

# A Review on Carbon-rich Molecules in Space

Franco Cataldo<sup>1,2</sup>, D. Aníbal García-Hernández<sup>3,4</sup>  
and Arturo Manchado<sup>3,4,5</sup>

<sup>1</sup>Istituto Nazionale di Astrofisica - Osservatorio Astrofisica di Catania, Via S. Sofia 78, 95123, Italy

<sup>2</sup>Actinium Chemical Research, Via Casilina 1626/A, 00133 Rome, Italy

<sup>3</sup>Instituto de Astrofisica de Canarias, Via Lactea s/n, E-38200, La Laguna, Tenerife, Spain

<sup>4</sup>Universidad de La Laguna (ULL), Dept. de Astrofisica, E-38205, La Laguna, Tenerife, Spain

<sup>5</sup>CSIC, Madrid, Spain

**Abstract.** We present and discuss carbon-rich compounds of astrochemical interest such as polyynes, acetylenic carbon chains and the related derivative known as monocyanopolyynes and dicyanopolyynes. Fullerenes are now known to be abundant in space, while fulleranes - the hydrogenated fullerenes - and other carbon-rich compounds such as very large polycyclic aromatic hydrocarbons (PAHs) and heavy petroleum fractions are suspected to be present in space. We review the synthesis, the infrared spectra as well as the electronic absorption spectra of these four classes of carbon-rich molecules. The existence or possible existence in space of the latter molecules is reported and discussed.

**Keywords.** Astrochemistry, molecular data, infrared: ISM

---

The review regards a series of carbon-rich molecules which were recently studied by the authors. First we will discuss the first class of carbon-rich molecules: the polyynes and the related molecules known as monocyanopolyynes and dicyanopolyynes. These molecules were detected by radioastronomy in carbon-rich Asymptotic Giant Branch (AGB) stars, in dense and dark interstellar clouds like TMC-1 and in hot molecular cores. Although polyynes are highly unstable in terrestrial conditions, Cataldo (2004, 2006a,b) has developed a synthesis of these molecules by using a carbon arc and trapping the molecules in a solvent. When the arc is struck in liquid hydrocarbons, all the polyynes homologue series from H-(C≡C)<sub>3</sub>-H to H-(C≡C)<sub>9</sub>-H is obtained and the electronic absorption spectrum of each individual polyne molecular specie has been recorded. The formation of polyynes is always accompanied by the formation of PAHs and carbon soot. Indeed, polyynes are considered the precursors of PAHs and carbon soot. When the carbon arc is struck in liquid ammonia or in acetonitrile, then a mixture of polyynes series and monocyanopolyynes series H-(C≡C)<sub>n</sub>-CN is obtained. Dicyanopolyynes NC-(C≡C)<sub>n</sub>-CN can be synthesized by striking the carbon arc in liquid nitrogen. It was proposed that the laboratory conditions of polyynes synthesis through the carbon arc are comparable to those existing in the circumstellar medium of certain AGB stars since both in laboratory conditions and in the circumstellar environment the mechanism of carbon chain formation follows a free radical path (Cataldo 2006a,b). More recent work has shown that polyynes are also formed in the gas phase by arcing graphite in a flow of argon, in which the addition of methane to Ar strongly enhances the formation of polyynes, which are then accompanied by PAHs such as naphthalene (Cataldo 2007). Polyynes are an endothermal compound with a positive free energy of formation from the elements at 298 K. However, their Gibbs free energy of formation becomes negative just above 4400 K, which is the temperature of the carbon arc. The polyynes are thermodynamically

stable and form quite easily at such high temperatures, but are then quenched to a lower temperature by the hydrocarbon solvent surrounding the arc and become trapped there, thus permitting their manipulation, separation and analysis (Cataldo 2007).

