Laboratoire de Chimie Physique, Bâtiment 350,
Université de Paris-Sud
91405 Orsay cedex, France

Chantal Houée-Levin
Professeur
Tel. 33/0 1 69 15 55 49
Fax 33/0 1 69 15 30 53
chantal.houee-levin@lcp.u-psud.fr

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This STSM is a part of long term collaboration between two scientific groups in Orsay (Prof. Ch. Houée-Levin) and Warsaw (Prof. K. Bobrowski) lasting since 1997. Primarily, this collaboration has been supported by the Program of the Scientific and Technological Collaboration between Poland and France POLONIUM. Moreover, both groups were partners in the EC founded Research Training Network "***Sulfur radical chemistry of biological significance: the protective and damaging roles of thiol and thioether radicals***", RTN SULFRAD HPRN-CT-2002-00184, completed in February 2006. Currently, both laboratories participate in the 3-rd Working Group (WG-3) (chaired by Dr. Kevin McGuigan) "***Radiation in Physiological Environments***", within the COST-P9 Action (RADAM).

Last year (January, 2005) Prof. Ch. Houée-Levin visited Warsaw within STSM in order to perform joint ESR experiments on two amino acids: asparagine and aspartic acid. Experimental results were compared with the theoretical ones performed by the French group by DFT methods. A first draft of the article was written. Its final version has been submitted during this STSM to Biophys. Chem. "EPR spectroscopy and theoretical study of γ–irradiated asparagine and aspartic acid in solid state", Authors: Grażyna Strzelczak, Jacqueline Bergès, Chantal Houée-Levin, Dariusz Pogocki and Krzysztof Bobrowski. The COST P9 action was acknowledged.

RESULTS OBTAINED DURING THIS STAY

We began to study by DFT methods the possible free radicals derived from dipeptides containing asparagine. The calculations concerned structures, charge distributions and stabilization energies of radicals formed and coupling constants and spin densities as well. The last two parameters will be compared with the experimental ones that will be obtained by EPR spectroscopy in further experiments performed in Warsaw.

We considered the dipeptides Gly Asn and Asn Gly. The structures of the peptides were optimized by DFT method (B3LYP/6-31G*), taking, as starting point, the experimental structure of the sequence 101-102 of hen egg white lysozyme. The optimized structures are very close to the experimental ones. As an example, the result for Asn Gly is shown on Figure 1.

