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Relative thermodynamic stability of the [C,N,O] linkages as an indication of the most abundant structures in the ISM

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ABSTRACT

Context. Most of the compounds detected in the interstellar medium (ISM) that possess isomers correspond to the thermodynamically most stable isomer of a given chemical formula. Using the minimum energy principle (MEP) as a pragmatic tool is particularly efficient for less than six atoms, but for larger systems combinatorial analysis gives an intractable numbers of isomers.

Aims. To make the MEP more applicable, we look for a chemical sieve to filter the thermodynamic data needed to determine which isomers of complex organic molecules (COMs) have higher chances of being present in the ISM. To do so, we investigate whether the nature of the [C,N,O] elementary fragment can be determinant for the stabilization of COMs, taking C2H2NO as a case study.

Methods. We employed standard quantum chemistry methods to determine the ordering of fragments and derivatives on the energy scale. Density functional theory treatments were systematically performed, together with high-level coupled cluster calculations to refine relative energies.

Results. For C2H2NO we find methyliisocyanate CH3NCO, which is a compound that was very recently detected in the ISM, to be the most stable isomer in a corpus of 40 isomers of lowest energy. In neutral form we find the stability ordering of NCO > ONC; the same is true for the negative ion. Attachments of R=H, CH3, OH, and metals Al and Mg to the nitrogen atom of the NCO fragment provide the most stable isomers. The energy differences between the successive isomers on the energy scale R-NCO, R-OCN, R-CNO, and R-ONC are of the same order of magnitude for all carbonaceous R.

Conclusions. Combining the criterion of most stable linkage with the MEP concept should greatly reduce the window of potential targets to be searched for in the ISM. Compounds containing the NCO linkage should be preferential targets of future research.

Key words. ISM: molecules – ISM: abundances

1. Introduction

More than 200 compounds have been detected in the interstellar medium (ISM) and many are organic compounds. The recent compilation by McGuire (2018) provides detailed information on this. Most of these molecules have a permanent dipole moment $\mu$ allowing detection by microwave or millimetric spectroscopy. The highest dipole moments point to the easiest detectable compounds since the line intensities scale with $\mu^2$, which could counterbalance a low abundance. Dipole moments and abundances are unrelated parameters, but both are critical for such detections.

Thus many nitriles were very easily detected because of their huge dipole moments. Carbon monoxide (Wilson et al. 1970; Solomon et al. 1971), propene (CH2CHCH3) (Marcelino et al. 2007) or methoxymethanol (CH3OCH2OH) (McGuire et al. 2017) are molecules with a small dipole moment and these were easily detected only because they are very abundant. On the other hand, to detect in the ISM compounds such as ethylene (Betz 1981), acetylene (Ridgway et al. 1976), dinitrogen (Kauth et al. 2004), and benzene (C6H6) (Cernicharo et al. 2001) is much more challenging and can only be done by infrared or UV spectroscopies. Dioxygen represents a rare example of a rotational detection of a symmetric species thanks to a non-zero magnetic dipole in the triplet ground state (Goldsmith et al. 2011).

Another protocol has sometimes been used, namely, the search for the protonated adducts of species with zero dipole such as dinitrogen (Turner 1974; Green et al. 1974) or cyanogen (Agúndez et al. 2015). Such an approach, often linked to H2 as proton carrier, provides an additional knowledge of the target environment. The abundances of both neutral and protonated species should be consistent with the abundance of the neutral is deduced from that of the protonated adduct detected in the same object. However, it is not always that simple since other mechanisms than direct proton transfer from H2 can be considered. In the case of CO2 the protonated form HOCO+ is also thought to be produced by reaction of HCO+ + OH (Bizzocchi et al. 2017, and references therein). In any case, it also gives a chemical constraint that could reflect the composition of the local environment. Now, the question is how to select new candidates for the ISM.

