1,3-Diazatricyclo[5.3.1.0^{5,11}]undecane-2,4-dione의 합성과 결정구조

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Synthesis and Crystal Structure of 1,3-Diazatricyclo[5.3.1.0^{5,11}]undecane-2,4-dione

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요 약

분자내 [2+2] 광고리화 반응을 통하여 pyridine의 새로운 N^1-pentenyl 유도체가 얻어졌다. 이 물질의 구조는 단결정 X-선 회절법에 의해 해석되었다. 이 화합물은 rhombohedral계(R$\bar{3}$, a=27.767(5)Å, c=6.390(2)Å)로 결정화된다. 이 구조에서는 2개의 6각 고리와 1개의 4각 고리가 N-C 또는 C-C bonds를 공유하면서 fuse되어 있고, pyridine 고리는 의자모양의 형태를 취하고 있다. 점대칭으로 연관된 한 쌍의 분자들이 uracil 부분의 N, O 원자 사이의 H를 통하여 수소결합을 생성하고 있는 것이 관찰되었다.

Abstract

A new N^1-pentenyl derivative of pyrimidines has been synthesized by an intramolecular [2+2] photocycloaddition and characterized by the single-crystal X-ray diffraction technique. The compound crystallizes in the rhombohedral system (R$\bar{3}$, a=27.767(5)Å c=6.390(2)Å). In this structure, two 6-membered rings and a 4-membered ring are fused by the N-N or N-C bonds and the pyridine part adopts chair conformation. A pair of molecules related by an inversion center are held together through the hydrogen bonding interactions between N and O atoms of the uracil moiety.

1. Introduction

Intramolecular [2+2] photocycloadditions of cyclic α,β-enone tethered to suitable alkenes afford the construction of carbocyclic and heterocyclic ring systems with high regio-and/or stereoselectivity.[1-7]

When combined with the subsequent cleavage of the cyclobutane ring of the photoproducts by various chemical means, the overall transformation constitutes an annelative two-carbon ring or carbon-hetero ring expansion of original enones. This process is now the most widely used photochemical reaction in synthetic organic chemistry.[8-13] In conjunction with ongoing studies in our laboratories on the synthesis of heterocyclic compounds containing[14] diaza group in analogy with previously reported routes, we report the intramolecular equivalent of this process using N^1-(4-Pentenyl)-uracil.

N^1-alkenylpyrimidine was prepared by alkylation
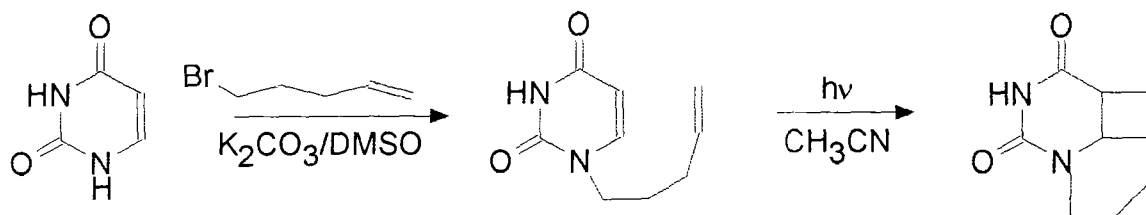
of uracil with 5-Bromo-1-pentene in the presence of potassium carbonate.

Direct and/or Pyrex-filtered irradiation of N^1-(4-pentenyl)uracil with a 150W medium pressure mercury lamp in CH$_3$CN at room temperature produced the intermolecular adduct on distillation of the solvent and separation by TLC.

Unambiguous assignments of the structure of photoproduct were a difficult task from ^{1}H and ^{13}C-NMR data alone due to long range couplings common to bi – or tricyclic ring compounds.[15,16] Thus, single crystal structure studies have been undertaken.

2. Experimental

Single crystals of the title compound were grown from methanol solution. A colorless crystal of dimensions 1.00 x 0.70 x 0.75mm^3 was taken and mounted at the tip of a glass fiber with silicone glue.

The cell parameters were derived from 23 reflections in the range 12° $\leq \theta \leq$ 15° that had been automatically centered on an MXC^3 diffractometer (MAC sciences). The parameters yielded a rhombohedral unit cell (a=27.767(5)Å, c=6.390(2)Å). Intensity data were collected at room temperature with the ω-2θ scan technique in the range 1.5° $\leq \theta \leq$ 22.5°. Extinction rule for hkl reflections (h-k+l=3n±1) was applied. During data collection 2 standard reflections measured every 100 reflections showed no significant variation in intensity. Data collection parameters and crystallographic details are given in Table I.