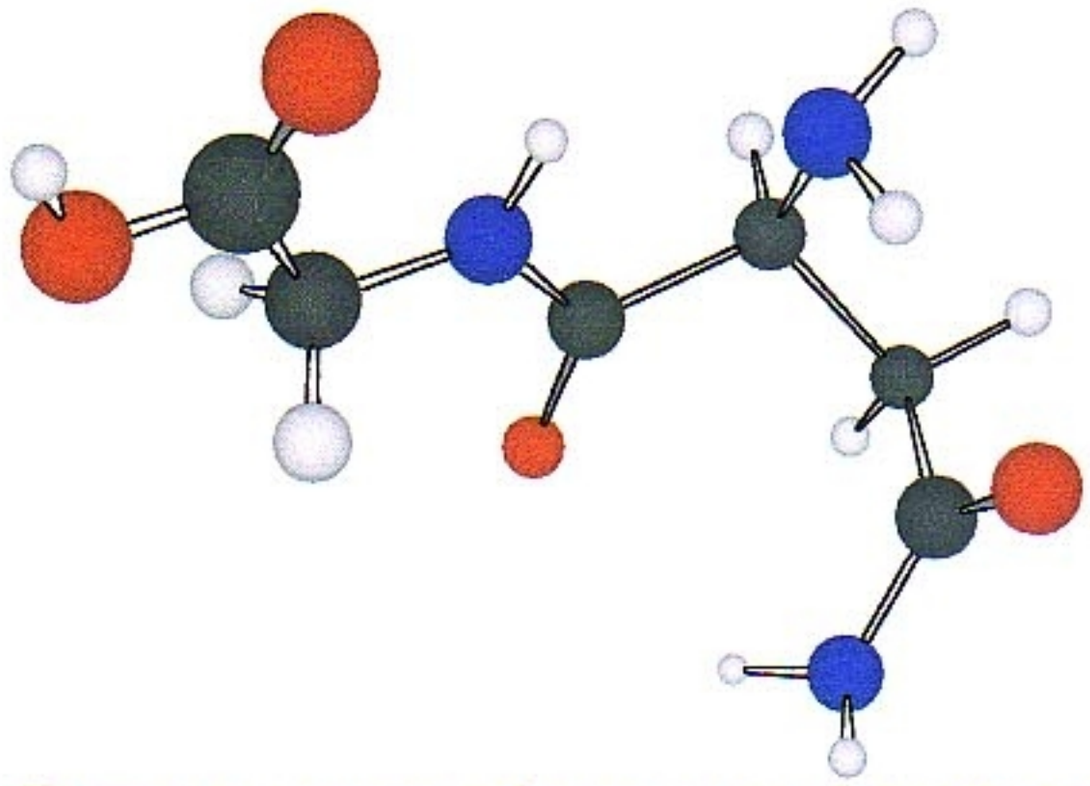

Figure 1: optimized structure of the dipeptide Asn Gly.

The radical anions and cations were then considered. Figure 2 displays the result concerning the radical cation.

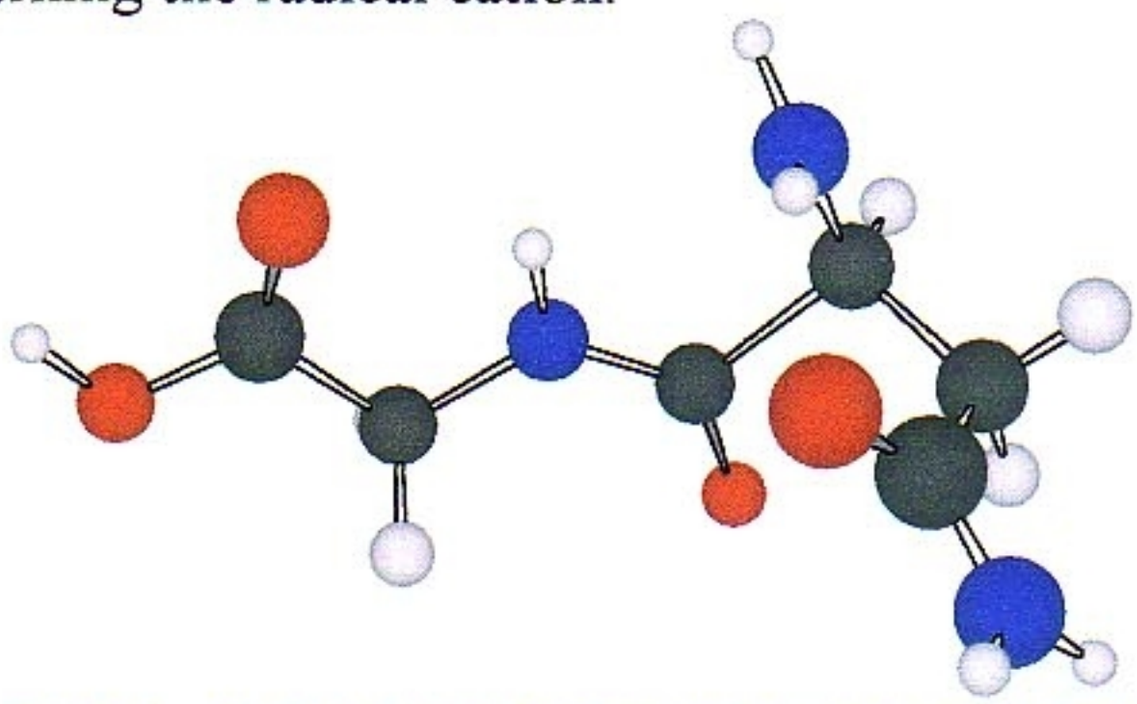

Figure 2: optimized structure of the dipeptide Asn Gly radical cation

In the radical cations from Asn Gly and Gly Asn, the spin density is mostly on the N-terminal. As for the radical anion, it is mostly on the carboxylic acid function.

We intend to continue this work by studying the following five dipeptides (Gly-Asn, Val-Asn, Met-Asn and Asn-Val and Asn-Met). These peptides were selected in order to study the influence of neighboring aminoacids and a sequence of amino acid residues on the character of radicals formed in asparagine residue. Some mechanism of formation and decay of free radicals can be deduced.

In addition, Prof. K. Bobrowski delivered a talk on Friday, May 12th. The title of his presentation was "Stabilization of sulfide radical cation: mechanisms relevant to oxidation of peptides and proteins containing Methionine". The support of the COST action was also acknowledged.