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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 minimun 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 C_2H_3NO 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 C_2H_3NO we find methylisocyanate CH_3NCO, 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, CH_3, C_2H_5, HC_2, H_2CCH, and C_6H_5 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)[1] provides detailed information on this. Most of these molecules have a permanent dipole moment μ allowing detection by microwave or millimetric spectroscopy. The highest dipole moments point to the easiest detectable compounds since the line intensities scale with μ^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 (CH_2CHCH_3) (Marcelino et al. 2007) or methoxymethanol (CH_3OCH_2OH) (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 (Knauth et al. 2004), and benzene (C_6H_6) (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 H_3^+ as proton carrier, provides an additional knowledge of the target environment. The abundances of both neutral and protonated species should be consistent since 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 H_3^+ can be considered. In the case of CO_2 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

[1] See https://cdms.astro.uni-koeln.de/classic/molecules or http://www.astrochymist.org/astrochymist_ism.html

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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 analogies. 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 (CH_3COOH), the most stable $C_2H_4O_2$ isomer, which is less abundant than methyl formate ($HCOOCH_3$), which could be explained by a much stronger adsorption of the former on the grain icy mantles (Lattelais et al. 2011). Another example, propadienone ($H_2C=C=C=O$) has not yet been detected, although thermodynamically more stable than the detected isomer 2-propynal ($HC\equiv CCH(O)$) 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 CH_2CHCO. This radical then reacts, without barriers, with an H atom to form propenal ($CH_2=CHCHO$), which was detected in the same regions as H_2C_3O (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 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 C_4H_5N (10 atoms) and C_4H_4O (9 atoms), in which pyrrole 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 CH_4N_2O (8 atoms) has been more successful in that urea $(NH_2)_2CO$ 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, CH_3NCO (Halfen et al. 2015; Cernicharo et al. 2016) and $HOCH_2CN$ (Zeng et al. 2019), the present work is a continuation in which we selected C_2H_3NO (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 C_2H_3NO series we focused on chemical analogs to find out if there is something specific with the NCO linkage, and more precisely with the [C,N,O] triad contained in R-NCO, R-OCN, R-CNO, R-ONC, with R=H, CH_3, C_2H_5, HC_2, H_2CCH, and C_6H_5. 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 C_2H_3NO formula. Section 4 focuses on the [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 C_2H_3NO 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 ~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 Hartre-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-pVTZ 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-[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 R=C_6H_5 the dipole moment was obtained at the B3LYP/aug-cc-pVTZ level. Each structure, either an isomer of C_2H_3NO or belonging

[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 (ΔE, in kcal mol^{-1}) and dipole moments (μ, in Debye) at different levels of theory.

