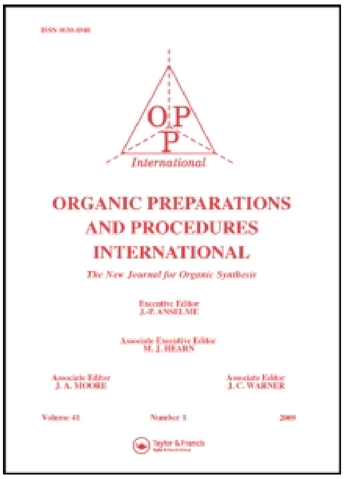

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

X-RAY CRYSTAL STRUCTURE ANALYSES OF ISOMERIC CYCLOADDUCTS OF 3-PICOLINE-N-OXIDE WITH *p*-CHLOROPHENYL ISOCYANATE

Takuzo Hisano[a]; Toshikazu Matsuoka[a]; Masataka Ichikawa[a]; Keiji Muraoka[a]; Tetsuya Komori[b]; Kazunobu Harano[b]; Yoshiteru Ida[b]; Arild T. Christensen[c]
[a] Faculty of Pharmaceutical Sciences, Kumamoto University, Kumamoto, JAPAN [b] Kyushu University Maidashi, Higashi-ku, Fukuoka, JAPAN [c] Syntex Analytical Instruments, Inc., Cupertino, CA, USA

To cite this Article Hisano, Takuzo , Matsuoka, Toshikazu , Ichikawa, Masataka , Muraoka, Keiji , Komori, Tetsuya , Harano, Kazunobu , Ida, Yoshiteru and Christensen, Arild T.(1978) 'X-RAY CRYSTAL STRUCTURE ANALYSES OF ISOMERIC CYCLOADDUCTS OF 3-PICOLINE-N-OXIDE WITH *p*-CHLOROPHENYL ISOCYANATE', Organic Preparations and Procedures International, 10: 6, 300 — 304

To link to this Article: DOI: 10.1080/00304947809355057

URL: http://dx.doi.org/10.1080/00304947809355057

6-Chloro-3,4-dihydroxycinnoline [IId, 1.04 g. (96%)] obtained as a yellow solid, mp. 180-181°, from 1 g (0.0055 mole) of 5-chloroisatin.

Anal. Calcd. for $C_8H_5N_2O_2Cl$: C, 48.87; H, 2.54; N, 14.25; Cl, 18.02.

Found: C, 48.52; H, 2.64; N, 13.98; Cl. 17.84.

IR (KBr, cm^{-1}): 3400-2300, 1675, 1575, 1495, 1480, 1465, 1420, 1370, 1270, 1250, 1235, 1165, 1035, 925, 860, 800, 775. NMR (DMSO-d_6, δ): 7.38-7.95 (m, 3H, 2H aromat. and 1 OH), 8.1-8.2 (m, 1H, aromat.), 12.6-14.6 (broad m, 1H, OH). MS: m/e (%): 196 (100, M^+), 197 (10), 198 (36), 179 (18), 152 (17), 124 (15), 122 (15), 111 (1), 76 (2).

X-RAY CRYSTAL STRUCTURE ANALYSES OF ISOMERIC CYCLOADDUCTS OF 3-PICOLINE-N-OXIDE WITH p-CHLOROPHENYL ISOCYANATE

Submitted by Takuzo Hisano,* Toshikazu Matsuoka, Masataka Ichikawa, and Keiji Muraoka
(6/14/78)

Faculty of Pharmaceutical Sciences
Kumamoto University
5-1 Oe-hon-machi
Kumamoto 862
JAPAN

Tetsuya Komori, Kazunobu Harano and Yoshiteru Ida

Faculty of Pharmaceutical Sciences
Kyushu University
Maidashi, Higashi-ku
Fukuoka 812
JAPAN

Arild T. Christensen

Syntex Analytical Instruments, Inc.
10040 Bubb Road
Cupertino, CA 95014
USA

The X-ray crystal analysis of the two products (I and II) isolated from the reaction of 3-picoline N-oxide with p-chlorophenyl isocyanate confirms[1] the 2,3-dihydropyridine structure of these adducts (Figs. 1 and 2).

