Benzocaine (BZ), butamben (BTN) and isobutamben (BTI) are local anesthetics characterized by a hydrophilic head and a lipophilic aliphatic tail linked by an aminobenzoate group. Previous rotational work on BZ (H$_2$N-C$_6$H$_4$-COO-Et)$^a$ showed that its ethyl aliphatic tail may adopt either in-plane (trans) or out of plane (gauche) conformations, with a low interconversion barrier below 50 cm$^{-1}$. Here we extend the rotational study to BTN and BTI, isolated in a supersonic jet expansion and vaporized either by heating or UV ps-laser ablation methods. Both molecules share a 14 heavy-atoms skeleton, differing in their butyl (-(CH$_2$)$_3$-CH$_3$) or isobutyl (-CH$_2$-CH(CH$_3$)$_2$) four-carbon tail. We detected a single conformer for BTN and two conformers for BTI. The two molecules do not adopt an all-trans carbon skeleton. Conversely, the $\beta$-ethyl carbon in BTN is gauche. For BTI the $\beta$-carbon may be either trans or gauche. The microwave spectrum covered the cm- (BTN, BTI, 6-18 GHz) and mm-wave (BTW, 50-75 GHz) frequency ranges. In all the cases, rotational and centrifugal distortion constants as well as the diagonal elements of the $^{14}$N nuclear quadrupole coupling tensor were accurately determined and compared to the theoretical results (ab initio and DFT). No transitions belonging to configurations predicted as higher minima of the PES were found, pointing out that conformational interconversions may take place in the jet.
