# Crystal Structure of Isoquinoline : Picric Acid Complex

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**The crystal structure of the isoquinoline : picric acid complex ($C_9H_7N \cdot C_6H_3N_3O_7$) was determined by means of X-ray crystal analysis. A proton of the hydroxyl group of picric acid was transferred to the nitrogen atom of the isoquinoline molecule in the complex. Isoquinoline and picric acid molecules are arranged alternately along the *b*-axis, making their molecular planes parallel to each other in the crystal. They overlap each other, and isoquinoline picrate is formed through both ionic interaction and $\pi$-bonding.**

**Keywords** isoquinoline; picric acid; ionic bonding; $\pi$-bonding; isoquinoline picrate; crystal structure; X-ray analysis

Picric acid forms picrates with various organic molecules through $\pi$-bonding or ionic bonding, and such picrates are convenient for identification and qualitative analysis of organic compounds. As part of a series of studies on the picrate of fundamental compounds, we have investigated the crystal structure of phenanthrene : picric acid complex,[1] benzene : picric acid complex,[2] and pyridine picrate.[3] From our studies and data on naphthalene[4] and anthracene picrates,[5] it is clear that stable picrates of fundamental aromatic hydrocarbons are formed through $\pi$-bonding. As for picrates of fundamental heterocyclic compounds, only a pyridine picrate is known, which is formed through ionic bonding. To get more information about the picrates of heterocyclic compounds, we have elucidated the crystal structure of isoquinoline picrate by X-ray crystal analysis.

## Experimental

The picrate used for X-ray analysis was prepared from equimolar isoquinoline and picric acid in methanol. Its melting point is 221—223 °C, which is similar to the reported value (224—225 °C).[6] The diffraction intensities were collected on a Rigaku AFC-5R automated four-circle X-ray diffractometer using graphite-monochromated Cu $K_\alpha$ ($\lambda = 1.54179$ Å) at 23 °C. Crystal data and other information are summarized in Table I. The $\omega$–$2\theta$ scan mode with a scan rate of 16°/min was employed with the $\omega$ scan range $(1.20 + 0.30 \tan\theta)°$. The collected reflection intensities were corrected for Lorentz and polarization factors, but not for absorption. The structure was solved by the direct method using the program MITHRIL.[7] The parameters of non-hydrogen atoms were refined by the full-matrix least-squares method with anisotropic temperature factors. The hydrogen atoms were located from a difference Fourier synthesis, and refined only the temperature factors isotropically. At the final refinement, 1939 reflections with $|F_O| > 3\sigma(|F_O|)$ were used. The final $R(R_w)$ was 0.066(0.065). Atomic scattering factors were taken from International Tables for X-Ray Crystallography (1974).[8] The final positional and thermal parameters of isoquinoline picrate are listed in Table II. No peak larger than 0.42 $e$ Å$^{-3}$ was found in the last difference electron density maps. All calculations were performed using the TEXSAN[9] crystallographic software package of Molecular Structure Corporation.

TABLE I. Crystallographic Details for Isoquinoline Picrate

| | |
|---|---|
| Formula | $C_9H_7N \cdot C_6H_3N_3O_7$ |
| Formula weight | 358.27 |
| Crystal system | Monoclinic |
| Space group | $P2_1/a$ |
| Size (mm) | $0.4 \times 0.4 \times 0.4$ |
| Lattice parameters | |
| $a$ (Å) | 14.924 (2) |
| $b$ (Å) | 7.377 (1) |
| $c$ (Å) | 13.542 (4) |
| $\beta$ (°) | 95.44 (1) |
| $Z$ value | 4 |
| $V$ (Å$^3$) | 1484 (1) |
| $\mu$ (Cu$K_\alpha$)/cm$^{-1}$ | 10.74 |
| $D_x$ (g/cm$^3$) | 1.603 |
| Function minimized | $\Sigma w(\|F_O\| - \|F_C\|)^2$ |
| $w$ | $4F_O^2/\sigma^2(F_O^2)$[a)] |

a) This formula is equivalent to the usual weight ($w = 1/\sigma^2(F_O)$).[2]