Intensities and the cell parameters were measured by a Syntex atuomated diffractometer ($P\bar{1}$) using Mo Kα radiation monochromated with a graphite crystal. The molecular structure of I was solved by the direct methods[2] using the MULTAN[3] series of programs and the UNICS-II system.[4] On the other hand, the structure II was solved by the same direct method using a SYNTEX-XTL program. Compound I, mp. 167°, $C_{13}H_{11}N_2O_2Cl$, gives orthorhombic crystals from ether-acetone; a = 9.010(4), b = 11.113(3), c = 12.150(3) Å, $Dm^5 = 1.414$ g. cm^{-3}, z = 4, space group $P2_12_12_1$. From the E map calculated by the set of phases which gave the figure of merit 1.008, 15 nonhydrogen atoms out of 18 independent ones were located. Subsequent Fourier synthesis and the refinement by the block-diagonal least-squares method revealed the molecular structure. After an anisotropic refinement of nonhydrogen atoms (R = 0.085), a difference Fourier map was calculated from which all the hydrogen atoms were located and were included in the final refinement assuming isotropic temperature factors. The final R value was 0.054 using 2069 independent reflections. Compound II, mp. 129-130°, $C_{13}H_{11}N_2O_2Cl$, monoclinic crystal class from ether-petr. ether; a = 12.664(3), b = 9.797(5), c = 9.751(4) Å, α = 90.00(4), β = 92.58(2), γ = 90.00(3)°, $Dm^5 = 1.463$ g. cm^{-3}, z = 4, space group $P2_1/A$. 2725 observed reflection ($Io \geqq 1.966\ Io$) were used for structure determination. From the E map calculated by the set of phases (figure of merit 1.0890), 18 nonhydrogen atoms were easily located. The refinement of the molecular structures was carried out by the Gauss-Seidel Block- and full matrix least squares-method and the R value reduced to 0.066 with anisotropic temperature factor. Calculated hydrogen atom coordinates were included in the final refinements and the final R value was 0.048.

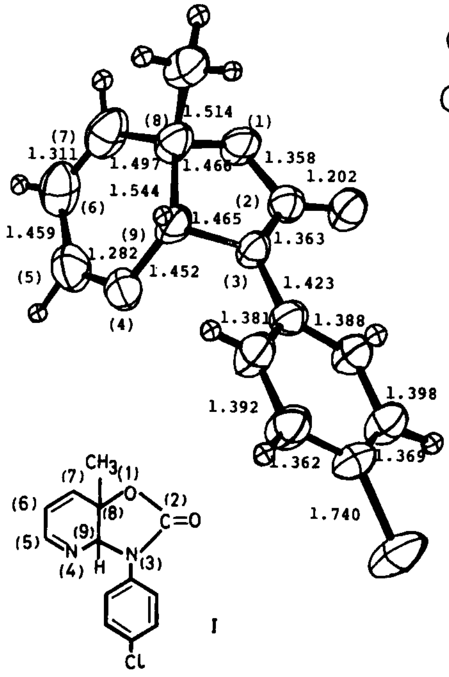

Fig. 1 (Å)

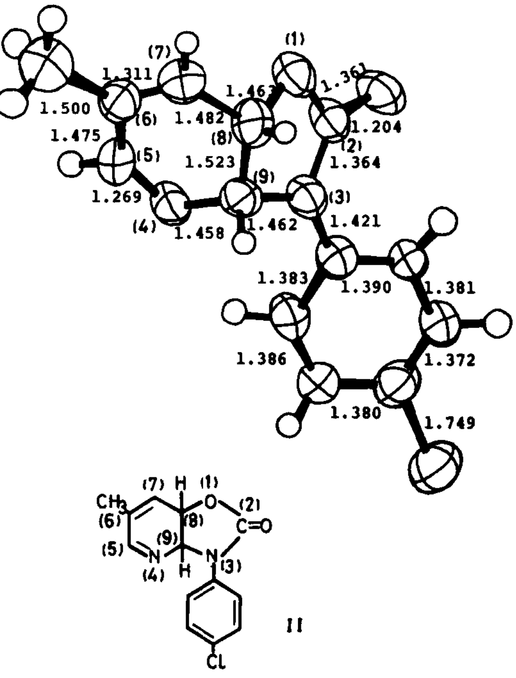

Fig. 2 (Å)

Table I: Bond angles (°) in I and II

	I (°)	II (°)
C(7)-C(8)-O(1)	108.02	110.21
C(7)-C(8)-C(9)	113.26	115.07
O(1)-C(8)-C(9)	104.00	103.88
N(4)-C(9)-C(8)	119.74	116.95
N(4)-C(9)-N(3)	109.46	110.10
C(8)-C(9)-N(3)	100.84	100.69

EXPERIMENTAL

All melting points were uncorrected. IR spectra were recorded on Nippon Bunko DS-301 infrared spectrophotometer equipped with grating. ^{1}H-NMR spectra were taken with JNM-MH-100 and JNM-C-60H spectrometer in ca. 5% (w/v) solution with tetramethylsilane as an internal standard and chemical shifts were expressed in τ value. MS spectra were taken with JEOL-JMS-01SG spectrometer.