On the basis of detected compounds, a chemistry for each cloud can be proposed with the help of theoretical calculations to take into consideration very low transition barriers that are consistent with the temperature of the environment. However, a weak understanding of these chemistries has led to work more, by analogy, with already detected compounds, adding some substituents or looking for isomers. Both approaches gave many candidates but only a few of these were detected in the end. This
could be explained by a lack of spectra not yet recorded in laboratories, an abundance that is too small, or a small dipole moment, as well as incorrect hypotheses or inappropriate analyses. About ten years ago, it was observed that for most of the formulas of compounds with at least one isomer present in the ISM, the detected isomer corresponds to that with the highest thermodynamic stability (Lattelais et al. 2009, 2010a). This relation has been given the name minimum energy principle (MEP)\(^2\). When several isomers are observed, the MEP concludes that the most abundant is the most stable. To date, only a few detections that do not satisfy this principle have been found and some of these are still being debated. As examples we may cite the case of acetic acid (\(\text{CH}_3\text{COOH}\)), the most stable \(\text{C}_2\text{H}_4\text{O}_2\) isomer, which is less abundant than methyl formate (\(\text{HCOOCH}_3\)), which could be explained by a much stronger adsorption of the former on the grain icy mantles (Lattelais et al. 2011). Another example, propadienone (\(\text{H}_2\text{C}==\text{C}==\text{C}==\text{O}\)) has not yet been detected, although thermodynamically more stable than the detected isomer 2-propynal (\(\text{HC}==\text{C}==\text{C}==\text{O}\)) but it should be noted that the isomerization enthalpy at 0 K is only of 0.6 kcal mol\(^{-1}\) at the highest level of theory (W2-F12) as pointed by Karton & Talbi (2014). Such energy difference between isomers is so small that any environmental effect such as the presence of H atoms in the environment could dramatically affect the relative abundances (Loomis et al. 2015). Indeed propadienone, in contrast to 2-propynal, is unstable against reaction with atomic hydrogen, leading to \(\text{CH}_2\text{CCHO}\). This radical then reacts, without barriers, with an H atom to form propenal (\(\text{CH}_3\text{C}==\text{CH}==\text{O}\)), which was detected in the same regions as \(\text{H}_2\text{C}_2\text{O}\) (Shingledecker et al. 2019).

Consequently, even if this principle is not a rule, it can be used as a pragmatic tool to predict with high efficiency the presence of interstellar molecules in the ISM. It should be noted that many compounds with a small number of atoms (two to six) have been detected in the ISM, a few less up to nine atoms and much less beyond. Considering \(\text{C, H, N, O}\) molecules, the number of isomers is increasing dramatically with the number of atoms, particularly when several hydrogens are present, which often also causes additional difficulties for the analysis of spectra. To summarize, predicting the presence of new molecules in the ISM is more and more challenging with an increasing number of atoms.

The aim of this paper is to help select candidates whose detections should have higher probability of success than the approaches based on empirical modeling of ISM chemistry or crude analogy with already detected species. This work follows a study on \(\text{C}_2\text{H}_4\text{N}\) (10 atoms) and \(\text{C}_2\text{H}_6\text{O}\) (9 atoms), in which pyrolysis and furan were calculated as the most stable isomers but have not yet been detected in the ISM (Lattelais et al. 2010b).

A similar study on \(\text{CH}_2\text{N}_2\text{O}\) (8 atoms) has been more successful in that urea (\(\text{NH}_2\text{CO}\)) was detected (Belloche et al. 2019) and previously calculated to be the most stable isomer by Fourré et al. (2016). Following recent discovery of two isomers, \(\text{CH}_3\text{NCO}\) (Halfen et al. 2015; Cernicharo et al. 2016) and \(\text{HOCH}_2\text{CN}\) (Zeng et al. 2019), the present work is a continuation in which we selected \(\text{C}_2\text{H}_5\text{NO}\) (7 atoms) for the role that several isomers could have played on the primitive Earth (Majumdar et al. 2018). Rather than targeting specific compounds, we looked for which isomer with this formula is thermodynamically the most stable. Based on the detection of the first members of the CHNO and \(\text{C}_2\text{H}_5\text{NO}\) series we focused on chemical analogs to find out if there is something specific with the NCO linkage, and more precisely with the \([\text{C, N, O}]\) triad contained in R-NCO, R-OCN, R-CNO, R-ONC, with \(\text{R}==\text{H, CH}_3, \text{C}_2\text{H}_5, \text{HC}_2, \text{H}_2\text{CCH}, \text{and C}_2\text{H}_3\). These substituents were chosen on the basis of their abundance in the interstellar molecules detected.

