Structure Analysis of Photo-induced Triplet Phenylnitrene Using Synchrotron Radiation

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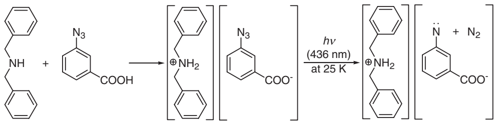
The crystal structures of $[(PhCH_2)_2NH_2]^+[m\text{-}C_6H_4(N_3)(COO)]^-$ before and after UV-irradiation were analyzed at 25 K by using an X-ray vacuum camera set up at the synchrotron laboratory (SPring-8). The C–N (nitrene) bond distance in the triplet state of the photo-induced *m*-carboxyphenylnitrene is determined to be 1.34(4) Å.

Photochemical reactions of phenyl azide derivatives have been intensively studied in a variety of fields such as synthetic and quantum chemistries, material sciences, industrial application, and so on.[1] Because the triplet nitrenes were produced when the phenyl azide derivatives were exposed to UV-light, a number of photo-induced nitrenes have been studied with spectroscopic methods. Therefore, we tried to analyze the structures of the photo-induced nitrenes from phenyl azides by X-ray crystallography, since we recently succeeded in analyzing the structures of reactive intermediates such as radicals and carbenes by X-ray technique at low temperatures as well as spectroscopy and theoretical calculation.[2] However, all the crystals of phenyl azides except azidebiphenyl were unreactive at 80 K or were easily broken when they were irradiated with a high-pressure mercury lamp. Although the nitrene and dinitrogen molecules were clearly observed in the difference Fourier map of the photo-irradiated azidebiphenyl crystal, the precise structures were not obtained because the structures of the produced nitrene and the original azidebiphenyl were closely overlapped each other. To obtain the precise structure, it is necessary to increase the concentration of the produced nitrene with retention of the single crystal form.



(**1**) (**2**) triplt nitrene

For the photoisomerization of cobaloxime complexes, host–guest complexes were produced to expand the void space around the reactive group, so-called reaction cavity.[3] The photoisomerization proceeded very quickly with retention of the single crystal form because the reaction cavity of the host–guest complex was expanded enough to accommodate the product.[4,5] This brought about an idea that the produced nitrene and dinitrogen molecules may be accommodated if the phenyl azide would make a salt with dibenzylamine. After many trials it was found that *m*-carboxylic phenyl azide (**1**) made a salt with dibenylamine in a ratio of 1:1. The crystal turned from colorless to pale yellow at low temperatures on exposure to the UV-light with retention of the crystallinity, although the crystal of *m*-carboxylic phenyl azide itself was easily broken upon irradiation.

Recently a new X-ray vacuum camera was designed and set up at SPring-8 to use synchrotron radiation as X-ray source. The structural change of the photo-induced radical was analyzed successfully at 23 K with the camera.[6] Furthermore, the structure of the excited state of a Pt complex has just observed at 25 K.[7] Here we report an unprecedented crystal structure of the photo-induced triplet phenylnitrene from the host–guest complex of $[(PhCH_2)_2NH_2]^+[m\text{-}C_6H_4(N_3)(COO)]^-$ (**2**) using the X-ray vacuum camera at SPring-8.

To a diethyl ether solution of **1**, an excess of dibenzylamine was added and stirred. The solution kept at room temperature overnight in the dark gave colorless plate crystals of **2** in high yields. X-ray diffraction measurement of **2** was performed at 80 K in our laboratory. There is one crystallographically independent host–guest complex in the $P2_12_12_1$ cell. The hydrogen atom of the carboxyl group of **1** is transferred to the imino group of dibenzylamine to become an ammonium-carboxylate pair.

Because the azide group occupies the peripheral part of the hydrogen bonding chain, the reaction cavity volume for N2 and N3 of the azide group of **2** at 80 K becomes 2.2 Å^3, which is considerably larger than that of **1** (1.6 Å^3) at 80 K. The shape of the cavity is suitable for trapping the produced dinitrogen molecule as well. The density of **2** (1.245 Mg/m^3 at 80 K) becomes considerably smaller than that of **1** (1.528 Mg/m^3 at 80 K), indicating that the molecules of **2** are more loosely packed than those of **1**. Such a change made it possible to increase the amount of the produced nitrene with retention of the crystal form at low temperatures and to perform in situ observation of photochemical reaction by X-ray analysis. When photolysis and X-ray analysis of **2** were performed at 80 K, a broad peak corresponding to a dinitrogen molecule rather than two peaks was found, indicating large thermal motions or a severely disordered structure.

The intensity data before irradiation were also collected at 25 K at the BL02B1 station of SPring-8.[8] Then the crystal was irradiated with a high-pressure mercury lamp through a band path filter (TOSHIBA CO39B) at 25 K for 2 h.[9] The intensity data were collected under the same conditions as those before irradiation.[10] In the difference Fourier map, the nitrene and released dinitrogen molecules were clearly observed, although the occupancy factor of the produced ones was only 0.075. Figure 1 shows the disordered molecular structure of the original and photo produced ones. The closest contact between the nitrene and dinitrogen molecules is found between N2R and N1R, 2.91(9) Å, which is significantly smaller than the sum of van der Waals radii (3.1 Å).[11] The bond length of N2R–N3R (0.97(8) Å) is shorter than that obtained in a gas phase (1.09 Å), probably because of the large thermal motion as indi-

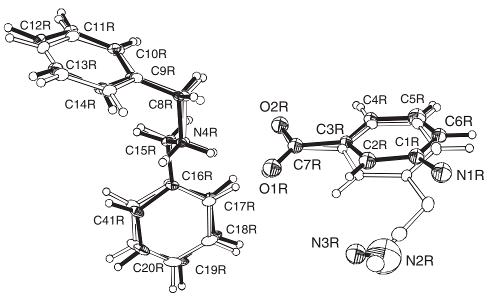


Figure 1. The disordered structure of **2** after irradiation: white bonds, the initial molecule of **2** before irradiation; black bonds, the photo-produced molecules after irradiation. Thermal ellipsoid are drawn at 50%.

