particularly noteworthy is the difference of kinetic stability between cyanobutadiyne (**2**) and methylcyanobutadiyne (**4**), which only differ from each other by a methyl group. Whereas compound **2** decomposes in the solid state from −40°C, **4** melts at 92°C without any apparent decomposition. This huge difference probably originates from the possibility for $HC_5N$ to polymerize because of the terminal acetylenic function.

By mixing different gases detected in the atmosphere of Titan and/or in the ISM, we demonstrated the formation of cyanobutadiyne by photolysis of cyanoacetylene or dicyanoacetylene with acetylene, or dicyanoacetylene with butadiyne at 185 nm.[15] In all cases, the addition of the $C_3N$ radical on acetylene or of the CN radical on butadiyne was proposed for the reaction pathway. Such a hypothesis was supported by the formation of other photoproducts, such as cyanoacetylene or a compound tentatively assigned to be cyanohexatriyne ($HC_7N$). The extension of this finding to the formation of the methylated cyanopolyynes by the use of propyne and 1,3-pentadiyne instead of acetylene and butadiyne would reinforce the proposed mechanism.

For this purpose, a lamp irradiating at 185, 193 and 254 nm was used. Moreover, two different cells were used: one in ordinary quartz, which absorbs most of the 185 nm radiation, and one with a Suprasil® window, which allows 185, 193 and 254 nm wavelengths to pass through. After some hours of irradiation, the volatile compounds were analyzed by $^1H$ NMR spectroscopy by trapping them in an NMR tube at low temperature. The presence of $MeC_5N$ could be confirmed or disconfirmed by comparison of spectra before and after subsequent addition of an authentic sample in the tube.

The photolysis of $HC_3N$ (**1**)[17] and propyne (**11**) gave trace amounts of $MeC_5N$ (**4**). However, particularly noteworthy is that the procedure did not give rise to $MeC_5N$ (**4**) with the Suprasil cell but with the quartz cell. This unexpected effect can be explained by the important coefficient absorption of 185 nm radiation by propyne (**11**; about 110 $amagat^{-1}cm^{-1}$ at 185 nm at 293 K).[18] Moreover, some studies have shown that the major product formed from photolysis of propyne at 193 nm is the propargyl radical,[19] which should not result to the formation of $MeC_5N$ at this wavelength. However, at this wavelength, the homolytic break of the C–H bond of $HC_3N$ also occurs,[20] but the absorption coefficient is approximately the same as that of propyne (about 10 $amagat^{-1}cm^{-1}$ at 293 K). Therefore, we conclude that the formation of the two radicals is in competition at 193 nm: the propargyl radical $CH_2$–CCH and CC–CN. At 185 nm, the formation of the propargyl radical is probably predominant because the absorption coefficient of propyne is ten-times higher than that of $HC_3N$, and this is the reason why the amount of $MeC_5N$ formed during this experiment is probably too low to be detected by $^1$H NMR spectroscopy.

This result gave us some information about the most likely mechanism of formation of $MeC_5N$. It suggests that $HC_3N$ (**1**) partially absorbs 193 nm radiation and is thus broken into two radicals H and $C_3N$. Radical $C_3N$ may then add on propyne, to give $MeC_5N$ and H (Scheme 1). This result is perfectly consistent with our previous study on $HC_5N$ (**2**), which could be formed from $HC_3N$ and acetylene (**12**) with this type of irradiation.[15]

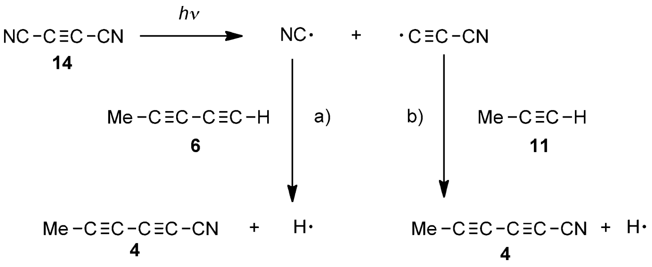


Scheme 1. Proposed mechanism of formation of $MeC_5N$ (**4**) from $HC_3N$ (**1**) and propyne (**11**).

To reinforce our hypothesis, a mixture of $HC_3N$ (**1**) and 1,3-pentadiyne (**6**) was also studied. If these products react in the same way as the $HC_3N$/propyne mixture, $MeC_5N$ (**4**) should *not* be obtained, but rather the superior counterpart $MeC_7N$ (**13**; methylcyanohexatriyne). Indeed, under the same conditions, no $MeC_5N$ could be detected. However, a peak around $\delta = 2.05$ ppm in the $^1$H NMR spectrum was observed that might be assignable to $MeC_7N$ (**13**), but no $^1$H NMR spectrum of this latter compound is currently available. Studies are currently in progress in our laboratory on this compound to confirm or disconfirm its formation.