The organization of the paper is as follows: Sect. 2 presents the theoretical approaches that were employed, given that a balance between accuracy and computational efficiency has to be reached. Section 3 is devoted to the study of the whole set of isomers of \(\text{C}_2\text{H}_5\text{NO}\) formula. Section 4 focuses on the \([\text{C, N, O}]\) triad. Our conclusions are given in Sect. 5.

### 2. Computational background

Before starting this study we had to decide which computational protocol to employ. To facilitate this choice we first had to determine the number of isomers to consider for the \(\text{C}_2\text{H}_5\text{NO}\) panel. To this end we used, in addition to chemical intuition, the SciFinder database, which lists 21 isomers and a software (named Isomers) recently developed by H. Chevreau at Sorbonne Université (Fourré et al. 2016). The list of isomers was a-priori limited to those \(\sim 6\) eV above the most stable compound and bicyclic compounds were not considered on the basis that such compounds with high energy have never been detected in the ISM.

From the results of the isomers count, comprising 40 isomers (not counting conformers), it then made sense to use methods capable of providing a reasonable balance between the quality of the electronic treatments and the required computing time. This is why the calculations were first performed using density functional theory (DFT)\(^3\) in the B3LYP formalism specially adjusted to reproduce the structures and the relative energies of a panel of representative organic molecules at lower cost (Becke 1993; Stephens et al. 1994, and references therein). More specifically, geometry optimizations were carried out using the Dunning aug-cc-pVTZ basis set of triple-zeta quality in the valence shell augmented with diffuse and polarization functions (Dunning 1989). The energies were refined by means of post Hartree-Fock (HF) coupled cluster CCSD and CCSD(T) calculations (Bartlett & Shavitt 1977; Raghavachari et al. 1989)\(^4\) on the previously optimized B3LYP geometries, using the same basis set. As some isomers were very close in energy, a final refinement of the energies was performed at the CCSD(T)/aug-cc-pVQZ level, to ensure convergence. Since dipole moments are not available at the CCSD(T) level, single point calculations were also performed at the CCSD/aug-cc-pVQZ level, which provides more reliable values than B3LYP. It should be noted that because some of the isomers are carbenes (RR'C:), these species may be either in a singlet or in a triplet spin state. Only the most stable species is considered.

Concerning the R-[\text{C, N, O}] compounds, the same formalism was employed, except that single point calculations were only performed at the CCSD(T)/aug-cc-pVTZ and that for \(\text{R}==\text{C}_2\text{H}_3\) the dipole moment was obtained at the B3LYP/aug-cc-pVTZ level. Each structure, either an isomer of \(\text{C}_2\text{H}_5\text{NO}\) or belonging

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\(^2\) Principle refers to laws which certain observations have first shown to be probable and to which the most extensive generality has then been given. We use the word principle, according to the definition given in the ARTFL Project, The University of Chicago (2001).

\(^3\) A comprehensive presentation of DFT methods and their application to reproduce the structural properties, energies, and spectroscopic parameters (vibration frequencies, dipole moments, ...) of organic molecules is provided in Lee & Scuseria (1995) and Koch & Holthausen (2001).

\(^4\) An easier insight into post HF methods is provided in Szabo & Ostlund (1996).
Table 1. Relative energies ($\Delta E$, in kcal mol$^{-1}$) and dipole moments ($\mu$, in Debye) at different levels of theory.

