

X-RAY ANALYSIS OF VARIOUS REACTION PATHWAYS THROUGH NITRENES

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It has been extensively studied in a variety of fields, such as synthetic and quantum chemistries, material sciences, industrial application, that the triplet nitrenes are produced when the phenyl azides are exposed to UV light. However, the structures have not been reported yet, because they are very unstable and active. Since the structures of unstable carbenes and radicals have been observed, we intended to analyse the structures of nitrenes. The first example is the nitrene produced from m-carboxylic phenyl azide, **1**. The bond distance of C-N(nitrene) distance is 1.34(4) Å.[1] The second example is transformation from nitrene to a hetero-ring. The crystal of 2-nitrophenylazide was exposed to a Hg lamp at 80 K. The analysed structure showed the formation of the five-membered ring and a nitrogen molecule. This suggested that the produced nitrene attacked to the neighbouring oxygen of the nitro group to form the five-membered ring and became benzofuroxan, **2**. [2]

In this work, the crystal of 4-carboxyphenylazide, **3**, was exposed to the Hg lamp and the intensity data were collected at 80 K using the SMART-CCD diffractometer. The analysed structure revealed that approximately 10 % of **3** turned to the dimer structure, **4**, and nitrogen molecules. In the original crystal lattice, the interatomic distance between the neighbouring nitrogen atoms, which are changed to the nitrene, is 4.067(1) Å. Moreover, the produced dimer structure occupies nearly the same position as that of the monomer molecule before photoirradiation. Although the dimer formation is most popular pathway when the unstable nitrene is produced in a solution, the dimerization was believed to be difficult in the solid state because of the large molecular motion.

The crystal of 2-carboxyphenylazide, **5**, was also exposed to the Hg lamp and the structure was analyzed by X-rays in the way similar to that of **3**. The analyzed structure clearly indicated that approximately 10% of **5** were transformed to the five-membered ring, **6**, and a nitrogen molecule.

These examples suggest that the in situ crystal structure analysis at low temperatures make it possible to follow the various reaction pathways.

References

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