

## Different Conformational Ground States of a *Pseudosaccharin Ether* in the Gaseous Phase and in Solid Krypton

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Benzisothiazoles are often vital structural units of biologically active systems. In particular, their use as herbicides and antibiotic agents has been extensively described [1]. Benzisothiazoles have also been described as phospholipase inhibitors efficient in the treatment of hepatic diseases [2].

In this work, the conformational space of the *pseudosaccharyl ether* 3-(allyloxy)-1,2-benzisothiazole 1,1-dioxide (ABID) has been studied by means of infrared spectroscopy and density functional theory (DFT) calculations. Five different low energy conformers (*TSk*, *TC*, *GSk*, *GSk'* and *GC*, with relative energies of 0.00, 1.97, 2.00, 3.82 and 6.02 kJ mol<sup>-1</sup>, respectively) were found on the DFT(B3LYP)/6-311++G(3df,3pd) potential energy surface of the molecule, all of them differing in the conformation of the allyl substituent. According to calculations, in the gaseous phase all conformers are significantly populated *TSk*:*TC*:*GSk*:*GSk'*:*GC* = 47%:16%:18%:12%:7%, at 350 K). However, in the cryogenic matrices only the *TSk* and *TC* conformers exist due to isomerization from the higher energy *gauche* forms to the most stable *trans* isomers during deposition of the matrix (conformational cooling). The observed conformational cooling is in consonance with the low calculated energy barriers for the *GSk*→*TSk*, *GSk'*→*TSk* and *GC*→*TC* isomerization processes. Results from annealing experiments in a krypton matrix doubtlessly show that in this matrix the order of stability of the *TSk* and *TC* conformers is reversed, with the more planar *TC* form becoming the most stable conformer.

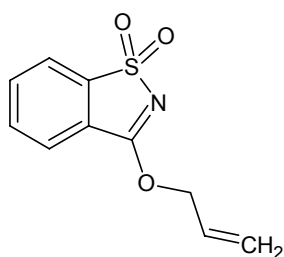


Fig. 1 Structure of ABID.

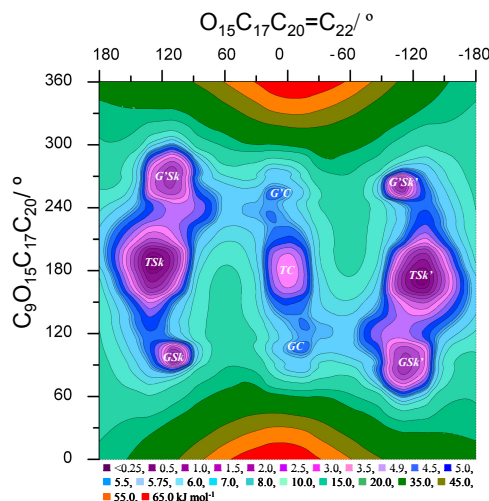


Fig. 2: DFT(B3LYP)/6-311++G(3df,3pd) potential energy (kJ mol<sup>-1</sup>) contour map for ABID as a function of the C<sub>9</sub>O<sub>15</sub>C<sub>17</sub>C<sub>20</sub> and O<sub>15</sub>C<sub>17</sub>C<sub>20</sub>=C<sub>22</sub> dihedral angles.

- [1] M. Otten, W. von Deyn, S. Engel, R. Hill, U. Kardorff, M. Vossen and P. Plath, Patent number WO9719076. Internationale Anmeldung veröffentlicht durch die Weltorganisation für geistiges Eigentum.
- [2] P.I. Eacho, P.S. Foxworthy-Mason, H.S. Lin, J.E. Lopez, M. Mosior and M.E. Richett, (2004) Patent number: WO2004094394. Internationale Anmeldung veröffentlicht durch die Weltorganisation für geistiges Eigentum.