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

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OUTLINE

- Cyanobutadiynes in the interstellar medium
- The technical stuff!
- IR results: experiment & theory
R-(C≡C)₂-CN

If R = H:

- Cyanobutadiyne (HC₅N) was detected in interstellar medium in 1976.*
- Higher homologues have been detected up to HC₁₁N (1997).** The abundance of the cyanopolyynes decreases with length, the decrement between one to the next being about six for the longer carbon chains.

Its methyl derivative (MeC₅N) 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

The bromine derivative (BrC₅N) was very recently (2015) obtained by Jean-Claude Guillemin & col.*

BrC₅N >> HC₇N >> MeC₇N

The IR spectrum of HC₅N: already studied in detail.**

Our goal: to study MeC₅N and BrC₅N to determine the effects of substituents on the C₅N group. The IR spectrum of MeC₅N gives a tool for its detection and quantification.

The synthesis of these substituted cyanobutadiynes is challenging. Compounds HC$_5$N, MeC$_5$N are obtained by dehydration of the corresponding amide.*

Synthesis of BrC$_5$N:  **

\[ \text{H-TIPS} \begin{align*} \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{O} + \text{MeO-P(OMe)}_2\text{N} & \xrightarrow{\text{Cs}_2\text{CO}_3, \text{MeOH}} \text{H-TIPS} \begin{align*} \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{H} \
\text{MeO-P(OMe)}_2\text{N} \end{align*} \\ \text{Br} \begin{align*} \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CN} \end{align*} & \xrightarrow{\text{NBS, AgF, MeCN}} \text{Br} \begin{align*} \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CN} \end{align*} \]

MeC₅N and BrC₅N 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

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$_5$N B 785.13 [778.04] MHz

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: BrC₅N > 44.4 cm⁻¹ (harm), 46.4 cm⁻¹ (anhar); MeC₅N > 13.7 cm⁻¹ (harm), 23.4 cm⁻¹ (anhar) – Agreement with QTAIM
- Stretching modes Me group 3000 cm⁻¹
- Single CC bonds - stretching modes around 1228 cm⁻¹
IR RESULTS: EXPERIMENT & THEORY

- BrC₅N - weak absorption around 760 cm⁻¹, C-Br stretching coupled with C-C stretching modes.
- MeC₅N- 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)
- BrC₅N - additional band - combination band involving the fundamental chain stretching band (c) and the fundamental C-Br stretching (327 cm⁻¹)

X = Br, CH₃
CONCLUSIONS

- The IR spectra of BrC₅N and MeC₅N 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).

- BrC₅N presents two well differentiated strong bands around 2250 cm⁻¹, MeC₅N 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.
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*Y. Benilan et al. J. Mol. Spectrosc. 2007, 245, 109 - 114

[Graph showing absorption spectra with labeled peaks and vibrational modes]
a) H-C≡C-CN \xrightarrow{193 \text{ nm}} H^+ + C≡C-CN

b) Me-\overset{\text{H}}{\text{C≡C-H}} + C≡C-CN \rightarrow Me-\overset{\text{H}}{\text{C≡C-C≡C-CN}} + H^+

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

\[ \text{NC-C≡C-CN} \xrightarrow{h\nu} \text{NC}^+ + C≡C-CN \]

\[ \text{Me-C≡C-C≡C-H} \]

\[ \text{Me-C≡C-C≡C-CN} \]

\[ \text{Me-C≡C-C≡C-CN} + H^+ \]

\[ \text{Me-C≡C-C≡C-CN} \]

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