

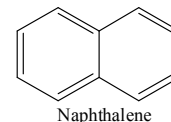
The role of structural isomers and resonance-stabilized radicals in photochemical pathways to fused-ring aromatics in Titan's atmosphere

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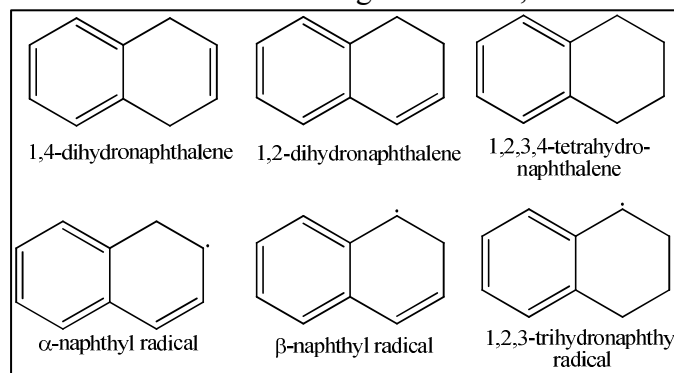
The Cassini mission and Huygens probe are providing compositional data on Titan's hydrocarbon-rich atmosphere of unprecedented detail and accuracy. This has challenged those modeling the altitude-dependent composition of the atmosphere to include in their models an ever-widening array of hydrocarbons, nitriles, free radicals, and ions.¹ Laboratory studies must determine the products formed, provide temperature-dependent reaction rates, and measure the product quantum yields under the conditions relevant to the atmosphere.

Naphthalene is the smallest polyaromatic hydrocarbon (C₁₀H₈), consisting of two fused rings. As such, it is especially important to establish pathways from benzene and its simple derivatives to naphthalene and its derivatives, since similar pathways are likely to operate in forming larger PAH. Current photochemical models lack structural detail in molecules beyond benzene, but recognize the need for extending the models.¹



This contribution will describe laboratory-based studies of possible formation pathways leading to naphthalene and its close structural analogs. We will particularly emphasize recent results from our laboratory that highlight the need for expansion of the current models along three lines. First, we have spectroscopically characterized a series of resonantly-stabilized radicals (RSR) that are likely intermediates along these pathways. RSRs will accumulate in the atmosphere by virtue of their unusual stability. The recombination of two RSRs is likely to be an important means of forming larger closed-shell products. Second, structural isomers of both stable molecules and free radicals are also increasingly pervasive at this large-molecule end of the photochemical model of Titan's atmosphere. Third, photoisomerization is a likely unimolecular process of some importance. We will present laboratory evidence that highlights the need for future models of these atmospheres to include a wider range of RSR's, structural isomers, and photoisomerization pathways.

Mass-selective ultraviolet spectra of jet-cooled 1,2- and 1,4-dihydronaphthalene (two C₁₀H₁₀ structural isomers), 1,2,3,4-tetrahydronaphthalene (C₁₀H₁₂), α -naphthyl and β -naphthyl radicals (C₁₀H₉ RSRs), and 1,2,3-trihydronaphthyl radical (C₁₀H₁₁ RSR) will be presented. The C₁₀H₉ data provide an accurate value for the H-atom affinity of naphthalene; that is, ΔE for the reaction:



C₁₀H₈(naphthalene) + H \rightarrow α -naphthyl or β -naphthyl radicals.

The data also provide accurate ionization potentials for the two isomeric C₁₀H₉ radicals, which produce protonated naphthalene through photoionization. Knowledge of these energetics may be important for connecting ion and neutral pathways, both of which are thought to play an important role in the chemistry of Titan's atmosphere.^{1,2}

¹ V. A. Krasnopolsky, *Icarus* **201** (1), 226 (2009); E. H. Wilson and S. K. Atreya, *Journal of Geophysical Research-Planets* **109** (E6) (2004).

² V. Vuitton, R. V. Yelle, and J. Cui, *Journal of Geophysical Research-Planets* **113** (E5) (2008); J. H. Waite, D. T. Young, T. E. Cravens, A. J. Coates, F. J. Crary, B. Magee, and J. Westlake, *Science* **316** (5826), 870 (2007).