## Discussion

A perspective drawing with the atomic-numbering system is given in Fig. 1. As can be seen in Fig. 1, the proton of the hydroxy group of picric acid was transferred to the nitrogen atom in the isoquinoline molecule, forming an N(4)–H···O(1) hydrogen bond with the distance of 1.683 Å. Similar intramolecular hydrogen bonding was

TABLE II. Fractional Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($B_{eq}$/Å$^2$) of Isoquinoline Picrate with Estimated Standard Deviations in Parentheses

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| O1 | 4699 (2) | 2234 (5) | 907 (2) | 6.1 (2) |
| O2 | 6267 (2) | 1800 (6) | 2057 (3) | 8.6 (2) |
| O3 | 6109 (2) | 3043 (5) | 3450 (2) | 6.9 (2) |
| O4 | 3701 (2) | 496 (5) | 5141 (2) | 5.9 (2) |
| O5 | 2551 (2) | −719 (4) | 4298 (2) | 5.2 (1) |
| O6 | 2165 (3) | 144 (7) | 782 (2) | 10.4 (3) |
| O7 | 3161 (3) | 1063 (1) | 17 (3) | 15.6 (4) |
| N1 | 5816 (2) | 2232 (5) | 2711 (3) | 5.0 (2) |
| N2 | 3268 (2) | 98 (5) | 43 (2) | 4.1 (2) |
| N3 | 2898 (3) | 699 (6) | 770 (2) | 5.4 (2) |
| N4 | 5256 (2) | 7270 (5) | 981 (2) | 4.8 (2) |
| C1 | 4371 (3) | 1628 (6) | 1656 (3) | 4.1 (2) |
| C2 | 4862 (2) | 1669 (5) | 2627 (3) | 3.6 (2) |
| C3 | 4510 (2) | 1241 (5) | 3478 (2) | 3.4 (2) |
| C4 | 3638 (2) | 608 (5) | 3440 (2) | 3.2 (2) |
| C5 | 3114 (2) | 418 (5) | 2542 (3) | 3.5 (2) |
| C6 | 3476 (3) | 909 (5) | 1690 (2) | 3.6 (2) |
| C7 | 4457 (3) | 6613 (6) | 1108 (3) | 4.7 (2) |
| C8 | 5581 (3) | 7595 (7) | 1760 (3) | 4.9 (2) |
| C9 | 5692 (3) | 7292 (6) | 2696 (3) | 4.5 (2) |
| C10 | 4841 (2) | 6631 (5) | 2876 (3) | 3.4 (2) |
| C11 | 4601 (3) | 6322 (6) | 3851 (3) | 4.2 (2) |
| C12 | 3765 (3) | 5659 (6) | 3984 (3) | 4.7 (2) |
| C13 | 3139 (3) | 5292 (6) | 3165 (4) | 5.2 (2) |
| C14 | 3345 (3) | 5559 (6) | 2223 (3) | 4.7 (2) |
| C15 | 4201 (2) | 6247 (5) | 2065 (3) | 3.6 (2) |

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}a_ia_j$.

