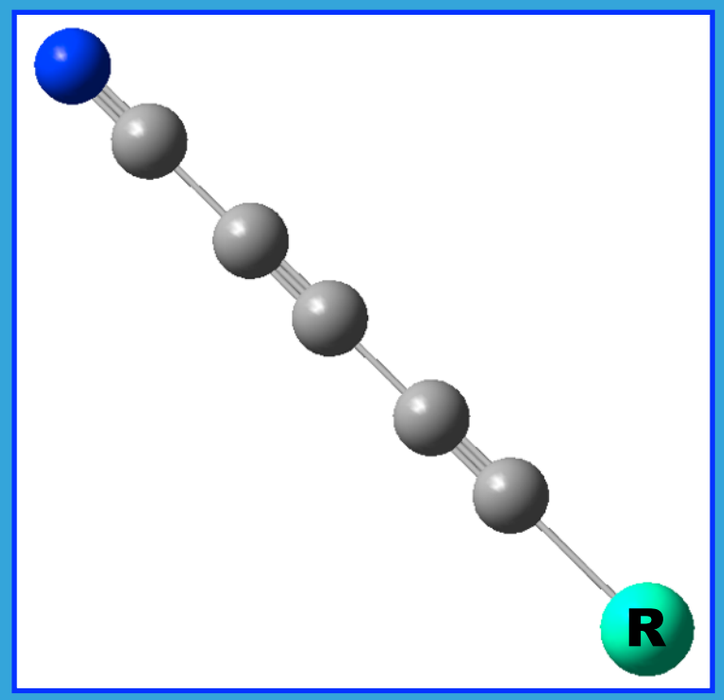


IDENTIFYING SUBSTITUTED CYANOBUTADIYNES BY GAS-PHASE IR SPECTROSCOPY: THEORY AND EXPERIMENT

M. M. Montero-Campillo
UNIVERSIDAD AUTÓNOMA DE MADRID

A. Benidar, C. Rouxel, N. Kerisit, Y. Trolez, J-C. Guillemin, Otilia Mó, Manuel Yáñez

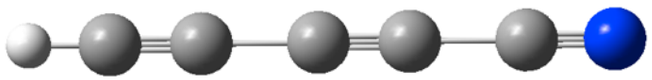
OUTLINE

- Cyanobutadiynes in the interstellar medium
- The technical stuff!
- IR results: experiment & theory

CYANOBUTADIYNES IN THE INTERSTELLAR MEDIUM

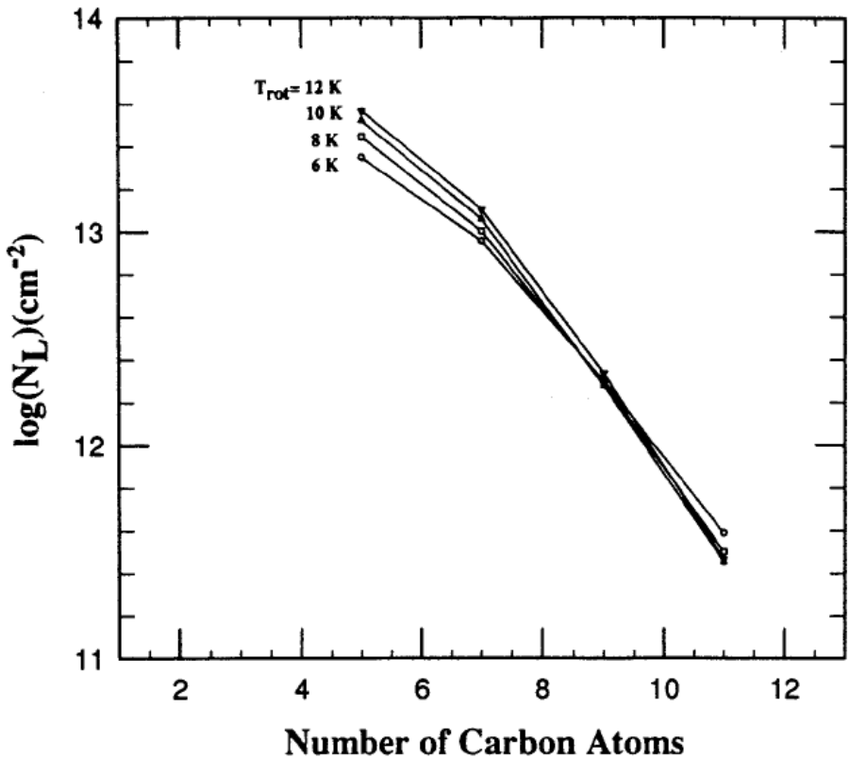
$R\text{-}(C{\equiv}C)_2\text{-}CN$

If R = H:



- Cyanobutadiyne (HC_5N) was detected in interstellar medium in 1976.*

Abundance of cyanopolyynes**

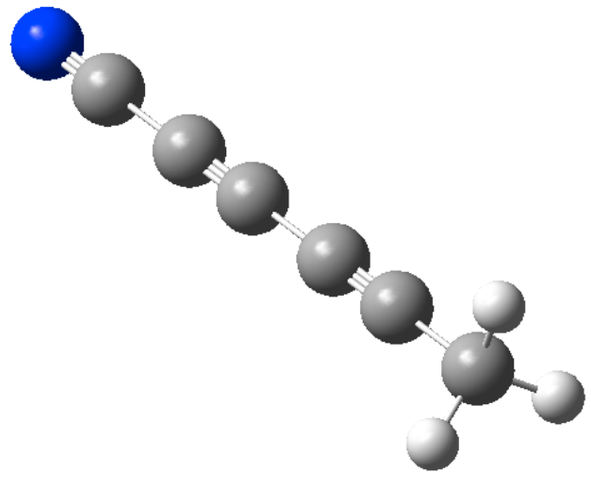


- Higher homologues have been detected up to $HC_{11}N$ (1997).** The abundance of the cyanopolyynes decreases with length, the decrement between one to the next being about six for the longer carbon chains.

*L.W.Avery et al, *Astrophys. J.* **1976**, *205*, L173 – L175; **M.B.Bell et al, *Astrophys. J.* **1997**, *483*, L61 – L64

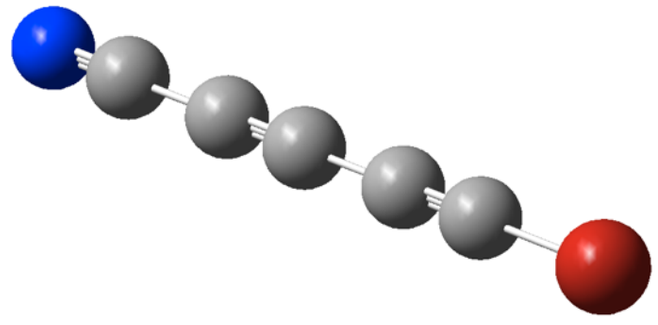
CYANOBUTADIYNES IN THE INTERSTELLAR MEDIUM

- Its methyl derivative (**MeC_5N**) was detected in that medium in 2006 in the cold dark dust cloud Taurus Molecular Cloud 1.*
- No larger methyl derivatives have been found by now.
- Methyl derivatives can serve as indicators of gas-phase production schemes.
- Importance of Me, C≡C, CN groups



*L.E. Snyder et al,*Astrophys. J.* **2006**, *647*, 412 – 417.