Another interesting carbon-rich class of molecules are fullerenes, which were recently detected in a series of astrophysical objects (Cami *et al.* 2010; García-Hernández *et al.* 2010, 2011a,b; Sellgren *et al.* 2010; Zhang & Kwok 2011). Fullerenes show considerable stability toward the action of high energy radiation so that they could survive for billions of years in the ISM under certain conditions (Cataldo *et al.* 2009). This fact may explain why fullerenes have been found in completely different astrophysical objects. To facilitate the search of C<sub>60</sub> and C<sub>70</sub> fullerenes in space, we have studied the dependence of infrared band pattern and band intensity of these molecules with temperature and measured the molar absorptivity for the quantitative determination of their abundance (Iglesias-Groth *et al.* 2011). Furthermore, the electronic absorption spectra of the radical cation of C<sub>60</sub> and C<sub>70</sub> in a very high dielectric constant medium has been determined (Cataldo *et al.* 2012). Fullerenes are very reactive with atomic hydrogen, and form fulleranes, which are hydrogenated fullerenes (Cataldo & Iglesias-Groth 2010). When heated or photolyzed, the fulleranes release molecular hydrogen yielding back the parent fullerene. Therefore, fullerenes may play a key role in the molecular hydrogen formation starting from atomic hydrogen. The photolysis rate constant of fulleranes appears of the same order of magnitude as that of polyynes (Cataldo & Iglesias-Groth 2009). Curiously, the fullerane C<sub>60</sub>H<sub>36</sub> shows an electronic absorption spectrum with a unique peak at 217 nm, exactly matching the UV “bump” of the interstellar light extinction curve (Cataldo & Iglesias-Groth 2009). The infrared spectra of a series of reference fulleranes have been recorded in the laboratory by Iglesias-Groth *et al.* (2012) together with the relative molar absorptivity. Consequently, since the reference spectra are now available, a search for fulleranes can now be made in space, and their possible detection in astrophysical environments is now only a matter of time and luck.

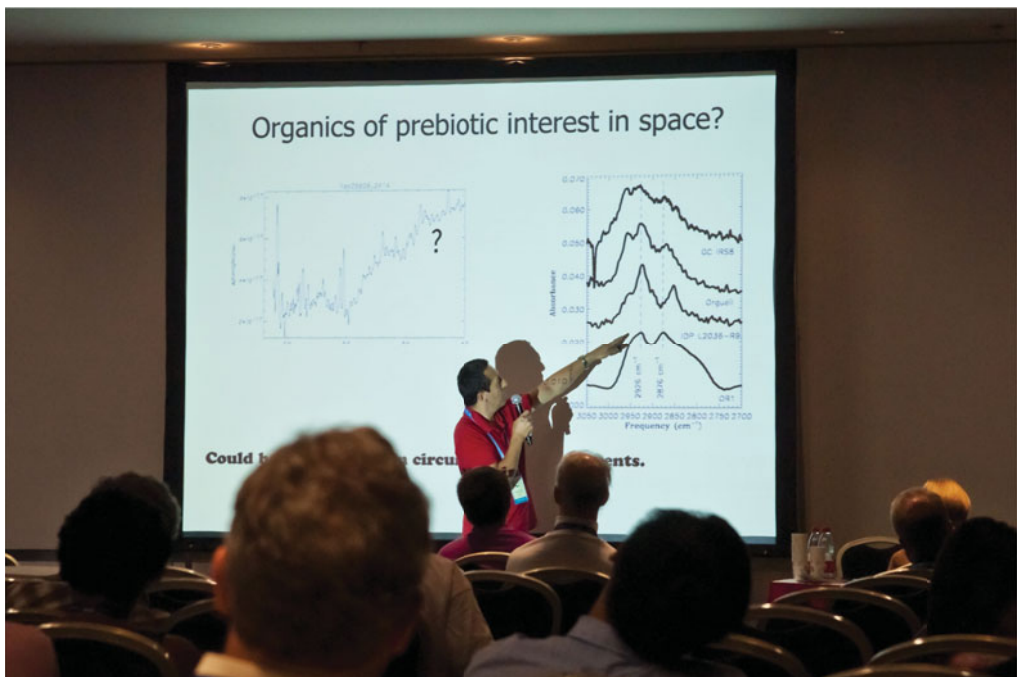
Coal was proposed by Papoular and colleagues (1989) as a possible model for matching the infrared band pattern of the unidentified infrared bands (UIBs) of certain planetary nebula (PNe) and proto-PNe (PPNe). However, anthracite, “mature” coal, is eminently aromatic with minor aliphatic components. More recently, Cataldo *et al.* (2002, 2004) and Cataldo & Keheyán (2003) have shown that certain heavy petroleum fractions are also able to match the band pattern of coal and of PPNe and PNe. Thus, petroleum fractions should be used as realistic model compounds since they are composed by a “core” of 3 to 4 condensed aromatic rings surrounded by cycloaliphatic (naphthenic rings) and chains of aliphatic *sp*<sup>3</sup> hybridized carbon. Thus, instead of searching for pure PAHs, the heavy petroleum fraction model offers molecules where the aromatic, naphthenic and aliphatic moieties co-exist, and match certain PPNe spectra where a mixture of aliphatic/cycloaliphatic and aromatic structures are evident.