Energy		B3LYP/B1		CCSD/B1		CCSD(T)/B1	CCSD(T)/B2
ordering	Isomer name	ΔE	μ	ΔE	μ	ΔE	ΔE
(1)	Methyl isocyanate	0.0	3.02	0.0	3.10	0.0	0.0
(2)	Hydroxyacetonitrile	18.6	3.03	10.8	2.97	12.1	12.7
(3)	Iminoacetaldehyde	22.8	2.34	18.3	2.27	18.9	19.3
(4)	N-methyleneformamide	21.5	3.05	18.5	2.97	19.0	19.3
(5)	Methyl cyanate	30.0	4.66	24.7	4.59	25.7	26.2
(6)	2-aminoethenone	28.5	2.55	26.6	2.52	27.3	27.3
(7)	Hydroxyisocyanomethane	36.4	3.07	28.7	3.08	30.4	30.9
(8)	Aziridin-2-one	37.9	3.43	35.2	3.42	35.4	35.5
(9)	2H-1,3-oxazete	42.6	0.95	36.1	0.87	36.1	36.4
(10)	2-oxiranimine	43.0	1.65	39.8	1.61	39.7	40.2
(11)	2-iminoethenol	41.8	0.92	40.6	0.93	41.1	41.1
(12)	2-hydroxy-3H-azirine	48.1	1.51	43.3	1.43	43.4	43.5
(13)	2-hydroxy-azirine	53.3	1.58	46.9	1.60	47.2	47.4
(14)	Hydroxy(methyleneamino)methylidene	53.1	0.70	55.5	1.02	54.7	54.9
(15)	Aminoethynol	57.1	0.77	54.9	0.77	56.2	55.7
(16)	Acetonitrile-N-oxyde	55.0	4.49	58.0	4.80	56.0	56.3
(17)	Formamidomethylidene	59.0	3.37	54.8	3.43	55.9	56.4
(18)	[(Z)-hydroxymethyleneamino]methylidene	61.4	3.62	63.3	3.75	62.6	62.9
(19)	Nitrosoethylene	67.6	3.35	65.5	2.99	64.5	65.1
(20)	N-hydroxyethenimine	65.6	0.42	66.7	0.50	65.9	66.4
(21)	3-methyloxazirine	72.1	4.02	69.4	3.99	65.3	66.4
(22)	4H-1,2-oxazete	72.2	3.56	66.9	3.61	65.9	66.6
(23)	3-hydroxy-iminoethylidene	73.7	2.74	68.3	2.79	69.1	69.7
(24) [(a)]	2-amino-2-oxoethylidene	70.9	3.05	68.1	3.16	70.8	71.5
(25)	2H-1,3-oxazet-3-ium-2-ide	79.6	2.62	79.0	2.65	75.2	75.2
(26)	3-methylenoxaziridine	79.6	1.91	77.0	1.98	75.7	76.5
(27)	2H-1,2-oxazete	83.6	1.91	80.0	2.04	78.9	79.2
(28)	1H-aziren-2-ol	84.8	1.33	81.5	1.25	80.8	80.9
(29)	methyl Isofulminate	85.9	4.16	81.2	4.13	81.7	82.6
(30) [(a)]	2-hydroxy-iminoethylidene	84.0	1.08	79.1	1.16	82.3	83.1
(31)	N-hydroxyethynamine	86.8	0.95	84.5	0.86	84.8	84.9
(32)	2,2-aminohydroxy-ethenylidene	95.9	2.71	91.4	2.56	91.7	92.0
(33)	Aminoxyethyne	94.9	1.98	92.8	1.92	92.9	93.3
(34)	1-oxo-2H-azirene	97.7	3.59	100.1	3.90	97.1	97.4
(35)	2-methyl-oxaziridin-3-ylidene	105.7	2.60	99.7	2.49	98.1	99.4
(36)	1-hydroxy-azirine	106.3	1.41	103.3	1.39	101.7	102.2
(37)	1,2-oxazetidin-3-ylidene	109.2	1.51	104.7	1.48	104.4	105.0
(38)	1-hydroxyaziridin-2-ylidene	117.7	1.58	115.0	1.58	114.1	114.6
(39) [(a)]	2-hydroxyimino-ethylidene	113.7	0.83	112.0	0.80	114.7	115.8
(40)	2-hydroxyamino-ethenylidene	133.4	3.07	129.6	2.89	129.2	130.2

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.

to the R-[C,N,O] family, fully optimized, was verified to be a stationary point by vibrational analysis. All calculations were done using the Gaussian package (Frisch et al. 2009).

3. Relative stability of C_2H_3NO 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_3NCO, CH_3OCN, and CH_3CNO 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_2H_3ON 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_2H_3NO. We also used the works of Badawi (2005) for 2-aminoethenone (6), Brahimi et al. (2006)