CYANOBUTADIYNES IN THE INTERSTELLAR MEDIUM



- The bromine derivative (**BrC_5N**) was very recently (2015) obtained by Jean-Claude Guillemin & col.*

- BrC_5N >> HC_7N >> MeC_7N

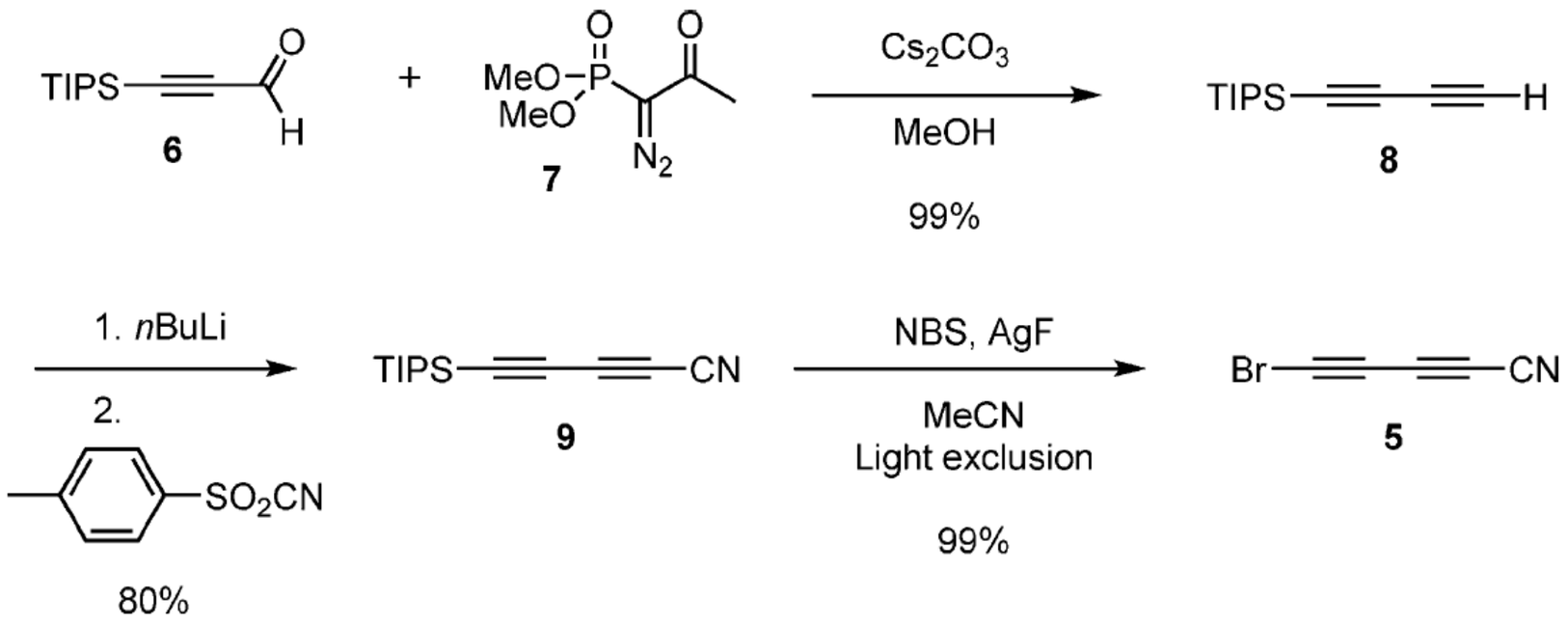
- The IR spectrum of HC_5N: already studied in detail.**

- Our goal: to study **MeC_5N** and **BrC_5N** to determine the effects of substituents on the C_5N group. The IR spectrum of MeC_5N gives a tool for its detection and quantification.

*N. Kerisit et al. *Chem. Eur. J.* **2015**, *21*, 6042 – 6047; **Y. Benilan et al. *J. Mol. Spectrosc.* **2007**, *245*, 109 – 114

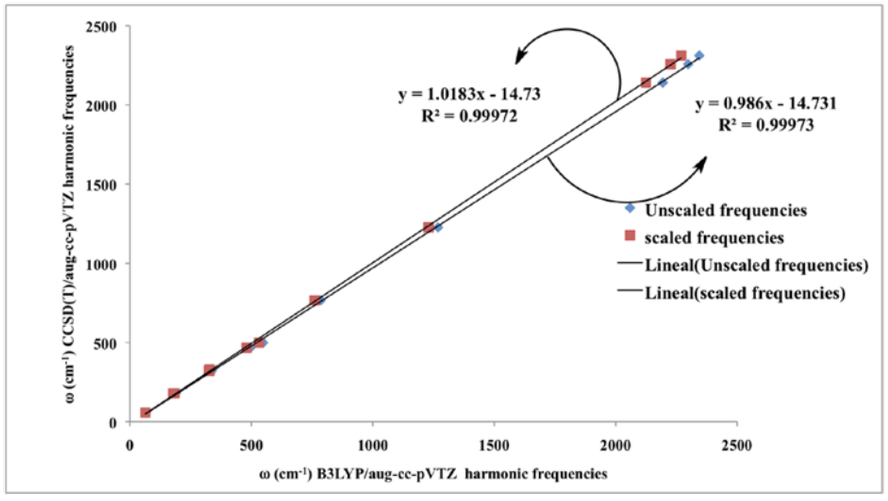
THE TECHNICAL STUFF!

- The synthesis of these substituted cyanobutadiynes is challenging. Compounds HC_5N, MeC_5N are obtained by dehydration of the corresponding amide.*
- Synthesis of BrC_5N: **



*N. Kerisit et al. *Chem. Eur. J.* **2013**, *19*, 17683 – 17686;**N. Kerisit et al. *Chem. Eur. J.* **2015**, *21*, 6042 – 6047

THE TECHNICAL STUFF!