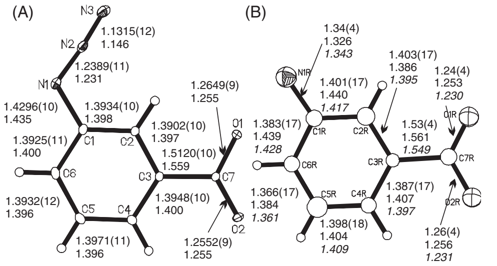


Figure 2. Bond lengths (Å) obtained by X-ray analysis at 25 K (upper) and theoretical calculations. (A) *m*-$C_6H_4(COO)(N_3)$ anion: upper with esd, X-ray; lower, DFT RB3LYP/6-31G*. (B) The triplet nitrene: upper with esd, X-ray analysis; middle, DFT UB3LYP/6-31G*; lower (italic), CASSCF(6,6)/6-31G*. For dinitrogen: N3R–N2R, 0.97(8); N3R–N1R 3.49(4); N2R–N1R, 2.91(9).

cated by the large thermal temperature factor of the nitrogen atoms.

Figure 2 shows the bond lengths of the azide and triplet nitrene obtained by X-ray analysis at 25 K and theoretical calculations.[12] The bond lengths calculated at the DFT B3LYP/6-31G* level of theory for *m*-$C_6H_4(N_3)$ (COO^-) anion show excellent agreement with those obtained by X-ray analysis except for that of C3–C7 (X-ray, 1.512(1) vs calc. 1.559 Å) partly because of no diffuse function included in the basis function. On the other hand, there are several discrepancies between X-ray and UB3LYP/6-31G* results for the triplet nitrene. The salient disagreements are found in the bond lengths around the C1R atom. To take into account the electronic correlation more precisely, we optimized the triplet nitrene structure at the CASSCF(6,6)/6-31G* level of theory.[13] The CASSCF result shows considerably better agreement with that obtained by X-rays. The X-ray result is the first experimental one suggesting that the electronic correlation should be taken into consideration even in the ground state when the optimization of open-shell species such as nitrene is performed.

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References and Notes

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8 X-ray data were collected on an X-ray vacuum camera equipped with an IP area detector.

9 The crystalline-state photoreaction of **2** was monitored by IR spectroscopy in a KBr matrix. Photolysis of **2** at 7 K caused clear spectral changes with isosbestic points, indicating a unique product, nitrene.

10 $C_{21}H_{20}N_4O_2$, $M_r = 360.41$, orthorhombic, space group $P2_12_12_1$, $\lambda = 0.61650$ Å, $T = 25(2)$ K, $a = 8.9550(2)$ Å, $b = 14.3420(3)$ Å, $c = 14.7720(3)$ Å, $V = 1897.21(7)$ Å^3, $Z = 4$, $d_{calcd} = 1.262$ Mg/m^3, crystal dimension $= 0.30 \times 0.12 \times 0.12$ mm^3. No decay was observed during the data collection. Isotropic and anisotropic least-squares refinement (289 parameters/45 restraints) on 8033 independent merged reflections ($R_{int} = 0.117$) converged at $wR_2(F^2) = 0.1699$ for all data; $R_1(F) = 0.0657$ for 6200 observed data ($(I) > 2\sigma(I)$), GOF = 1.084. An initial molecule (occupancy factor = 0.925(3)) was treated as a rigid group allowed rotating and translating where the thermal temperature factors were anisotropically refined. A nitrene (occupancy factor = 0.075(3)) was isotropically refined without any restraint/constraint except for a restraint applied to a CO_2 group. A few restraints were applied to two disordered ammonium cations where the thermal temperature factors were anisotropically refined with constraints forcing the same values for each corresponding atom. Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 215565-215568.

11 We observed such a short contact between a dinitrogen molecule and a triplet diphenylcarbene in a crystal. See the Ref. 2d.

12 The triplet state of the product was confirmed by ESR as expected from Ref. 1c. Ab initio molecular orbital calculations were carried out using the GAUSSIAN 98 program. Optimized geometries were obtained at the (U)B3LYP/6-31G* and CASSCF/6-31G* levels of theory. For a triplet nitrene the active space used in CASSCF calculations comprised of 6 electrons in 6 MOs (two π and three π^* MOs plus a σ one) denoted as CASSCF(6,6).

13 Because the result of the CASSCF calculation depends on the combination of the selected active spaces, several combinations and sizes of them were tested. Despite many attempts, the CASSCF calculations using the active spaces larger than (6,6) have been yet unsuccessful, resulting in non-convergence of SCF calculations. See the following excellent review about calculations on open-shell molecules: T. Bally and W. T. Borden, *Rev. Comput. Chem.*, **13**, 1 (1999).

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