| Energy ordering | Isomer name                  | B3LYP/B1 $\Delta E$ | CCSD/B1 $\Delta E$ | CCSD(T)/B1 $\Delta E$ | CCSD(T)/B2 $\Delta E$ |
|-----------------|------------------------------|----------------------|---------------------|------------------------|-----------------------|
| (1)             | Methyl isocyanate          | 0.0                  | 0.0                 | 0.0                    | 0.0                   |
| (2)             | Hydroxycetonitrile         | 18.6                 | 10.8                | 2.97                   | 12.1                  |
| (3)             | Iminoacetaldehyde          | 22.8                 | 18.3                | 2.27                   | 18.9                  |
| (4)             | N-methyleneformamide       | 21.5                 | 18.5                | 2.97                   | 19.0                  |
| (5)             | Methyl cyanate            | 30.0                 | 24.7                | 4.59                   | 25.7                  |
| (6)             | 2-aminoetheneone          | 28.5                 | 26.6                | 2.52                   | 27.3                  |
| (7)             | Hydroxyisocyano methane    | 36.4                 | 28.7                | 3.08                   | 30.4                  |
| (8)             | Aziridin-2-one            | 37.9                 | 35.2                | 3.42                   | 35.4                  |
| (9)             | 2H-1,3-oxazete            | 42.6                 | 36.1                | 0.87                   | 36.1                  |
| (10)            | 2-oxiramine                | 43.0                 | 39.8                | 1.61                   | 39.7                  |
| (11)            | 2-iminothiol               | 41.8                 | 40.6                | 0.93                   | 41.1                  |
| (12)            | 2-hydroxy-3H-azirine       | 48.1                 | 43.3                | 1.43                   | 43.4                  |
| (13)            | 2-hydroxy-azirine          | 53.3                 | 46.9                | 1.60                   | 47.2                  |
| (14)            | Hydroxy(methyleneamino)methylidene | 53.1   | 55.5                | 1.02                   | 54.7                  |
| (15)            | Aminoethenyl              | 57.1                 | 54.9                | 0.77                   | 56.2                  |
| (16)            | Acetonitrile-N-oxide       | 55.0                 | 58.0                | 4.80                   | 56.0                  |
| (17)            | Formamidomethylidene       | 59.0                 | 54.8                | 3.43                   | 55.9                  |
| (18)            | [(Z)-hydroxymethyleneamino]methylidene | 61.4   | 63.3                | 3.75                   | 62.6                  |
| (19)            | Nitrosoethylene           | 66.7                 | 65.5                | 2.99                   | 65.1                  |
| (20)            | N-hydroxethylamine        | 65.6                 | 66.7                | 0.50                   | 65.9                  |
| (21)            | 3-methyloxazirine         | 72.1                 | 69.4                | 3.99                   | 65.3                  |
| (22)            | 4H-1,2-oxazete           | 72.2                 | 66.9                | 3.61                   | 65.9                  |
| (23)            | 3-hydroxy-iminothiolidene | 73.7                 | 68.3                | 2.79                   | 69.1                  |
| (24) ($^a$)     | 2-amino-2-oxoethylenide  | 70.9                 | 68.1                | 3.16                   | 70.8                  |
| (25)            | 2H-1,3-oxazet-3-ium-2-ide | 79.6                 | 79.0                | 2.65                   | 75.2                  |
| (26)            | 3-methylenoxazidine       | 79.6                 | 77.0                | 1.98                   | 75.7                  |
| (27)            | 2H-1,2-oxazete           | 83.6                 | 80.0                | 2.04                   | 78.9                  |
| (28)            | 1H-aziren-2-ol           | 84.8                 | 81.5                | 1.25                   | 80.8                  |
| (29)            | methyl Isolufinate        | 85.9                 | 81.6                | 4.13                   | 81.7                  |
| (30) ($^a$)     | 2-hydroxy-iminothiolidene | 84.0                 | 79.1                | 1.16                   | 82.3                  |
| (31)            | N-hydroxyethynilene       | 86.8                 | 84.5                | 0.86                   | 84.8                  |
| (32)            | 2,2-aminoxydroxy-ethenyliene | 95.9   | 91.4                | 2.56                   | 91.7                  |
| (33)            | Aminoxethylethyene        | 94.9                 | 92.8                | 1.92                   | 92.9                  |
| (34)            | 1-oxo-2H-azirene          | 97.7                 | 100.1               | 3.90                   | 97.1                  |
| (35)            | 2-methyl-oxaziridin-3-ylidene | 105.7  | 99.7                | 2.49                   | 98.1                  |
| (36)            | 1-hydroxy-azirine         | 106.3                | 103.3               | 1.39                   | 101.7                 |
| (37)            | 1,2-oxazetidin-3-ylidene  | 109.2                | 104.7               | 1.48                   | 104.4                 |
| (38)            | 1-hydroxyaziridine-2-ylidene | 117.7  | 115.0               | 1.58                   | 114.1                 |
| (39) ($^a$)     | 2-hydroxyimino-ethylidene | 113.7                | 112.0               | 0.80                   | 115.7                 |
| (40)            | 2-hydroxyiminoothiolidene | 133.4                | 129.6               | 2.89                   | 129.2                 |

Notes. These relative energies and dipole moments use a two basis set (B1 = aug-ccc-pVTZ, B2 = aug-cc-pVQZ): B3LYP/B1 full optimizations with zero-point (ZPE) correction included, CCSD/B1, CCSD(T)/B1, and CCSD(T)/B2 single points calculated at the B3LYP optimized geometries. For single points the ZPE is taken at the B3LYP level. The corresponding structures are represented in Fig. 1. $^a$Isomer whose electronic ground state is a triplet state.