From intensity comparisons, Laue class was determined to be 3. Since this crystal system is reverse setting, collected reflections transformed to obverse setting and all data reported here refer to this crystal system.[17] The systematic absences (-h+k+l=3n±1, for hkl reflections ; l=3n±1, for 00l

Table I. Crystal data and structure refinement for 1,3-Diazatricyclo[5.3.1.0^{5,11}]undecane - 2,4-dione

Empirical formula	C9 H12 N2 O2
Formula weight	180.21
Temperature	293 K
Diffratometer used	MAC Sciences MXC^3
	Graphite monochromated Mo Kα
	λ =0.71073 Å
Crystal system	Rhombohedral(hexagonal setting)
Space group	R$\overline{3}$
Unit cell dimensions	a = 27.767(5) Å
	c = 6.390(2) Å
Volume	4267(2) Å^3
Z	18
Density (calculated)	1.262 g/cm^3
Linear absorption coefficient	0.091 mm^{-1}
F(000)	1728
Crystal size	1.00 x 0.75 x 0.70 mm^3
θ range for data collection	1.5 to 22.50°
Scan type	ω-2θ scan
Scan rate	5.00 deg/min
Scan width, deg	1.25+0.35tanθ
Index ranges	-29 $\leq$ h $\leq$ 29, 0 $\leq$ k $\leq$ 29, 0 $\leq$ l $\leq$ 6
Reflections collected	1431
Independent reflections	1245 [R(int) = 0.0062]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1245 / 0 / 119
Goodness-of-fit on F^2	1.168
Final R indices [Fo>4σ(Fo)]	R1 = 0.0741
R indices	wR2 = 0.2785
Extinction coefficient	0.005(2)

reflections) are indicative of the space groups C_{3i}^2 − R$\overline{3}$ or C_3^4 −R3. Centrosymmetric R$\overline{3}$ was assumed and this was confirmed by a successful structure solution.

All calculations were performed on a PC with the programs, SHELXS-86[18] and SHELXL-93.[19] The structures were solved by the direct method. All reflections were not corrected for absorption effect because of the small linear absorption coefficient(μ= 0.091mm^{-1}). Parameter refinements were carried out with the use of the method of the full-matrix least squares on F^2. In this refinement, anisotropic temperature parameters were used for all 13 non-hydrogen atoms and isotropic temperature parameters were used for all 12 hydrogen atoms. Atomic positions of hydrogen atoms were generated with the riding model technique of SHELXL-93.

With 1245 unique reflections and 119 variables, the final cycle of refinement was performed. The final values of R on F_o and R_w on F_o^2 are 0.0776 and 0.2785 respectively. The value of the conventional R index on F for those 1137 reflections having $F_o > 4\sigma(F_o)$ is 0.0741. In the final refinement cycles, Δ/σ are not exceeding 0.005. Also, the final difference electron density map exhibite no features. The error in an observation of unit weight is 1.168.

Final atomic positions for non-hydrogen atoms and hydrogen atoms are listed in Table II and III,

Table II Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2 x10^3$) for 1,3- Diazatricyclo [5.3.1.0^{5,11}]undecane-2,4-dione.

	x	y	z	U(eq)*
O(2)	2680(1)	1462(1)	-2374(4)	65(1)
O(4)	3783(1)	829(1)	52(5)	80(1)
N(1)	2266(1)	701(1)	-307(4)	46(1)
N(3)	3198(1)	1085(1)	-1310(4)	51(1)
C(2)	2706(1)	1098(1)	-1374(5)	46(1)
C(4)	3325(2)	779(2)	20(5)	51(1)
C(5)	2863(2)	400(1)	1444(5)	51(1)
C(6)	2272(1)	241(1)	822(5)	48(1)
C(7)	1786(2)	765(2)	74(5)	54(1)
C(8)	1781(2)	919(2)	2341(6)	62(1)
C(9)	1737(2)	451(2)	753(6)	67(1)
C(10)	2143(2)	263(2)	3157(6)	55(1)
C(11)	2779(2)	644(2)	3503(5)	57(1)

* U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table. III. Hydrogen coordinates (x10^4) and isotropic displacement parameters (Å^{2}x10^3) for 1,3-Diazatricyclo[5.3.1.0^{5,11}] undecane-2,4-dione.

	x	y	z	U
H(3)	3450(1)	1291(1)	-2200(4)	61
H(7A)	1448(2)	420(2)	-243(5)	65
H(7B)	1801(2)	1053(2)	-827(5)	65
H(6)	2056(1)	-125(1)	163(5)	58
H(10)	2024(2)	-101(2)	3792(6)	65
H(9A)	1804(2)	579(2)	5192(6)	80
H(9B)	1362(2)	136(2)	3671(6)	80
H(5)	2885(2)	65(1)	1738(5)	62
H(8A)	1468(2)	975(2)	2592(6)	75
H(8B)	2120(2)	1263(2)	2660(6)	75
H(11A)	2905(2)	1038(2)	3439(5)	69
H(11B)	2920(2)	553(2)	4740(5)	69