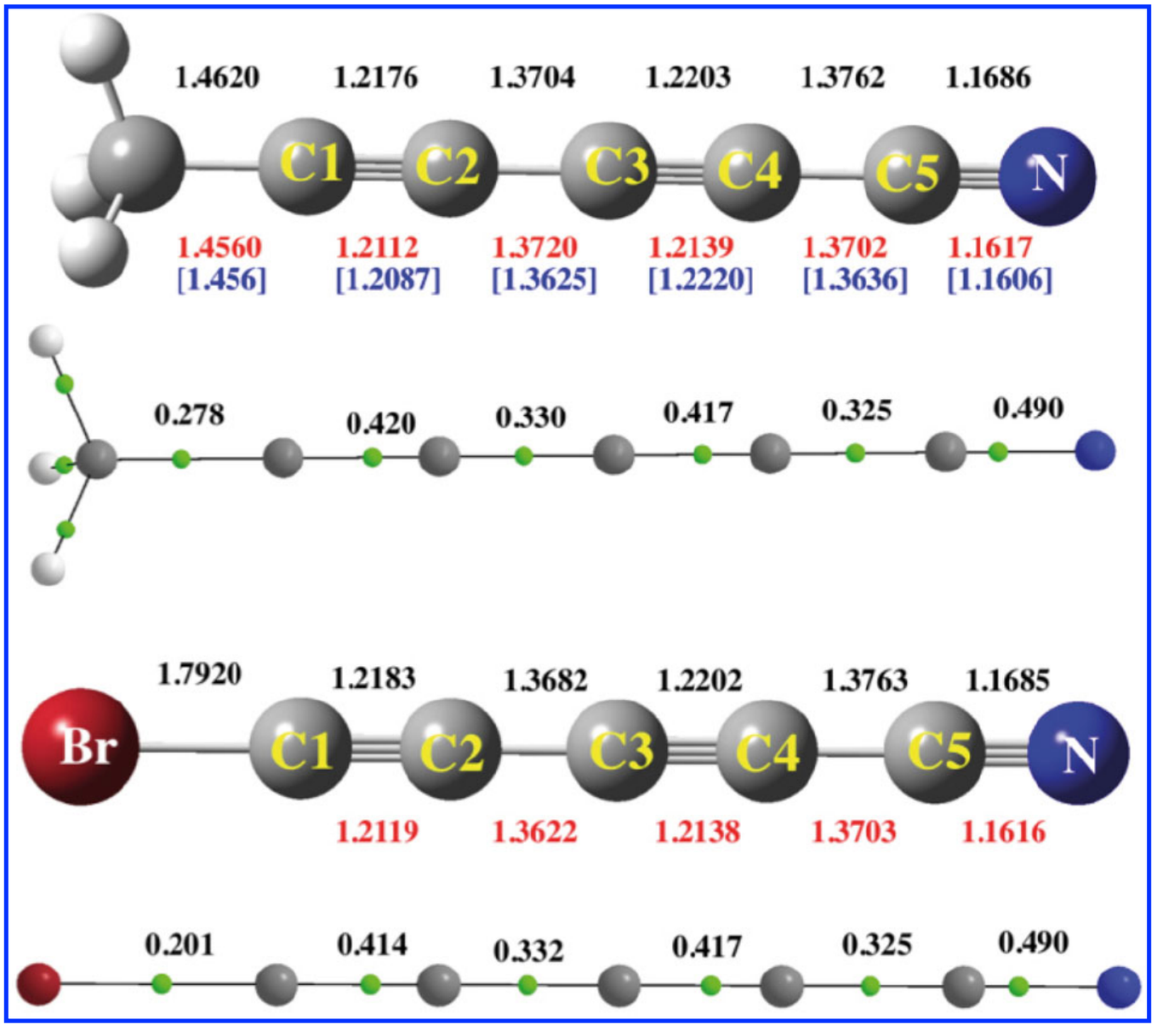
- MeC_5N and BrC_5N have been prepared
- IR in the 500-4000 cm^{-1} spectral range
- Ab initio and DFT calculations - MOLPRO & Gaussian09
  CCSD(T) cc-pVTZ + harmonic frequencies
  B3LYP cc-pVTZ/cc-pV5Z + harmonic frequencies - Scaled & Not scaled
  B3LYP and CCSD(T) -agreement
  Best agreement with the experiment: scaled B3LYP cc-pVTZ
- QTAIM

M.M. Montero-Campillo et al. *ChemPhysChem* **2016**, DOI 10.1002/cphc.201501153

IR RESULTS: EXPERIMENT & THEORY

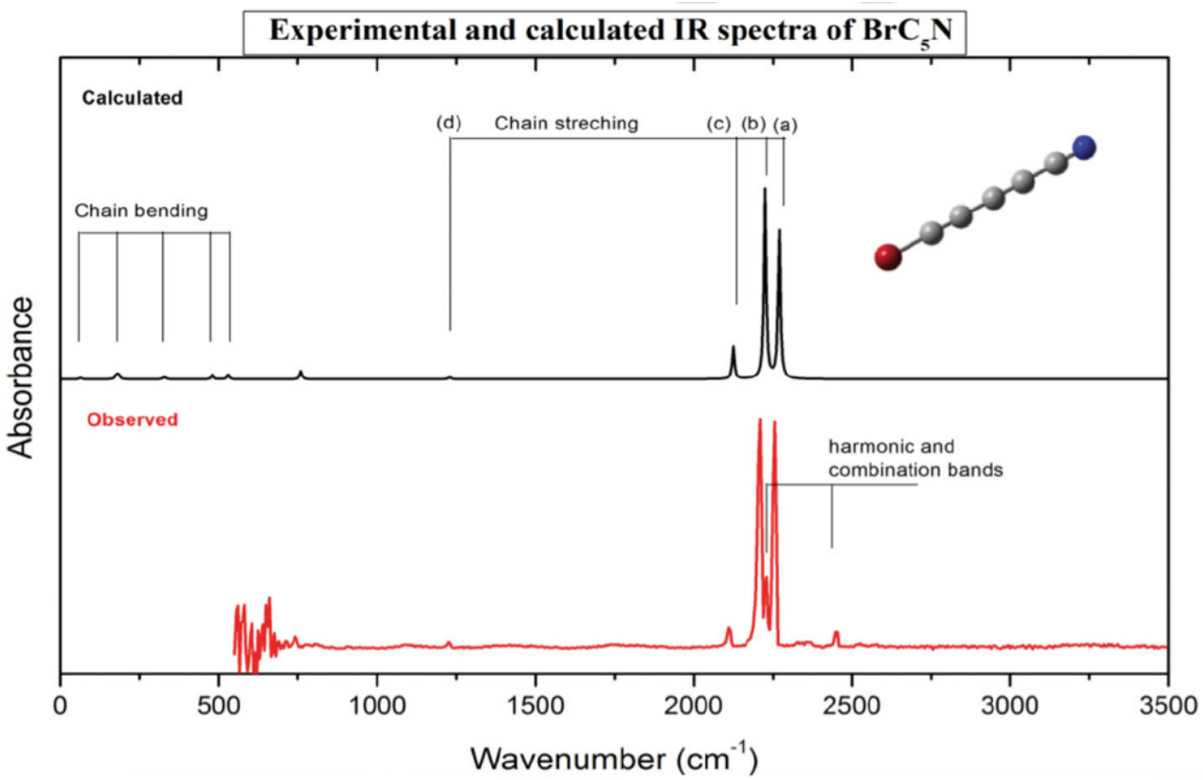
- CCSD(T)
- CCSD(T) corrected *
- MW (exp)
- QTAIM

