Crystal Structure of 6-Chloro-2-ethoxy-13-methoxy-12-methyl-11-phenyl-9,11,13,15-tetraazatetracyclo[7.6.0.0^{1,12}.0^{3,8}]pentadeca-3,5,7-triene-10,14-dione

Kazuyoshi SEGUCHI,[†] Satoko TANAKA, and Ai KOBAYASHI

School of Human Environmental Sciences, Mukogawa Women's University, Nishinomiya 663-8558, Japan

The title compound was synthesized and its structure characterized by X-ray diffraction. This compound crystallizes in monoclinic space group $P2_1/n$ with cell parameters $a = 7.3400(4)\text{\AA}$, $b = 11.4484(5)\text{\AA}$, $c = 23.342(1)\text{\AA}$, $\beta = 91.5490(8)^\circ$, and $Z = 4$; the final residual factor is $R = 0.048$ for 4152 reflections.

(Received July 5, 2004; Accepted August 10, 2004; Published on web October 25, 2004)

Naturally occurring polyquinanes with fused five-membered carbocyclic frameworks have attracted attention due to their specific structures and biological activities.¹ During the course of our continuous investigation on the stereoselective syntheses of hetero angular polyquinane analogues from active urazole (1),^{2,3} we isolated an intricate cyclic urea including an indoline skeleton (title compound, 2) as a racemate by an alkali-treatment of photoproduct (3) of 1 with ethanol. Since the ¹H and ¹³C-NMR analyses did not permit identification of the framework and the stereochemistry of 2, the crystal structure was determined by X-ray analysis.

The synthetic procedure of 2 was as follows. A powder of sodium hydroxide (150 mg) was added to an ethanolic solution (20 ml) of 3 (100 mg) and heated at reflux for 5 h. After removing the solvent on a rotary evaporator, the resulting solid was chromatographed on silica gel with dichloromethane as an eluent. The isolated white solid recrystallized from ethanol to afford crystals appropriate for X-ray analysis.

X-ray data collection was performed on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite-

monochromated Mo K_α radiation ($\lambda = 0.71069\text{\AA}$) at 123 K. The crystal data and the experimental details are given in Table 1. The crystal structure was solved by a direct method with SIR97.⁴ The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located by a geometrical calculation, and were not refined. The refined atomic parameters and equivalent isotropic temperature factors for the non-hydrogen atoms are given in Table 2. The selected bond lengths and bond angles are given in Table 3. An ORTEP drawing of compound 2 is illustrated in Fig. 2.

The structure of 2 consists of one indoline and two imidazolidinone rings, and these rings are fused at the axis of C1-N4 and of C1-C3. Three C-N bond lengths (N1-C2; 1.364(3) $\text{\AA}$, N4-C; 1.383(3) $\text{\AA}$, and N3-C2; 1.386(3) $\text{\AA}$), and two C=O bond lengths (O1-C2; 1.210(3) $\text{\AA}$ and O3 - C4; 1.213(3) $\text{\AA}$) of the cyclic urea moiety are consistent with those of values reported by Dekaprilevich *et al.*,⁵ but the other C-N bond length (N2-C2; 1.416(3) $\text{\AA}$) is longer. However, these bond lengths are very consistent with the values of a related compound that we previously analyzed.⁶ The stereochemistry between the ethoxyl group in the indoline ring and the cyclic urea having the *N*-methoxyl group is *cis*-configuration. The torsion angle of O4-C11-C1-N1 is 29.1 $^\circ$.

Fig. 1 Reaction scheme.

Fig. 2 ORTEP drawing of the title compound along with the atomic labeling scheme.

[†] To whom correspondence should be addressed.
E-mail: seguchi@mwu.mukogawa-u.ac.jp

Table 1 Crystal and experimental data

Formula: C ₂₁ H ₂₁ ClN ₄ O ₄
Formula weight = 428.87
Crystal size(mm): 0.25 × 0.20 × 0.07
Crystal system: monoclinic
Space group: P2 ₁ /n Z = 4
a = 7.3400(4) Å
b = 11.4484(5) Å β = 91.5490(8)°
c = 23.342(1) Å
V = 1960.8(2) Å ³
D _x = 1.453 g/cm ³
μ(Mo Kα) = 2.33 cm ⁻¹
T = 123 K
F(000) = 896.00
Radiation: graphite monochromated Mo Kα λ = 0.71069 Å
R, R _w = 0.048, 0.049
No. of reflections used = 4152 [I > 2.00σ(I)]
2θ _{max} = 54.8°
(Δσ) _{max} = 0.000
(Δρ) _{max} = 0.69 eÅ ⁻³ (around Cl(1))
(Δρ) _{min} = -0.66 eÅ ⁻³
Measurement: Rigaku/ RAXIS-RAPID Imaging Plate
Program system: teXsan
Structure determination: direct method (SIR97)
Refinement: full-matrix least-squares

Table 2 Atomic coordinates and equivalent isotropic parameters(Å²)