3. Relative stability of C$_2$H$_3$NO isomer

Only 12 species with 7 atoms have been observed in the ISM so far, representing 5% of all the molecules detected. Methyl isocyanate is one of these molecules. By analogy with the CHON series in which HNCO (Snyder & Buhl 1972), HOCN (Marcelino et al. 2009), and HCNO (Brünken et al. 2009) had been detected, we expected that the -CH$_3$ substituted CH$_3$NCO, CH$_3$OCN, and CH$_3$CNO would be the next isomers to be observed.

Quantum calculations were already reported at various levels of theory for some of the 40 isomers listed by increasing energy in Table 1; the corresponding structures are represented in Fig. 1. In this work only the most stable conformer of each of the C$_2$H$_3$ON isomers was considered and hereafter these are referred to either by name or serial number.

For their investigation of the reaction of vinyl radical with nitric oxide, Sumathi et al. (2000) optimized the structures of 25 different isomers of C$_2$H$_3$NO. We also used the works of Badawi (2005) for 2-aminoethenone (6), Brahimi et al. (2006)
Fig. 1. Structures of C$_2$H$_3$NO isomers as ordered in Table 1 by increasing energy. The black boxes correspond to the HNCO isomers (Table 2), the orange box corresponds to the second isomer HOCH$_2$CN identified recently. (a) Isomer whose electronic ground state is a triplet state.

The corresponding 40 optimized structures were ranked in increasing order of relative stability at the CCSD(T)/aug-cc-pVQZ level (Table 1, Fig. 1). The most stable isomer (1) is methyl isocyanate (CH$_3$NCO) with a dipole moment of 3.1 Debye at the CCSD level. The second most stable isomer (2), hydroxyacetonitrile (HOCH$_2$CN), also known as glycolonitrile, is 12.7 kcal mol$^{-1}$, which is higher on the energy scale with a similar dipole moment. The third and fourth isomers, iminoacetaldehyde (3) (HC(O)–CH=NH) and N-methyleneformamide (4) (H$_2$C=NCHO), with dipole moments of 2.3 and 3.0 Debye, respectively, are degenerated at the CCSD(T)/aug-cc-pVQZ level, at 19.3 kcal mol$^{-1}$ above methyl isocyanate. From that point, the energy difference between each isomer is at most 8 kcal mol$^{-1}$, the highest relative energies exceeding 100 kcal mol$^{-1}$ (Table 1). Surprisingly, several three- and four-atom rings are within 50 kcal mol$^{-1}$ of methyl isocyanate. Indeed, because the small cycles are subjected to strong tensions, we would have thought that these isomers would be higher in energy. On the other hand, we find that carbenes (RR'C:) are among the least stable isomers with energies of more than 50 kcal mol$^{-1}$ above CH$_3$NCO.

Of the 11 optimized carbenes, (14, 17, 23, 24, 30, 32, 35, 37, 38, 39, 40) only three (24, 30, 39) are more stable in the triplet state. It should be mentioned that for this family of compounds as for some others (Lattelais et al. 2010a), compounds with single or double NO bonds, unsaturated small cycles and carbenes are never in the thermodynamically most stable range of the isomers list. Only two isomers have been observed so far, methyl isocyanate (1) which is the thermodynamically most stable isomer and hydroxyacetonitrile (2) (Zeng et al. 2019) about 13 kcal mol$^{-1}$ above (Halfen et al. 2015; Cernicharo et al. 2016; Zeng et al. 2019).