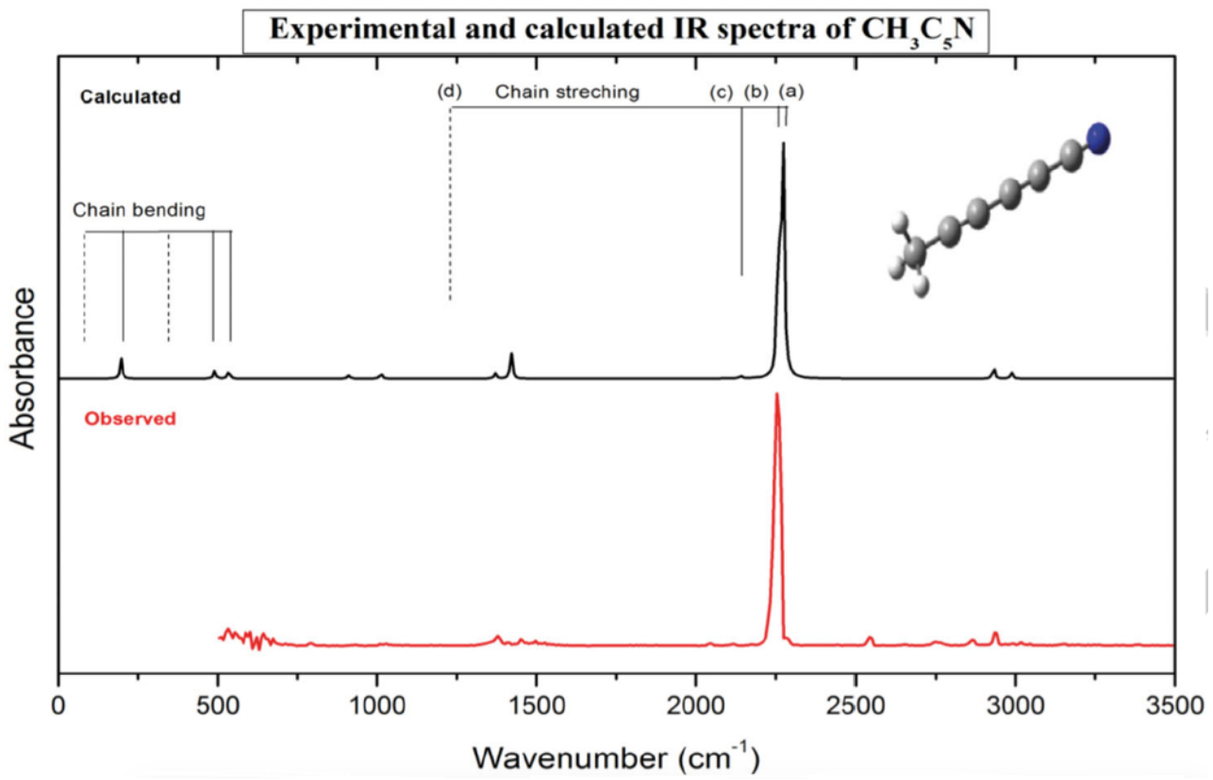
- Average deviation is 0.004 Å
- Subtle differences on bonding
  that will be reflected in the IR spectra
- Rotational constant MeC_5N
  B 785.13 [*778.04*] MHz



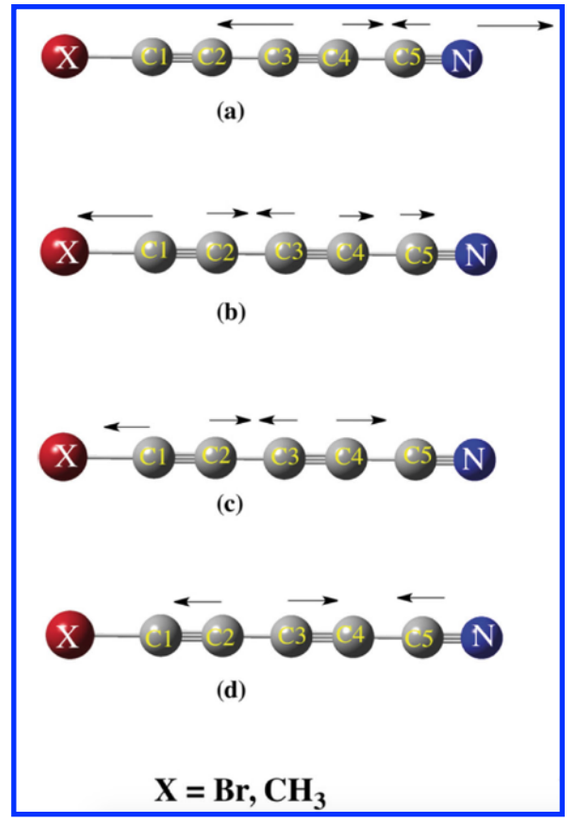
* P. Botschwina. *PhysChemChemPhys* 2003, 5, 3337-3348

