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Benzimidazole: One molecule - two photoreactions

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Monomers of benzimidazole trapped in an argon matrix at 15 K were characterized by vibrational spectroscopy and identified as 1H-tautomers exclusively. The photochemistry of matrix-isolated 1H-benzimidazole was induced by excitations with a frequency-tunable narrowband UV light and followed spectroscopically. Hitherto unobserved photoproducts were identified as 4H- and 6H-tautomers.[1] Simultaneously, a family of photoproducts bearing the isocyano moiety was identified.[1] Thereby, the photochemistry of benzimidazole was hypothesized to follow two reaction pathways: the fixed-ring and the ring-opening isomerizations.

The former reaction channel is initiated by cleavage of the NH bond and formation of a benzimidazolyl radical and an H atom. The latter reaction channel involves cleavage of the five-membered ring and concomitant shift of the H-atom from the CH bond of the imidazole moiety to the neighboring NH group, leading to 2-isocyanoaniline (ICA) and subsequently to isocyanoanilinyl radical (and an H-atom). Recombination of the radical pairs yields a variety of photoproducts. The mechanistic analysis of the observed photochemistry will be presented, demonstrating that the photochemistry of benzimidazole occupies an intermediate position between the earlier studied prototype cases of indole [2] and benzoxazole,[3] which exhibit exclusively the fixed-ring and the ring-opening photochemistries, respectively.

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