It should be noted that the microwave and millimetric spectra of iminoacetaldehyde (3), of N-methyleneformamide (4) and aminoethenone (6) have never been recorded and that we cannot reach a conclusion concerning their absence or presence in the ISM. Among the compounds for which such spectra were available the case of hydroxyacetonitrile is of interest since it was easy to imagine and to demonstrate its formation on grains by laboratory experiments (Danger et al. 2014).

For methyl cyanate (5) (Kolesniková et al. 2016) and acetonitrile-N-oxide (16) (Galica et al. 1984), the recording of their spectra did not allow their detection in the ISM so far. This result cannot be explained by the dipole moment, which is in all cases comparable to that of methyl isocyanate. Nevertheless, it was interesting to try to find some explanation to the formation of CH$_3$NCO in the ISM and on the possible isomerization of isomers under irradiation (Majumdar et al. 2018). It should be mentioned that methyl isocyanate (1) has never been detected in the photolysis of hydroxyacetonitrile (2) and the thermolysis of
this latter led to hydrogen cyanide and formaldehyde. The case of methyl cyanate (5) was discussed recently and it was evidenced that the free monomeric species in the gas phase did not rearange on heating into the isocyanate isomer, but this reaction could occur on the grains or in a bimolecular process (Koch et al. 2012).

A great number of isomers with a C$_2$H$_4$NO formula have never been synthesized. Many of these isomers are probably kinetically unstable, strongly limiting photochemical studies, and thermolysis of isomers to have a better knowledge of the most often formed species.

**4. Carbon, nitrogen, oxygen atomic triad**

Only 13 organic molecules detected in the ISM contain carbon, nitrogen, and oxygen simultaneously. Eleven of these contain the three CNO atoms directly linked together (Table 2). At least one such structure has been found for each series of molecules comprising from 3 to 9 atoms. It suggests that the CNO linkage should be a widespread fragment, possibly substituted by various chemical functional groups.

### 4.1. R-NCO isomers already observed

The simplest example is the triatomic species itself, which has been identified recently by Marcelino et al. (2018) in the form of a free radical. The same structure had also been proposed in the form of a negative ion to interpret IR spectra in interstellar ices (Gibb et al. 2000). A radical or negative ion, NCO is more stable than CNO by ~62.5 kcal mol$^{-1}$ (Pak et al. 1997; Saito & Amano 1970). It is of the same order of magnitude as the energy separation between HNCO and HCNO (Table 3).

With four atoms we find the only example of three species detected so far in a given series, which suggests that knowing their relative energies could be used for calibration of the energy scale. Two of these, HNCO (Snyder & Buhl 1972) and HOCN (Brünken et al. 2009) have been identified in the same region (Sgr B2), whereas HCNO (Marcelino et al. 2009) has been found in dark clouds (B1, L1544, L193, L1527).

With five atoms, the target must contain one more atom than any isomer of HNCO. Only HC(=O)CN is observed in the form of a neutral species (Remijan et al. 2008) but it is not structured around the CN bond. However, from an energetical point of view, it is the lowest energy isomer, calculated below HC(=O)NC and HCCNO by 11.5 and 80.6 kcal mol$^{-1}$, respectively. The first and most stable CNO species observed is H$_2$NCO$^+$ (Gupta et al. 2013), that is, the protonated ion of the most stable HNCO isomer.

With six atoms there are six stable isomers, five of which have a linear backbone. The most stable of these is formamide (NH$_2$CHO), which is often taken as the first example of a peptide bond model (Lattelais et al. 2010a). It is the only isomer detected so far (Rubin et al. 1971). It must be stressed that all isomers containing a NO bond are 50 kcal mol$^{-1}$, at least, higher in energy (Lattelais et al. 2010a).

With seven atoms there are six stable isomers, five of which have a linear backbone. The most stable of these is formamide (NH$_2$CHO), which is often taken as the first example of a peptide bond model (Lattelais et al. 2010a). It is the only isomer detected so far (Rubin et al. 1971). It must be stressed that all isomers containing a NO bond are 50 kcal mol$^{-1}$, at least, higher in energy (Lattelais et al. 2010a).

With seven atoms, CH$_2$NCO (1) is the most stable isomer in the panel of 40 isomers (Table 1 and Sect. 3). The energy spread between isomers Fig. 1 and Table 3 is about the same as for HNCO, that is, the same ordering and similar energy differences. We note that CH$_4$OCN (16) is closer to CH$_4$OCN.

