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The Effect of Linker Length on the Photomodification of Tyr Residue in N-(Tyrosyl)-N'-(5-azido-2-nitrobenzoyl)diaminoalkanes

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Abstract—*N*-(Tyrosyl)-*N*'-(5-azido-2-nitrobenzoyl)-1,4-diaminobutane containing a Tyr residue connected with the photoreactive aryl azide group through a diaminobutylene linker was synthesized as a model for studying the photomodification of Tyr residues in proteins. This compound and the compound with a shorter, 1,2-diaminoethylene linker, obtained previously, were subjected to a computer modeling to find their minimal energy conformations. The aromatic rings of Tyr and 5-azido-2-nitrobenzoic acid residues in the latter compound were localized in parallel planes at a distance of approximately 0.3 nm between them and were shown to be implicated in stacking interaction. On the contrary, the planes of aromatic rings of the former compound with a longer diaminobutylene linker were found to be situated perpendicularly to each other, with the distance between the centers of the rings being approximately 0.6 nm. The computer analysis was confirmed by experimental results: when studying the photomodification of the compound with the diaminobutylene linker, neither stable products of the Tyr photomodification nor unstable products capable of transformation into stable products in the dark were found. On the contrary, such products were previously identified in the case of the compound with diaminoethylene linker. The formation of amino, nitro, azoxy and azo derivatives was common for the photomodification of both compounds.

Key words: amino acid photoderivatives; tyrosine, 5-azido-2-nitrobenzoyl derivatives, photoderivatives