Very large PAHs (VLPAs) are not easily accessible but of high interest as reference molecules for the explanation of the diffuse interstellar bands (DIBs) of the interstellar medium (ISM). Using the Scholl reaction, we have synthesized a series of VLPAs ranging from dicoronylene to quaterrylene to hexabenzocoronene. Dicoronylene was also obtained by the thermal dimerization of coronene. If the thermal treatment of coronene is prolonged, the oligomerization of coronene proceeds further, yielding a black oligomer, which is probably a trimer or a higher homologue. It is shown that from coronene oligomerization it is possible to build a sheet of graphene.

## References

Cami, J., Bernard-Salas, J., Peeters, E., & Malek, S. E. 2010, *Science* 329, 1180

- Cataldo, F. 2004, *Int. J. Astrobiol.* 3, 237
- Cataldo, F. 2006a, *Int. J. Astrobiol.* 5, 37
- Cataldo, F. 2006b, *OLEB* 36, 467
- Cataldo, F. 2007, *Fullerenes Nanotubes Carbon Nanostructures* 15, 291
- Cataldo, F. & Iglesias-Groth, S. 2009, *MNRAS* 400, 291
- Cataldo, F. & Iglesias-Groth, S. 2010, *Fullerenes: The Hydrogenated Fullerenes*, (Dordrecht: Springer)
- Cataldo, F. & Keheyan, Y. 2003, *Int. J. Astrobiol.* 2, 41
- Cataldo, F., Keheyan, Y., & Heymann, D. 2002, *Int. J. Astrobiol.* 1, 79
- Cataldo, F., Keheyan, Y., & Heymann, D. 2004, *OLEB* 34, 13
- Cataldo, F., Strazzulla, G., & Iglesias-Groth, S. 2009, *MNRAS* 394, 615
- Cataldo, F., Iglesias-Groth, S., & Manchado, A. 2012, *Fullerenes Nanotubes Carbon Nanostructures* 20, 656
- García-Hernández, D. A., Manchado, A., García-Lario, P., Stanghellini, L., Villaver, E., Shaw, R. A., Szczerba, R., & Perea-Calderón, J. V. 2010, *ApJ* 724, L39
- García-Hernández, D. A., Iglesias-Groth, S., Acosta-Pulido, J. A., Manchado, A., García-Lario, P., Stanghellini, L., Villaver, E., Shaw, R. A., & Cataldo, F. 2011a, *ApJ* 737, L30
- García-Hernández, D. A., Kameswara Rao, N., & Lambert, D. L. 2011b, *ApJ* 729, 126
- Iglesias-Groth, S., Cataldo, F., & Manchado, A. 2011, *MNRAS* 413, 213
- Iglesias-Groth, S., Garcia-Hernandez, A., & Cataldo, F., Manchado A. 2012, *MNRAS* 423, 2868
- Papoular, R., Conrad, J., Giuliano, M., Kister, J., & Mille, G. 1989, *A&A* 217, 204
- Sellgren, K., Werner, M. W., Ingalls, J. G., Smith, J. D. T., Carleton, T. M., & Joblin, C. 2010, *ApJ* 722, L54
- Zhang, Y. & Kwok, S. 2011, *ApJ* 730, 126



Guillermo Muñoz Caro addressing the problem of formation of prebiotic organics on interstellar grains.