Two other sets of experiments were carried out by substituting $HC_3N$ (**1**) by dicyanoacetylene ($C_4N_2$; **14**).[21] The same trend was observed: trace amounts of $MeC_5N$ were observed when mixtures of $C_4N_2$ and propyne were illuminated in an ordinary quartz cell, but not with a Suprasil window. The same reason as mentioned above can be invoked. However, when 1,3-pentadiyne was used, $MeC_5N$ was formed with and without Suprasil. Nevertheless, particularly noteworthy is that the formation seems to be less favorable with a Suprasil window, according to the intensity of the $^1$H NMR peak in both experiments. As for the propyne case, 185 nm radiation should involves the formation of more undesired radicals that might inhibit the formation of $MeC_5N$.

The same pathway of formation can be suggested from the breaking of $C_4N_2$ (**14**) into $C_3N$ and CN radicals (Scheme 2). The fact that both propyne (**11**) and 1,3-pentadiyne (**6**) lead to the formation of $MeC_5N$ (**4**) with $C_4N_2$ (**14**) is consistent with the initial formation of $C_3N$ and CN radicals from $C_4N_2$ (**14**), which then react with propyne or 1,3-pentadiyne, respectively, to give $MeC_5N$ (**4**).



Scheme 2. Proposed mechanism of formation of $MeC_5N$ (**4**) from $C_4N_2$ and: a) 1,3-pentadiyne (**6**), or b) propyne (**11**).

In conclusion, a new and convenient synthesis of $MeC_5N$ (**4**), which has also been applied to the synthesis of $HC_5N$ (**2**), is proposed. Photolysis experiments in the gas phase were carried out to investigate the possibility of $MeC_5N$ (**4**) formation in the ISM from relevant precursors. Indeed, binary mixtures of $HC_3N$ (**1**) or $C_4N_2$ (**14**), and propyne or 1,3-pentadiyne led to the detection of trace amounts of $MeC_5N$ (**4**) under certain irradiation conditions. However, it is likely that other cyanopolyynes were formed during these experiments. In particular, methylcyanohexatriyne ($MeC_7N$; **13**) could be formed in some cases. However, we currently do not have an authentic sample of this compound that could allow us to be sure of its formation. Therefore, experiments are currently underway in our laboratory to find a convenient synthesis of $MeC_7N$ (**13**).

## Experimental Section

Experimental details can be found in the Supporting Information. CCDC-935292 (**4**) and 884433 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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**Keywords:** cyanopolyynes · interstellar chemistry · methylcyanobutadiyne · synthetic methods · photochemistry

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[1] $HC_3N$: B. E. Turner, *Astrophys. J.* **1971**, *163*, L35–L39; $HC_5N$: L. W. Avery, N. W. Broten, J. M. MacLeod, T. Oka, H. W. Kroto, *Astrophys. J.* **1976**, *205*, L173–L175; $HC_7N$: H. W. Kroto, C. Kirby, D. R. M. Walton, L. W. Avery, N. W. Broten, J. M. MacLeod, T. Oka, *Astrophys. J.* **1978**, *219*, L133–L137; $HC_9N$: N. W. Broten, T. Oka, L. W. Avery, J. M. MacLeod, H. W. Kroto, *Astrophys. J.* **1978**, *223*, L105–L107; $HC_{11}N$: M. B. Bell, P. A. Feldman, M. J. Travers, M. C. McCarthy, C. A. Gottlieb, P. Thaddeus, *Astrophys. J.* **1997**, *483*, L61–L64.

[2] L. C. L. Huang, Y. T. Lee, R. I. Kaiser, *J. Chem. Phys.* **1999**, *110*, 7119–7122.

[3] a) V. G. Kunde, A. C. Aikin, R. A. Hanel, D. E. Jennings, W. C. Maguire, R. E. Samuelson, *Nature* **1981**, *292*, 686–688; b) A. Coustenis, T. Encrenaz, B. Bézard, B. Bjoraker, G. Graner, G. Dang-Nhu, E. Arié, *Icarus* **1993**, *102*, 240–260.

[4] D. Bockelée-Morvan, D. C. Lis, J. E. Wink, D. Despois, J. Crovisier, R. Bachiller, D. J. Benford, N. Biver, P. Colom, J. K. Davies, E. Gérard, B. Germain, M. Houde, D. Mehringer, R. Moreno, G. Paubert, T. G. Phillips, H. Rauer, *Astron. Astrophys.* **2000**, *353*, 1101–1114.