### Table 2. Complex organic molecules detected in space so far containing C, H, N, O atoms as a function of the total number of atoms.

| Substituent | RNCO | ROCN | RCNO | RONC |
|-------------|------|------|------|------|
| NCO (8)     | NCO$^+$ (1) | HCNO (9) | H$_2$NCO (3) | NH$_2$CHO (4) |
| HNCO (2)    | CH$_3$NCO (5) | HCO (10) | HOCH$_2$CN (11) | (NH$_2$)$_2$CO (6) |
| H$_2$NCO (3) | CH$_3$CONH$_2$ (7) | CH$_3$NHCHO (12) | | |
| HOCN (13)   | | | | |

### Table 3. Computed relative stabilities with respect to the minimum energy isomer in each series $\Delta$E (kcal mol$^{-1}$), dipole moments $\mu$ (Debye).

| Substituent | RNCO $\Delta$E | ROCN $\Delta$E | RCNO $\Delta$E | RONC $\Delta$E |
|-------------|-----------------|-----------------|-----------------|-----------------|
| None (anion)$^{(a)}$ | 0.0 | 1.62 | 67.1 | |
| None (radical)$^{(b)}$ | 0.0 | 0.64 | 62.0 | |
| H            | 0.0 | 2.13 | 24.3 | 3.86 | 68.8 | 3.59 | 82.5 | 3.48 | |
| CH$_3$       | 0.0 | 3.10 | 25.7 | 4.59 | 56.0 | 4.80 | 81.7 | 4.13 | |
| CH$_2$CH$_2$ | 0.0 | 3.37 | 23.6 | 5.00 | 58.1 | 4.92 | 79.6 | 4.53 | |
| H$_2$C=C     | 0.0 | 2.31 | 28.2 | 4.24 | 59.0 | 4.35 | 84.7 | 3.72 | |
| HC≡C         | 0.0 | 1.49 | 39.5 | 3.20 | 52.5 | 3.68 | 95.9 | 2.83 | |
| C$_6$H$_5$   | 0.0 | 2.53 | 27.2 | 4.65 | 59.0 | 4.58 | 83.9 | 4.01 | |
| Al$^{(c)}$   | 0.0 | 2.02 | 16.6 | 5.12 | 83.9 | 2.93 | 80.5 | |
| Mg$^{(d)}$   | 0.0 | 4.84 | 15.8 | 7.59 | 81.7 | 81.0 | |

**Notes.** Conversion factors: 1 kcal mol$^{-1}$ = 349.7 cm$^{-1}$ = 503.2 K.

**References.** (1) Soifer et al. (1979); (2) Snyder & Buhl (1972); (3) Gupta et al. (2013); Marcelino et al. (2018); (4) Rubin et al. (1971); (5) Halfen et al. (2015); Cernicharo et al. (2016); (6) Remijan et al. (2014); (7) Hollis et al. (2006); (8) Marcelino et al. (2018); (9) Marcelino et al. (2009); (10) Remijan et al. (2008); (11) Zeng et al. (2019); (12) Belloche et al. (2017, 2019); (13) Brünken et al. (2009).
(5) than HCN is to HOCN. The reason has to be found in the linear arrangement of the CCNO backbone that maximizes the hyperconjugation interaction stabilizing the whole structure5.

With eight atoms, urea, (NH2)2CO, tentatively detected by Remjaj et al. (2014) and confirmed unambiguously by Belloche et al. (2019) presents a double NCO arrangement that makes it the most stable compound as shown by Fourré et al. (2016); replacing oxygen by sulfur leads to thiourea, which is predicted by the same authors to be the most stable of the sulfurred series.

With nine atoms, we find the next amide isomers after formamide, (H2NCHO), namely, acetamide, (H2NCO(CH3)) (Hollis et al. 2006) and N-methyl formamide, (CH3NCHO) (Belloche et al. 2017, 2019) predicted as the second species on the energy scale of the C2H5NO series (Lattelais et al. 2010a). These are the only isomers detected. It is worth mentioning that when adding one CH2 group the next more stable species in the C3H7NO series are also 3 amides in the panel of 25 molecules of lowest energies (Lattelais et al. 2010a).