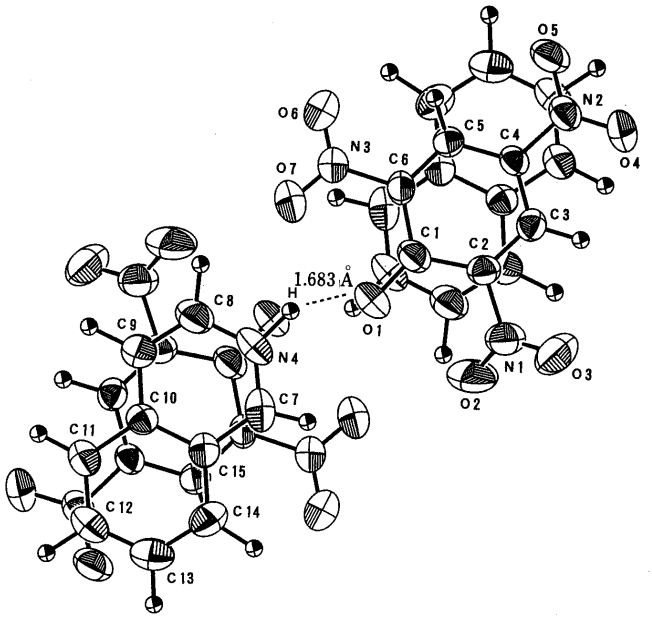


Fig. 1. Perspective Drawing of the Structure of Isoquinoline Picrate with the Atomic-Numbering System Viewed along the *b*-Axis

A broken line shows a hydrogen bond.

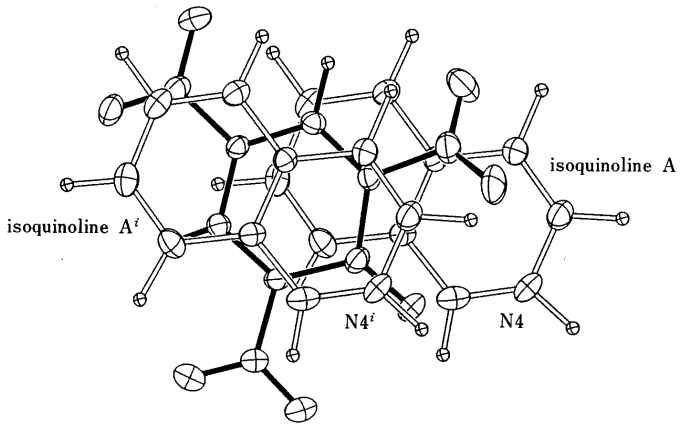


Fig. 2. Overlap of Picric Acid and Isoquinoline Molecules in Sections Parallel to the Phenyl Ring ($i$, $x$, $1+y$, $z$)

observed in pyridinium picrate.[3] The C(1)–O(1) bond length (1.250 Å) of picric acid is rather shorter than the normal value of phenols (1.335 Å),[10,11] but close to that of carbonyls. Thus, isoquinoline picrate is considered to be formed through ionic bonding. Molecules of both picric acid and isoquinoline lie approximately in (010) parallel to each other, stacking alternately, and isoquinoline picrate forms one-dimensional columns along the *b*-axis. The plane of the phenyl ring of picric acid makes angles of 3.17° with the overlapping planes of both the isoquinoline ring A and isoquinoline ring A$^i$ ($i$, $x$, $1+y$, $z$). The average interplanar distances between the phenyl ring of picric acid and the neighboring isoquinoline rings in the complexes are 3.42 (phenyl ring–isoquinoline A) and 3.48 Å (phenyl ring–isoquinoline A$^i$). The overlap diagram of the complex is shown in Fig. 2. The overlapping of the phenyl ring and the neighboring isoquinoline rings was calculated from the overlapping areas between the phenyl ring and the projection of the isoquinoline plane on it, as shown in Fig. 2. The values obtained were 38 (phenyl ring–isoquinoline A) and 86% (phenyl ring–isoquinoline A$^i$). Consequently the $\pi$-electron clouds of the neighboring rings are thought to be interacting by overlapping each other. Thus, isoquinoline picrate is also considered to be formed through $\pi$-bonding. In the crystal of naphthalene picrate[4] structural disorder is observed, but not in either phenanthrene picrate[1] or isoquinoline picrate.

Through our studies on picrates of fundamental aromatic compounds,[1-3] we have clarified that the picrates of benzene, naphthalene, and phenanthrene are formed through $\pi$-bonding, and the picrate of pyridine is formed by ionic bonding.[3] But from this study on isoquinoline picrate, we found that the crystal structure of isoquinoline picrate involves both ionic bonding (including hydrogen bonding), and $\pi$-bonding. To our knowledge, isoquinoline picrate is the first compound which has both ionic and $\pi$-bonding in one molecule.

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