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 {4*Z*,10*E*}, {4*Z*,10*Z*}, {4*E*,10*E*}, and {4*E*,10*Z*} [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 {4*Z*,10*E*}–{4*Z*,10*Z*} and {4*E*,10*E*}–{4*E*,10*Z*} isomerization was detected and was confirmed by exchange cross-peaks in the ROESY map. The molecular structures of the {4*Z*,10*E*} and {4*E*,10*E*} stereoisomers were established by X-ray analysis. Density functional theory (DFT) was applied to model the molecular and electronic structure of {4*Z*,10*E*}, {4*Z*,10*Z*}, {4*E*,10*E*}, and {4*E*,10*Z*}. The very small energy difference observed between suitable diastereomers accounts for their coexistence in solution (0.48 kcal/mol for {4*Z*,10*E*}, {4*Z*,10*Z*}; 0.63 kcal/mol for {4*E*,10*E*}, {4*E*,10*Z*}).

Słowa kluczowe

phorphyrinoids, photooxidation, Degradation, isomerization, cleavage reactions

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