Table IV Anisotropic displacement parameters (A^2 x 10^3) for 1,3- Diazatricyclo[5.3.1.0^{5,11}]undecane-2,4-dione.*

	U11	U22	U33	U23	U13	U12
O(2)	63(2)	69(2)	68(2)	27(1)	19(1)	38(1)
O(4)	62(2)	118(3)	76(2)	23(2)	14(1)	57(2)
N(1)	47(2)	49(2)	43(2)	5(1)	3(1)	25(1)
N(3)	49(2)	57(2)	46(2)	11(1)	13(1)	26(1)
C(2)	52(2)	46(2)	39(2)	6(1)	6(1)	25(2)
C(4)	50(2)	62(2)	47(2)	-1(2)	3(1)	32(2)
C(5)	56(2)	53(2)	50(2)	8(2)	4(2)	31(2)
C(6)	51(2)	38(2)	51(2)	0(1)	1(1)	19(2)
C(7)	50(2)	55(2)	57(2)	9(2)	5(2)	26(2)
C(8)	62(2)	66(2)	68(3)	-1(2)	11(2)	39(2)
C(9)	62(2)	85(3)	52(2)	11(2)	14(2)	35(2)
C(10)	54(2)	55(2)	50(2)	17(2)	10(2)	24(2)
C(11)	56(2)	70(2)	43(2)	1(2)	-1(2)	29(2)

* The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2a^{*2}U_{11} + k^2b^{*2}2U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*\cos\gamma^*U_{12} + 2hla^*c^*\cos\beta^*U_{13} + 2klb^*c^*\cos\alpha^*U_{23}]$

respectively. Anisotropic thermal parameters are presented in Table IV.

3. Results and Discussion

A view of the compound is given in Fig. 1. A list of bond distances and angles may be found in Table V. The title compound is structurally similar to the tricyclic compound reported earlier [20] except that a five-membered ring in the tricyclic compound changed into a six-membered ring. In this tricyclic system, the three rings(4, two 6-membered) are fused by the C5-C6, C6-C10, and N1-C6 bonds.

The cyclobutane part is nearly planar – except the C11 atom that deviates 0.587Å from the least-squares plane defined by C5, C6, and C10 atoms(Table VI) – with the average bond angles of 87.89°. The torsion angle of C5-C6-C10-C11 is also 21.83°. There is no significant change between the torsion angle of this system and that of the
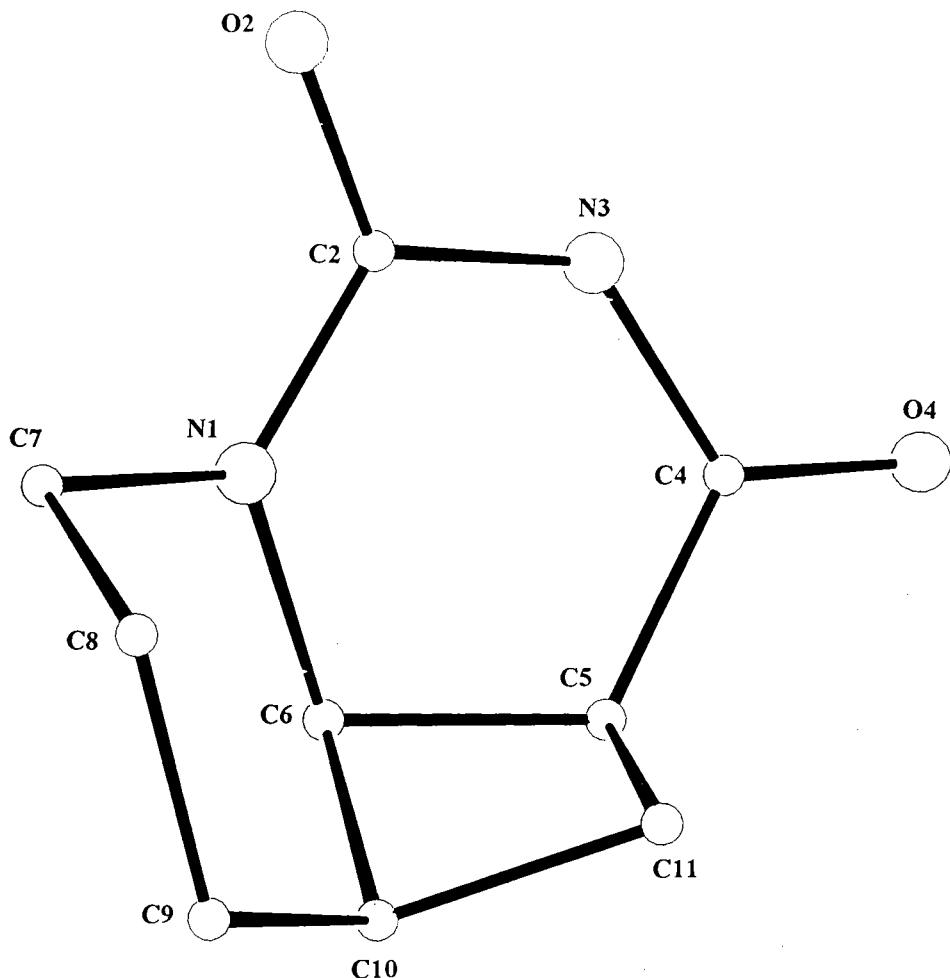
Fig. 1. Structure of 1,3-Diazatricyclo[5.3.1.0^{5,11}]undecane-2,4-dione.