IR RESULTS: EXPERIMENT & THEORY

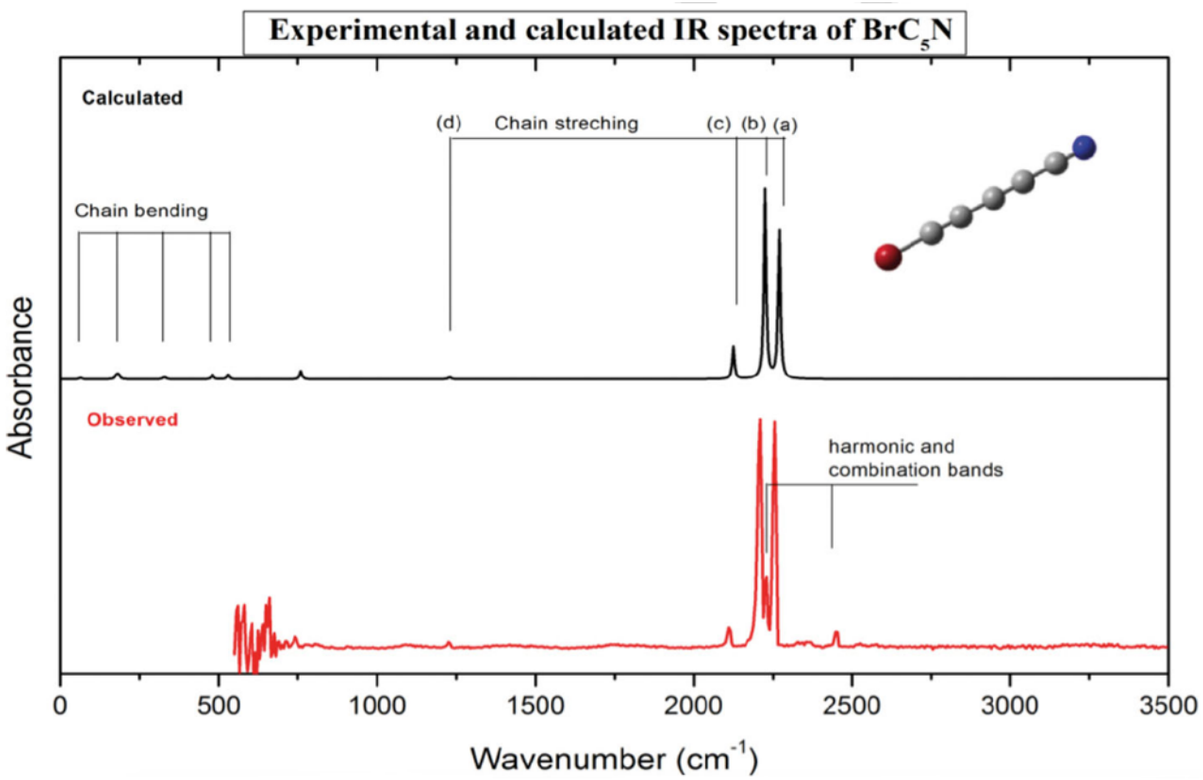


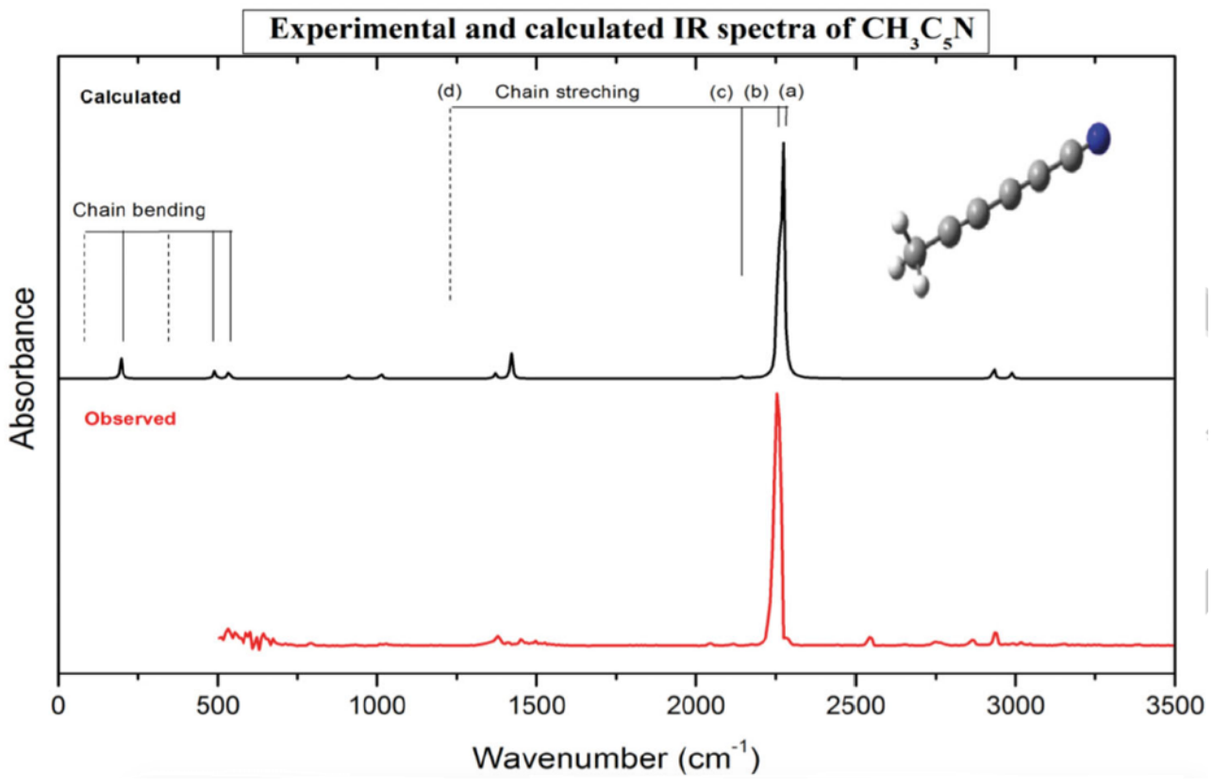


- Main peaks: coupling between triple carbon bond stretching displacements and the cyano group stretching, modes (a) and (b).