Atom	x	y	z	B _{eq}
Cl(1)	0.43564(9)	-0.12207(7)	0.44936(3)	2.28(2)
O(1)	1.0623(2)	0.0838(2)	0.13874(8)	2.35(5)
O(2)	0.8137(2)	0.0026(2)	0.06042(7)	1.75(4)
O(3)	0.4872(2)	-0.2428(2)	0.22521(7)	1.30(4)
O(4)	0.5701(2)	0.2507(2)	0.21908(7)	1.51(4)
N(1)	0.8210(2)	0.0891(2)	0.20029(8)	1.27(5)
N(2)	0.7897(3)	-0.0161(2)	0.11996(8)	1.25(5)
N(3)	0.5140(3)	-0.1113(2)	0.15015(8)	1.12(5)
N(4)	0.6146(3)	-0.0588(2)	0.23711(8)	1.05(5)
C(1)	0.6369(3)	0.0476(2)	0.20138(10)	1.29(6)
C(2)	0.9092(4)	0.0577(2)	0.1520(1)	1.50(6)
C(3)	0.6003(3)	0.0012(2)	0.14003(10)	1.16(6)
C(4)	0.5352(3)	-0.1494(2)	0.2063(1)	1.19(6)
Cl(1)	0.43564(9)	-0.12207(7)	0.44936(3)	2.28(2)
C(5)	0.5500(3)	-0.0230(2)	0.2921(1)	1.25(6)
C(6)	0.5349(3)	-0.0925(2)	0.3397(1)	1.50(6)
C(7)	0.4670(3)	-0.0370(2)	0.38799(10)	1.46(6)
C(8)	0.4206(3)	0.0797(2)	0.3884(1)	1.53(6)
C(9)	0.4331(3)	0.1461(2)	0.3388(1)	1.53(6)
C(10)	0.4980(3)	0.0932(2)	0.2905(1)	1.19(6)
C(11)	0.5059(3)	0.1365(3)	0.2283(1)	1.45(6)
C(12)	0.4912(3)	0.0844(2)	0.1017(1)	1.55(6)
C(13)	0.8573(3)	-0.1061(2)	0.0324(1)	1.87(6)
C(14)	0.4854(3)	-0.1947(2)	0.1046(1)	1.17(6)
C(15)	0.5913(3)	-0.2931(2)	0.1016(1)	1.15(6)
C(16)	0.5754(4)	-0.3665(2)	0.0543(1)	2.42(7)
C(17)	0.4540(4)	-0.3373(3)	0.0098(1)	2.62(8)
C(18)	0.3437(4)	-0.2414(3)	0.0137(1)	2.24(7)
C(19)	0.3583(3)	-0.1693(2)	0.0613(1)	1.59(6)
C(20)	0.4338(4)	0.3395(2)	0.2249(1)	2.61(8)
C(21)	0.4644(4)	0.4331(2)	0.1802(1)	2.49(7)

$$B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha).$$

Table 3 Selected bond lengths(Å) and bond angles(°)

Bond length			
O(1) - C(2)	1.210(3)	O(2) - N(2)	1.422(2)
O(2) - C(13)	1.446(3)	O(3) - C(4)	1.213(3)
O(4) - C(20)	1.435(3)	N(1) - C(1)	1.433(3)
N(1) - C(2)	1.364(3)	N(2) - C(2)	1.416(3)
N(2) - C(3)	1.492(3)	N(3) - C(3)	1.457(3)
N(3) - C(4)	1.386(3)	N(4) - C(1)	1.488(3)
N(4) - C(4)	1.383(3)	N(4) - C(5)	1.440(3)
C(1) - C(3)	1.544(3)	C(1) - C(11)	1.545(3)
C(3) - C(12)	1.520(3)	C(10) - C(11)	1.537(3)
Bond angle			
N(2)-O(2)-C(13)	110.4(2)	C(11)-O(4)-C(20)	113.9(2)
C(1)-N(1)-C(2)	113.3(2)	O(2)-N(2)-C(2)	109.6(2)
C(2)-N(2)-C(3)	115.3(2)	C(2)-N(2)-C(3)	108.9(2)
C(3)-N(3)-C(4)	113.2(2)	C(3)-N(3)-C(14)	121.4(2)
C(4)-N(3)-C(14)	120.0(2)	C(1)-N(4)-C(4)	111.9(2)
C(1)-N(4)-C(5)	108.1(2)	C(4)-N(4)-C(5)	122.2(2)
N(1)-C(1)-N(4)	113.5(2)	N(1)-C(1)-C(3)	103.8(2)
N(1)-C(1)-C(11)	112.7(2)	N(4)-C(1)-C(3)	102.6(2)
N(4)-C(1)-C(11)	103.4(2)	C(3)-C(1)-C(11)	120.6(2)
O(1)-C(2)-N(1)	127.6(2)	O(1)-C(2)-N(2)	125.4(2)
N(1)-C(2)-N(2)	107.0(2)	N(2)-C(3)-N(3)	110.3(2)
N(2)-C(3)-C(1)	101.3(2)	N(2)-C(3)-C(12)	112.3(2)
N(3)-C(3)-C(1)	102.7(2)	N(3)-C(3)-C(12)	115.1(2)
C(1)-C(3)-C(12)	113.9(2)	O(3)-C(4)-N(3)	126.6(2)
O(3)-C(4)-N(4)	126.5(2)	N(3)-C(4)-N(4)	106.9(2)
N(4)-C(5)-C(6)	126.3(2)	O(4)-C(11)-C(1)	109.5(2)
O(4)-C(11)-C(10)	117.7(2)	C(1)-C(11)-C(10)	102.2(2)

References

1. G. Mehta and A. Srikrishna, *Chem. Rev.*, **1997**, 97, 671.
2. S. Tanaka, K. Seguchi, and A. Sera, *J. Chem. Soc. Perkin Trans. 1*, **1995**, 519.
3. S. Tanaka, K. Seguchi, K. Itoh, and A. Sera, *Bull. Chem. Soc. Jpn.*, **1996**, 69, 3533.
4. A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, and R. Spagna, *J. Appl. Cryst.*, **1999**, 32, 115.
5. M. O. Dekaprilevich, L.I. Suvorova, L. I. Khmel'nitskii, and Y. T. Struchkov, *Acta Cryst.*, **1994**, C50, 2056.
6. S. Tanaka, K. Kato, H. Kimoto, and K. Seguchi, *Anal. Sci.*, **1999**, 15, 817