4.2. R-NCO isomers to come

The panel of isomers to probe can be extended by adding the ethyl substituent to the alkyl list (Table 3). After H, CH2 and C2H2, which do not allow any possibility of conjugation, we consider the case of delocalized substituents. There are more than ten species observed containing C=C triple bonds but only two benzene derivatives, namely, benzene (C6H6) (Cernicharo et al. 2001) and benzonitrile (C6H5CN) (McGuire et al. 2018b) have been unambiguously detected. This prompted us to consider vinyl (HC2CH), ethynyl (HC≡C), and benzyl (C6H5) as alternate substituents to the CNO triad.

A simple look at Table 3 shows three fundamental results.

(i) RNC and ROCN are always the most stable isomers whatever R=H, CH3, H2C=CH, HC≡C, C2H2 or metal, M = Al and Mg. Increasing the electronic delocalization on R does not affect the relative stability ordering of the lowest two isomers.

(ii) The stability ordering, from most to less stable, is RNCO > ROCN > RCNO > RONC when R is a carbonaceous fragment6. For R=H a complete survey of the potential energy surface was reported by Mebel et al. (1996). The energy difference between the most stable isomer, RNC, and those higher in energy have a rather limited spread for each type of isomer (kcal mol\(^{-1}\)), that is, \(~25 \pm 3\) for ROCN, \(~63.5 \pm 5\) for RNCO, and \(~82 \pm 3\) for RONC; this suggests strong stability of the NCO linkage in every circumstance.

(iii) For metal substituents the energy gap between the lowest two linked to the NCO linkage looses one-third of its value. The other two linked to CNO are now very close in energy with a gap between M–NCO and M–ONC about six times that between M–CNO and M–ONC. A reason for that can be found in a bonding analysis carried out by Vega-Vega et al. (2017).

In the end it is worth noting that all dipole moments are large enough to stimulate future search in the ISM.

5. Conclusions

We first confirm that the two detected C2H3NO isomers, that is, methyl isocyanate (1) and hydroxycetonitrile (2) rank in first and second positions on the stability scale. According to the MEP, without “chemical sieve”, the following isomer to be searched for in the ISM should be N-methyleneformamide (4) in preference to iminoacetaldehyde (3), which is isoe nergetic but possesses a smaller dipole moment). Then we focus on the simplified vision of organic compounds as represented by the crude naming of “CHON” species. All the molecules considered in this work have been chosen so as to contain a unique triatomic arrangement that may serve as baseline for comparison with all isomers of R-CNO type. A thorough screening of the molecules detected in the ISM showed a list of 13 species limited to 9 atoms (Table 2). These molecules belong principally in two large categories, amides and cyanates. The radical or negative ion, NCO is more stable than CNO by about 63 kcal mol\(^{-1}\). It is of the same order of magnitude as the energy separation between RNC (resp. ROCN) and RCNO (resp. RONC) in the series of isomers (Table 3). More precisely, we have HNCO above HCNO, CH3NCO above CH2CNO by 68.8 and 56.0 kcal mol\(^{-1}\), etc. Similarly one has HOCN above HONC, CH3OCN above CH2CNO. At the end of this inventory of the molecules already detected, we show that all those containing the N,C,O linkage satisfy the MEP (Lattelais et al. 2010a) and, that the connexion of the substituent to the nitrogen atom is energetically favored.

The present study offers a generalization in that it is consistent with the fact that the R-NCO arrangement is the most stable whether R=H, CH3 and C2H2, C2H4, CH, C2H5 or metals. Extension to other R functional groups is beyond the scope of this work. The case of metals might be not as simple as it appears in this work if transition metals are implied. It is therefore reasonable to consider the above species as most plausible targets among the molecules containing the NCO arrangement.

In the end, the fact that only the thermodynamically most stable isomers have been detected for C2H3NO species should be put back in a global context. It is more than plausible that many other compounds are also present in the ISM but cannot be detected to date owing to the absence of recorded millimeter spectra. Beyond the R-NCO structures the energetic ranking of C2H5NO isomers on the energy scale suggests that H2C=NCHO (4), HN=CHCHO (3) and NH2CHCNO (6) should be targets worth considering in the laboratory in view of future observations.

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A&A 639, A16 (2020)
I. Fourré et al: Thermodynamics as a tool

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