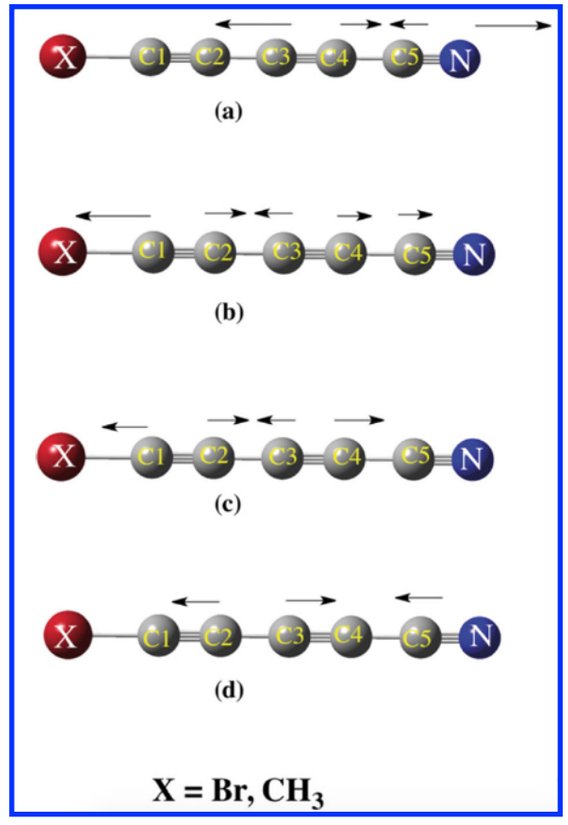


IR RESULTS: EXPERIMENT & THEORY

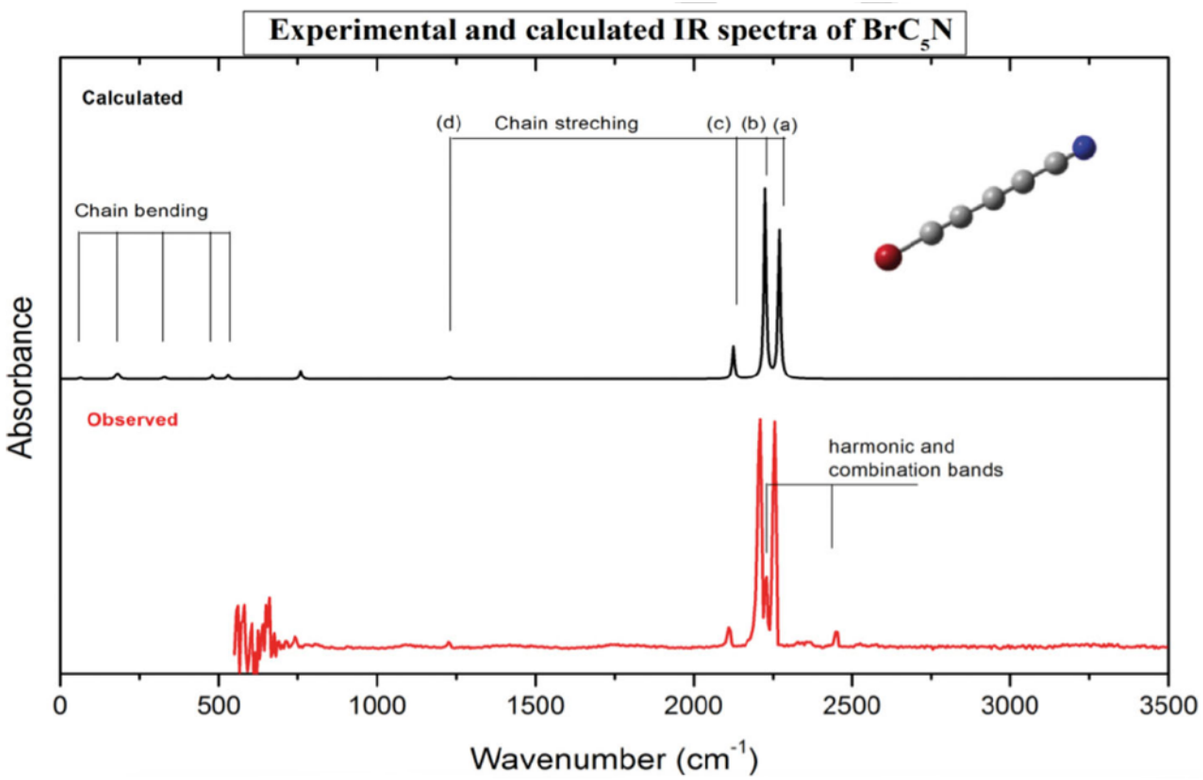


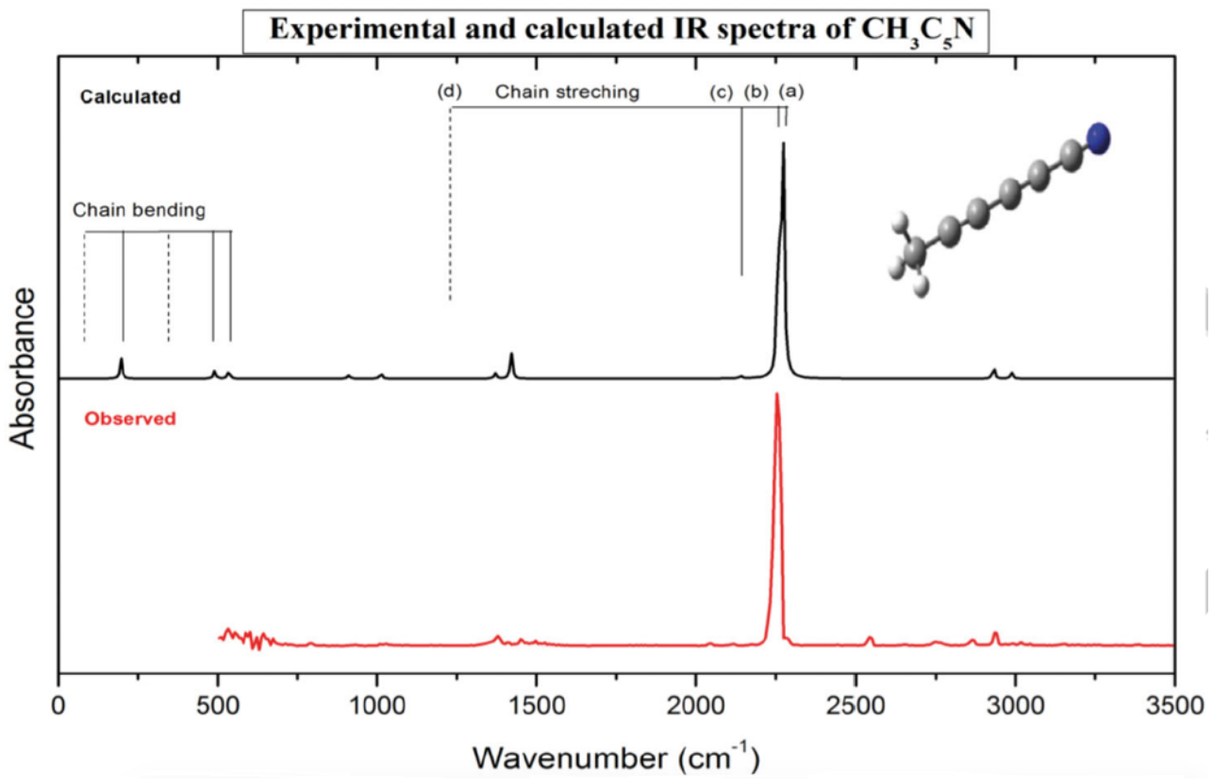


- Gap between bands: BrC_5N > 44.4 cm-1 (harm), 46.4 cm-1 (anharm); MeC_5N > 13.7 cm-1 (harm), 23.4 cm-1 (anharm) – Agreement with QTAIM
- Stretching modes Me group 3000 cm-1
- Single CC bonds - stretching modes around 1228 cm-1

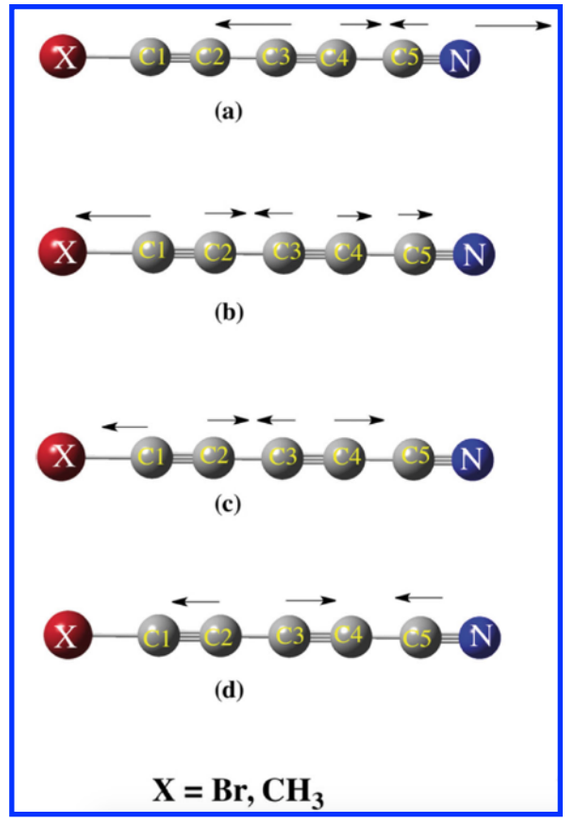


IR RESULTS: EXPERIMENT & THEORY





- BrC_5N - weak absorption around 760 cm-1, C-Br stretching coupled with C-C stretching modes.
- MeC_5N- 1400 cm-1 deformation displacements Me group, 1000 cm-1 rocking displacements Me group.
- Some features cannot be explained considering fundamental vibrational modes: 2500 cm-1 - 1st overtone chain-stretching fundamental band (d)
- BrC_5N - additional band - combination band involving the fundamental chain stretching band (c) and the fundamental C-Br stretching (327cm-1)



CONCLUSIONS

- The IR spectra of BrC_5N and MeC_5N have been recorded within the 4000-500 cm-1 spectral region and calculated by means of ab initio and DFT calculations.
- They look quite similar but there are subtle differences mainly in the strength of the C≡C bond directly attached to the substituent (distances & AIM results).
- BrC_5N presents two well differentiated strong bands around 2250 cm-1, MeC_5N one single band. In both cases these bands are the result of a coupling between C≡C and C≡N stretching displacements.
- The MeC5N spectrum gives a tool for its detection and quantification. The comparison with HC5N and BrC5N evidences the importance of the substituents in their spectral fingerprints.