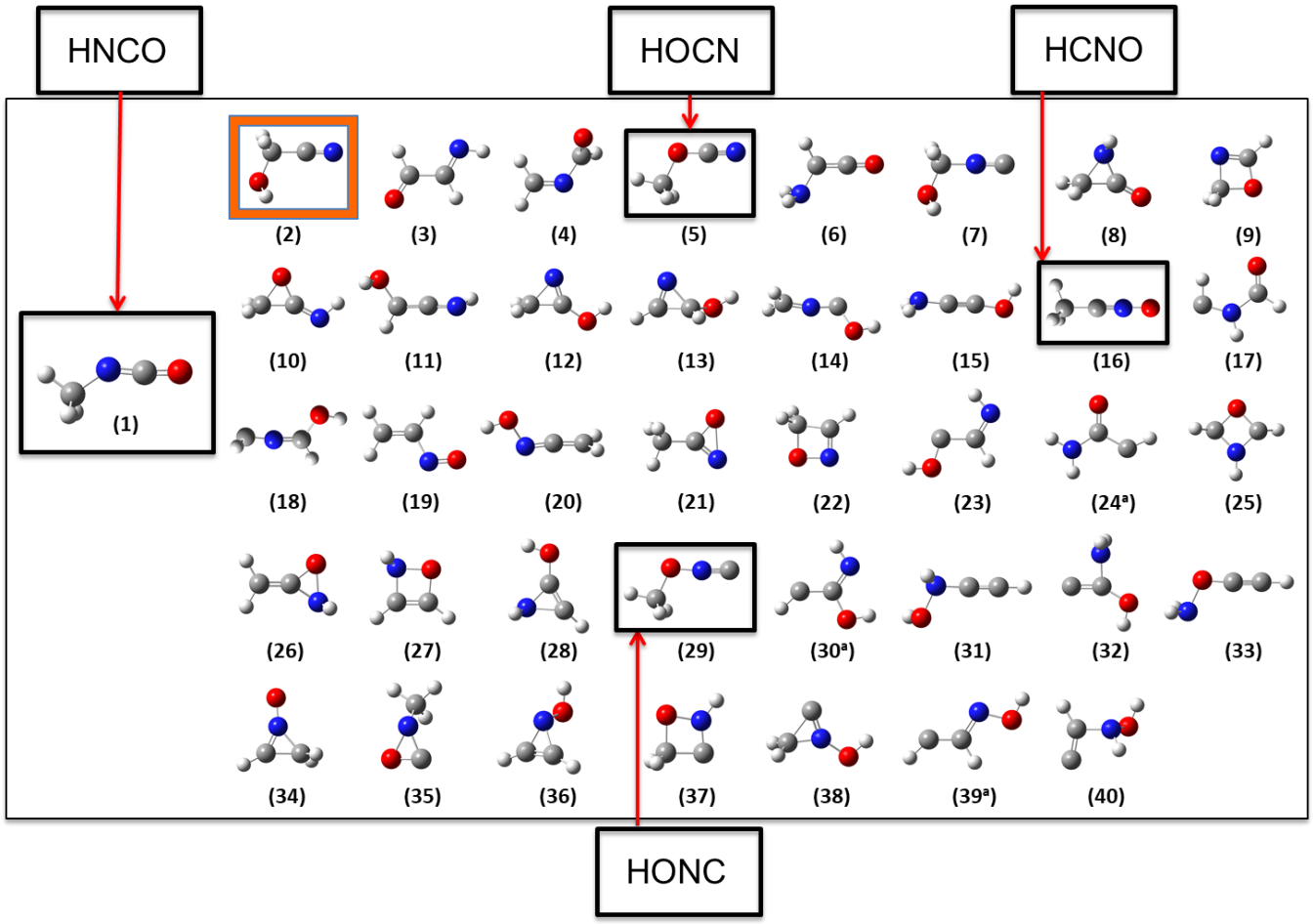


Fig. 1. Structures of C_2H_3NO isomers as ordered in Table 1 by increasing energy. The black boxes correspond to the HNCO isomers (Table 2), the orange box corresponds to the second isomer $HOCH_2CN$ identified recently. [(a)] Isomer whose electronic ground state is a triplet state.

and Afanas'yev & Prosyanik (2005) for N-methyleneformamide (4), Arulmozhiraja & Kolandaivel (1998) for nitrosoethylene (19) and 4H-1,2-oxazete (22), Liu et al. (2004) for 3-methyloxazirine (21) as starting points of our own treatments.

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_3NCO) with a dipole moment of 3.1 Debye at the CCSD level. The second most stable isomer (2), hydroxyacetonitrile ($HOCH_2CN$), 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_2C=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_3NCO.

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_3NCO 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

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.

