

Photooxidation of dithiaethyneporphyrin.

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Streszczenie

The oxidative degradation of the contracted carbaporphyrinoid 3,8,13,18-tetraphenyldithiaethyneporphyrin, which contains an acetylene moiety embedded in the macrocyclic framework, was investigated. The light-induced, regioselective cleavage of the macrocyclic ring was observed during exposure to dioxygen affording four open-chain diastereomers terminated by carbonyl groups. Studies on the regioselectivity of the process showed that the thiophene was cleft together with the 8-aryl substituent, which proved the primary attack of dioxygen at the C8–C9 bond. Diastereomers {4Z,10E}, {4Z,10Z}, {4E,10E}, and {4E,10Z} [the arrangement with respect to C4–C5 and C10···C13 conjugated bonds given] differ by the orientation of the terminal pyrrolone unit with respect to the 5-phenyl substituent and by the geometry around the cumulene fragment. Thermal {4Z,10E}–{4Z,10Z} and {4E,10E}–{4E,10Z} isomerization was detected and was confirmed by exchange cross-peaks in the ROESY map. The molecular structures of the {4Z,10E} and {4E,10E} stereoisomers were established by X-ray analysis. Density functional theory (DFT) was applied to model the molecular and electronic structure of {4Z,10E}, {4Z,10Z}, {4E,10E}, and {4E,10Z}. The very small energy difference observed between suitable diastereomers accounts for their coexistence in solution (0.48 kcal/mol for {4Z,10E}, {4Z,10Z}; 0.63 kcal/mol for {4E,10E}, {4E,10Z}).

Słowa kluczowe

porphyrinoids, photooxidation, Degradation, isomerization, cleavage reactions

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