CHEM. EUR. J. 2013, 19, 17683 – 17686;
CHEM. EUR. J. 2015, 21, 6042 – 6047

CHEM PHYS CHEM 2016,
DOI 10.1002/CPHC.201501153

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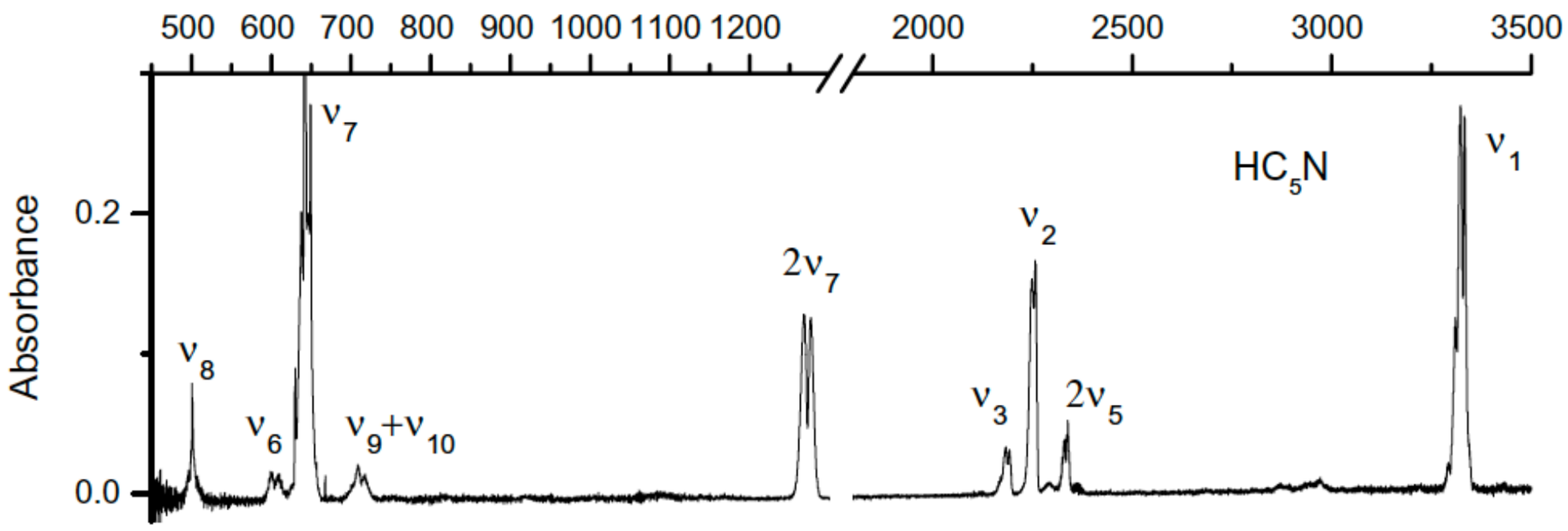
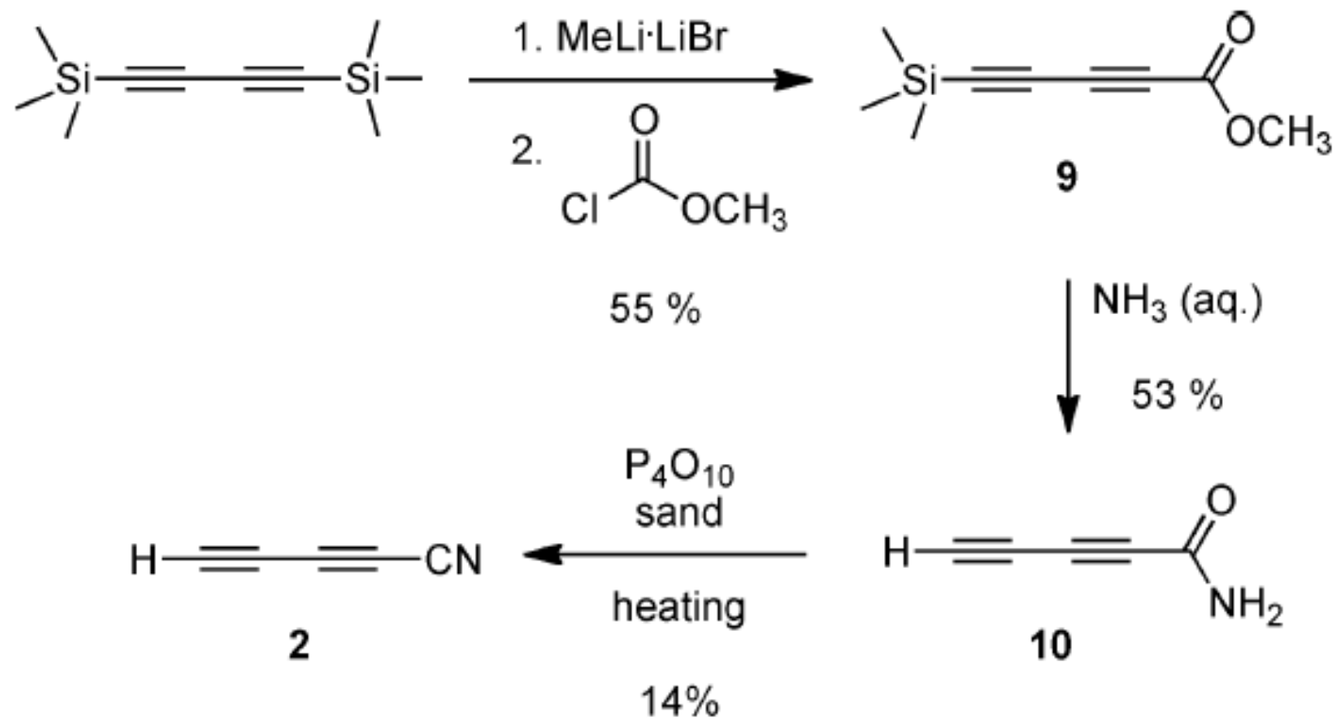
Otilia Mó, Manuel Yáñez