3	4	5	6	7	8	9
NCO^- (1) NCO (8)	HNCO (2) HCNO (9) HOCN (13)	H_2NCO+ (3) HC(O)CN (10)	NH_2CHO (4)	CH_3NCO (5) $HOCH_2CN$ (11)	$(NH_2)_2CO$ (6)	CH_3CONH_2 (7) CH_3NHCHO (12)

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).

Table 3. Computed relative stabilities with respect to the minimum energy isomer in each series ΔE (kcal mol^{-1}), dipole moments μ (Debye).

	RNCO		ROCN		RCNO		RONC	
Substituent	ΔE	μ	ΔE	μ	ΔE	μ	ΔE	μ
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_3CH_2	0.0	3.37	23.6	5.00	58.1	4.92	79.6	4.53
$H_2C{=}C$	0.0	2.31	28.2	4.24	59.0	4.35	84.7	3.72
$HC{\equiv}C$	0.0	1.49	39.5	3.20	52.5	3.68	95.9	2.83
C_6H_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. [a]Pak et al. (1997); [b]Saito & Amano (1970); [c]Trabelsi et al. (2019); [d]Vega-Vega et al. (2017).

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 rearrange 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_2H_3NO 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 CNO triad. 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_2NCO^+ (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_2CHO), 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_3NCO (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_3CNO (16) is closer to CH_3OCN

(5) than HCNO 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 structure[5].

With eight atoms, urea, $(NH_2)_2CO$, tentatively detected by Remijan 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 sulfurated series.

With nine atoms, we find the next amide isomers after formamide, (H_2NCHO), namely, acetamide, ($H_2NCO(CH_3)$) (Hollis et al. 2006) and N-methyl formamide, (CH_3NHCHO) (Belloche et al. 2017, 2019) predicted as the second species on the energy scale of the C_2H_5NO series (Lattelais et al. 2010a). These are the only isomers detected. It is worth mentioning that when adding one CH_2 group the next more stable species in the C_3H_7NO 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, CH_3 and C_2H_5, 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 (C_6H_6) (Cernicharo et al. 2001) and benzonitrile (C_6H_5CN) (McGuire et al. 2018b) have been unambiguously detected. This prompted us to consider vinyl (H_2CCH), ethynyl (HC_2), and benzyl (C_6H_5) as alternate substituents to the CNO triad.

A simple look at Table 3 shows three fundamental results.

(i) RNCO and ROCN are always the most stable isomers whatever R=H, CH_3, H_2C=CH, HC≡C, C_6H_5 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 fragment[6]. 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, RNCO, and those higher in energy have a rather limited spread for each type of isomer (kcal mol^{-1}), that is, ∼25 ± 3 for ROCN, ∼63.5 ± 5 for RCNO, and ∼82 ± 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 isomers 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 betwe-en M–NCO 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] Hyperconjugation refers in this work to the stabilizing interaction of the electron density of a delocalized system (e.g., C=N=O) with that of a localized adjacent group (e.g., CH_3).

[6] Though reported ∼40 yr ago it should not be forgotten that qualitatively similar results were obtained by simple Hartree-Fock calculations for R=H, CH_3 and C_6H_5 without correlation effects by Poppinger et al. (1977) and Poppinger & Radom (1978).

5. Conclusions

We first confirm that the two detected C_2H_3NO isomers, that is, methyl isocyanate (1) and hydroxyacetonitrile (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 isoenergetic 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 RNCO (resp. ROCN) and RCNO (resp. RONC) in the series of isomers (Table 3). More precisely, we have HNCO above HCNO, CH_3NCO above CH_3CNO by 68.8 and 56.0 kcal mol^{-1}, etc. Similarly one has HOCN above HONC, CH_3OCN above CH_3ONC. 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, CH_3 and C_2H_5, C_2H_3, C_2H, C_6H_5 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 two most stable isomers have been detected for C_2H_3NO 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 C_2H_3NO isomers on the energy scale suggests that H_2C=NCHO (4), HN=CHCHO (3) and NH_2CHCO (6) should be targets worth considering in the laboratory in view of future observations.

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