[5] a) M. C. McCarthy, P. Thaddeus, *Chem. Soc. Rev.* **2001**, *30*, 177–185; b) P. Botschwina, *Phys. Chem. Chem. Phys.* **2003**, *5*, 3337–3348; c) C. Crépin, M. Turowski, J. Ceponkus, S. Douin, S. Boyé-Péronne, M. Gronowski, R. Kolos, *Phys. Chem. Chem. Phys.* **2011**, *13*, 1678–16785; d) D. K. Böhme, *Phys. Chem. Chem. Phys.* **2011**, *13*, 18253–18263; e) R. I. Kaiser, A. M. Mebel, *Chem. Soc. Rev.* **2012**, *41*, 5490–5501.

[6] a) R. A. Sanchez, J. P. Ferris, L. E. Orgel, *Science* **1966**, *154*, 784–785; b) M. W. Powner, B. Gerland, J. D. Sutherland, *Nature* **2009**, *459*, 239–242.

[7] a) P. Coll, D. Coscia, N. Smith, M.-C. Gazeau, S. I. Ramirez, G. Cernagora, G. Israel, F. Raulin, *Planet. Space Sci.* **1999**, *47*, 1331–1340; b) E. de Vanssay, M.-C. Gazeau, J.-C. Guillemin, F. Raulin, *Planet. Space Sci.* **1995**, *43*, 25–31.

[8] a) P. Coll, D. Coscia, M. C. Gazeau, E. de Vanssay, J. C. Guillemin, F. Raulin, *Adv. Space Res.* **1995**, *16*, 93–103; b) E. Herbst, *Chem. Soc. Rev.* **2001**, *30*, 168–176; c) R. I. Kaiser, N. Balucani, *Acc. Chem. Res.* **2001**, *34*, 699–706.

[9] N. W. Broten, J. M. MacLeod, L. W. Avery, W. M. Irvine, B. Höglund, P. Friberg, A. Hjalmarson, *Astrophys. J.* **1984**, *276*, L25–L29.

[10] L. E. Snyder, J. M. Hollis, P. R. Jewell, F. J. Lovas, A. Remijan, *Astrophys. J.* **2006**, *647*, 412–417.

[11] W. Chen, J.-U. Grabow, M. J. Travers, M. R. Munrow, S. E. Novick, M. C. McCarthy, P. Thaddeus, *J. Mol. Spectrosc.* **1998**, *192*, 1–11.

[12] A. J. Alexander, H. W. Kroto, M. Maier, D. R. M. Walton, *J. Mol. Spectrosc.* **1978**, *70*, 84–94.

[13] H. D. Verkruijsse, L. Brandsma, *Synth. Commun.* **1991**, *21*, 141–144.

[14] D. E. Woon, E. Herbst, *Astrophys. J. Suppl. Ser.* **2009**, *185*, 273–288.

[15] Y. Trolez, J.-C. Guillemin, *Angew. Chem.* **2005**, *117*, 7390–7392; *Angew. Chem. Int. Ed.* **2005**, *44*, 7224–7226.

[16] An alternative method consists in preparing the bistributylstannylbutadiyne and treating it with tosyl cyanide, but it does not give better results: J.-C. Guillemin, Y. Trolez, A. Moncomble, *Adv. Space Res.* **2008**, *42*, 2002–2007.

[17] a) C. Moureu, J.-C. Bongrand, *C. R. Hebd. Seances Acad. Sci.* **1910**, *151*, 946–948; b) F. A. Miller, D. H. Lemmon, R. E. Witkowski, *Spectrochim. Acta* **1965**, *21*, 1709–1716.

[18] A. Jolly, personal communication: http://www.lisa.univ-paris12.fr/GPCOS/SCOOPweb/index.html.

[19] a) D. B. Atkinson, J. W. Hudgens, *J. Phys. Chem. A* **1999**, *103*, 4242–4252; b) R. H. Qadiri, E. J. Feltham, E. E. H. Cottrill, *J. Chem. Phys.* **2002**, *116*, 906–912; c) J. D. DeSain, C. A. Taatjes, *J. Phys. Chem. A* **2003**, *107*, 4843–4850; d) A. Fahr, A. H. Laufer, *J. Phys. Chem. A* **2005**, *109*, 2534–2539.

[20] D. W. Clarke, J. P. Ferris, *Icarus* **1995**, *115*, 119–125.

[21] C. Moureu, J.-C. Bongrand, *C. R. Hebd. Seances Acad. Sci.* **1910**, *4*, 225–227.

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