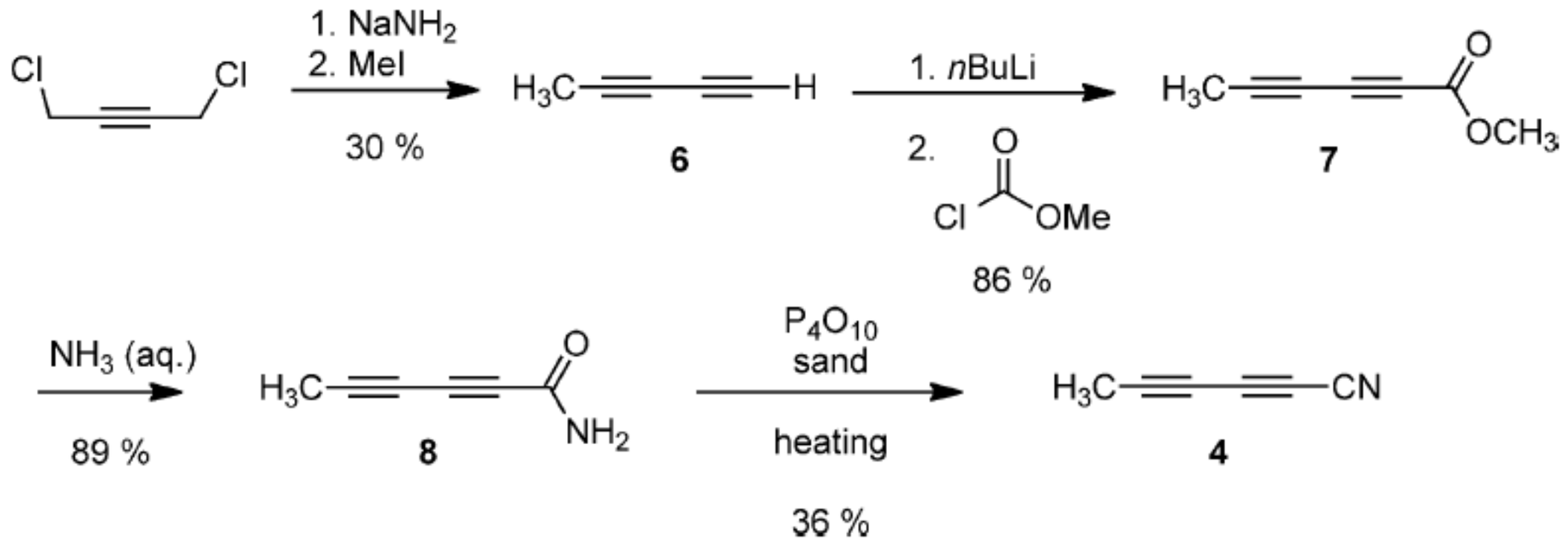
SUPPLEMENTARY DATA

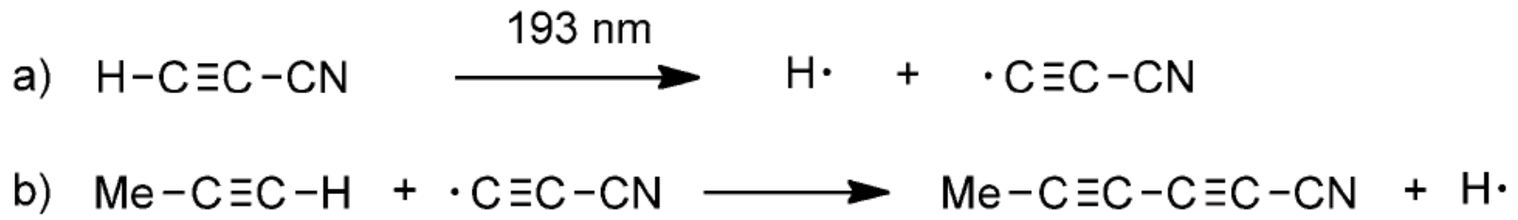
*Y. Benilan et al. *J. Mol. Spectrosc.* **2007**, *245*, 109 – 114





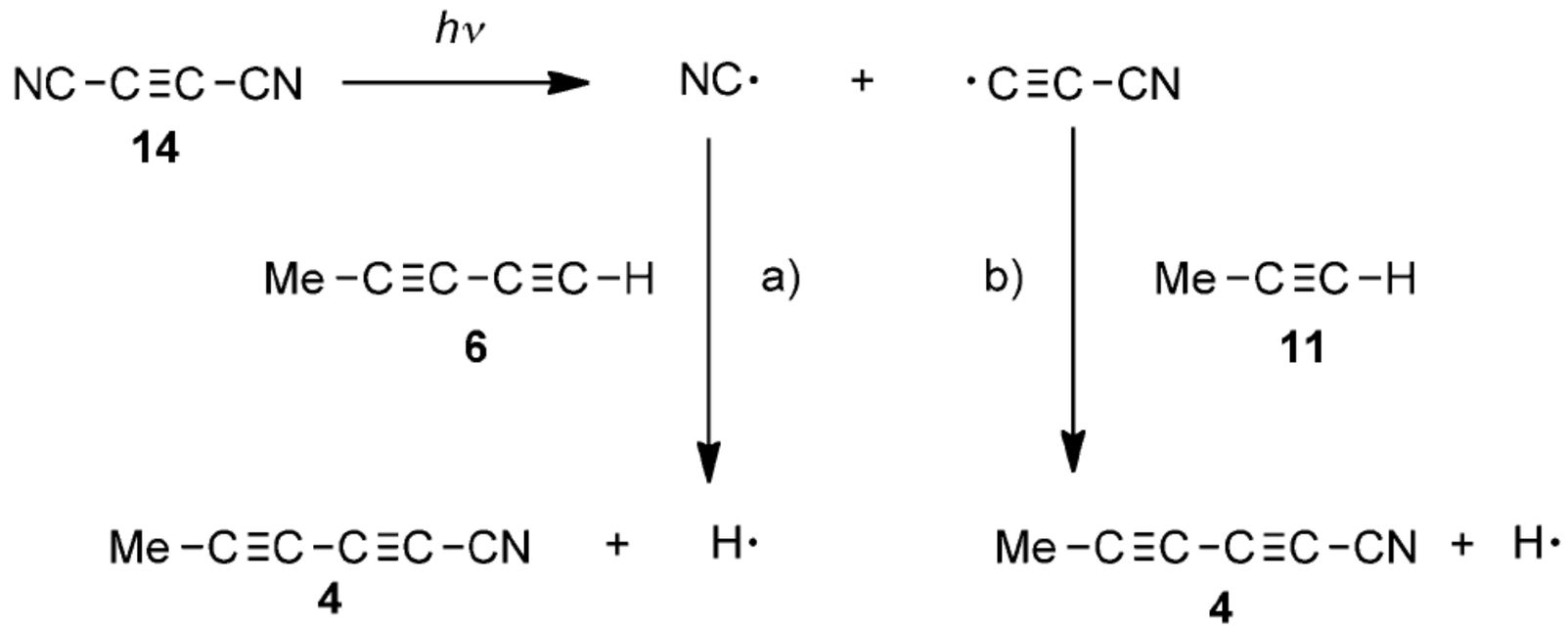
*N. Kerisit et al. *Chem. Eur. J.* **2013**, *19*, 17683 – 17686





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

*N. Kerisit et al. *Chem. Eur. J.* **2013**, *19*, 17683 – 17686



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