Reaction of 3-Picoline-N-oxide with p-Chlorophenyl Isocyanate.- To a solution of 2.73 g. (0.025 mole) of 3-picoline-N-oxide in 20 ml. of DMF, 7.68 g.

(0.050 mole) of p-chlorophenyl isocyanate was added dropwise with stirring at room temperature and the mixture heated at 110° for 7 hrs.

a) Isolation of I.- After the reaction was over, the reaction mixture was evaporated in vacuo below 70° and the residue dissolved in 20 ml. of ether. The ethereal solution was kept overnight below 5° and the precipitated colorless crystals were collected and washed with a small amount of cold ether. The crystalline mass was recrystallized from benzene to give an analytical sample of I, mp. 167° as colorless needles, in 29.6% yield. IR(KBr): C = 0 1725 cm^{-1}. NMR($CDCl_3$, 60 Mc): τ 8.37 (3H, s, $-CH_3$), 4.59 (1H, d, J = 2.5 Hz, C_9-H), 3.85-4.25 (2H, m, C_6-H and C_7-H), 2.20-3.00 (5H, m, aromatic and C_5-H). MS m/e: 262 and 264 (M^+; relative intensity, 3:1), 218 and 220 ($M^+ - CO_2$).

Anal. Calcd. for $C_{13}H_{11}N_2O_2Cl$: C, 59.44; H, 4.22; N, 10.66.

Found: C, 59.70; H, 4.20; N, 10.58.

b) Isolation of II.- After removal of I, the filtrate was evaporated in vacuo. After the tarry residue had been treated with hot n-hexane, the residue was dissolved in 10 ml. of ether and then kept overnight below 5°. The separated crystals were collected and recrystallized from n-hexane-benzene to give II, mp. 129-120° as colorless prisms, in 11.1% yield. IR(KBr): C = 0 1730 cm^{-1}. NMR($CDCl_3$, 60 Mc): τ 8.08 (3H, br. s, $-CH_3$), 5.12 (1H, d-d, J_{8-9} = 9 Hz, J_{8-7} = 6 Hz, C_8-H), 4.36 (1H, d-d, J_{9-8} = 9 Hz, J_{9-7} = 2.5 Hz, C_9-H), 3.95-4.20 (1H, m, C_7-H), 2.30-3.00 (5H, m, aromatic and C_5-H). MS m/e: 262 and 264 (M^+; relative intensity, 3:1), 218 and 220 ($M^+ - CO_2$).

Anal. Calcd. for $C_{13}H_{11}N_2O_2Cl$: C, 59.44; H, 4.22; N, 10.66.

Found: C, 59.65; H, 4.15; N, 10.68.

ACKNOWLEDGEMENT.- The authors wish to acknowledge the members of the Analytical Department of this Faculty for the microanalyses and spectral measurements, and also are grateful to Prof. T. Kawasaka and Prof. M. Hamana of Kyushu University for their encouragement throughout this work and helpful suggestions.

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2. All the calculations were performed on the FACOM M-190 computer in the computer center of Kyushu University

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4. The universal Crystallographic Computation Program System UNICS II (Sakurai, Iwasaki, Watanabe, Kobayashi, Bando and Nakamichi, 1974).

5. The densities of I and II are measured by the floating method used a mixture of n-hexane and CCl_4.

SELECTIVE REACTIVITY OF THE BISENAMINE OF PIPERAZINE-CYCLOHEXANONE WITH BENZOYL CHLORIDE

Submitted by Robert E. Lyle*
(9/19/78)

Department of Chemistry
North Texas State University
Denton, Texas 76203

Brian P. Coppola and Jose E. Saavedra†

Department of Chemistry
University of New Hampshire
Durham, New Hampshire 03824

Gloria G. Lyle

Basic Health Sciences
Texas College of Osteopathic Medicine
Denton, Texas 76203

The selective benzoylation of bis-enamine I affords a novel path to N-benzoylpiperazine.[1,2]