other related tricyclic compound, 1,3-Diazatricyclo[5.2.1.0^{5,10}]decane-2,4-dione(17.4°).[20] In other related tricyclic systems, the ring often adopts "butterfly" conformation with two bond angles near 80°.[21-24]

The uracil part is almost planar(max. dev. ≤ 0.06Å except the C6 atom that deviates 0.387Å from the least-squares plane defined by N1, C2, N3, C4, and C5 atoms. The pyridine part has chair conformation that is usual in the other pyridine system. This is indicative of largely deviated C7, C10 atoms (Table VI).

As shown in the other related tricyclic compounds,[20] the two molecules in this tricyclic system related by the inversion symmetry pairing together by the hydrogen bonding interactions between N3 and O2' (d(N3-O2')=2.902(4)Å, ∠(N3-H3--O2')=169.7(1)°), where O2' is related to

Table V. Bond lengths [A] and angles [deg] for 1,3-Diazatricyclo[5.3.1.05,11]undecane- 2,4-dione.

O(2)-C(2)	1.228(4)
O(4)-C(4)	1.210(4)
N(1)-C(2)	1.350(4)
N(1)-C(7)	1.452(4)
N(1)-C(6)	1.474(4)
N(3)-C(4)	1.367(5)
N(3)-C(2)	1.385(4)
C(5)-C(4)	1.494(5)
C(5)-C(11)	1.560(5)
C(6)-C(5)	1.523(5)
C(6)-C(10)	1.542(5)
C(7)-C(8)	1.512(5)
C(9)-C(8)	1.536(6)
C(10)-C(9)	1.509(6)
C(10)-C(11)	1.554(5)
O(2)-C(2)-N(1)	122.2(3)
O(2)-C(2)-N(3)	120.1(3)
O(4)-C(4)-N(3)	121.5(3)
O(4)-C(4)-C(5)	123.6(3)
N(1)-C(2)-N(3)	117.7(3)
N(1)-C(6)-C(5)	110.7(3)
N(1)-C(6)-C(10)	109.7(3)
N(1)-C(7)-C(8)	109.5(3)
N(3)-C(4)-C(5)	114.8(3)
C(2)-N(1)-C(7)	119.8(3)
C(2)-N(1)-C(6)	123.8(3)
C(4)-N(3)-C(2)	126.8(3)
C(4)-C(5)-C(6)	117.8(3)
C(4)-C(5)-C(11)	118.2(3)
C(5)-C(6)-C(10)	88.5(3)
C(5)-C(11)-C(10)	87.1(3)
C(6)-C(5)-C(11)	88.4(3)
C(6)-C(10)-C(11)	87.6(3)
C(7)-N(1)-C(6)	115.6(3)
C(7)-C(8)-C(9)	109.4(3)
C(9)-C(10)-C(6)	119.0(3)
C(9)-C(10)-C(11)	121.3(3)
C(10)-C(9)-C(8)	112.8(3)

Table VI. Least-squares planes for 1,3-Diazatricyclo [5.3.1.0^{5,11}] undecane-2,4-dione.

Crystallographic Equation of Plane No.1

$$- 2.37 (4) x + 18.15 (3) y + 4.496 (8) z = 0.66 (1)$$

atom	distance
*N1	-0.059(2)
*C2	0.077 (2)
*N3	-0.034 (2)
*C4	-0.022 (2)
*C5	0.039 (2)
C6	-0.387 (5)
O4	-0.026 (5)
O2	0.294 (5)

Crystallographic Equation of Plane No.2

$$17.64(4)x + 6.69(6)y + 2.72(1)z = 4.388(6)$$

atom	distance
C7	-0.706 (5)
*C8	0.004 (2)
*C9	-0.004 (2)
*C6	0.004 (2)
*N1	-0.004 (2)
C10	0.425 (5)

Crystallographic Equation of Plane No.3

$$6.47(7)x + 26.51(2)y - 0.60(2)z = 0.88(2)$$

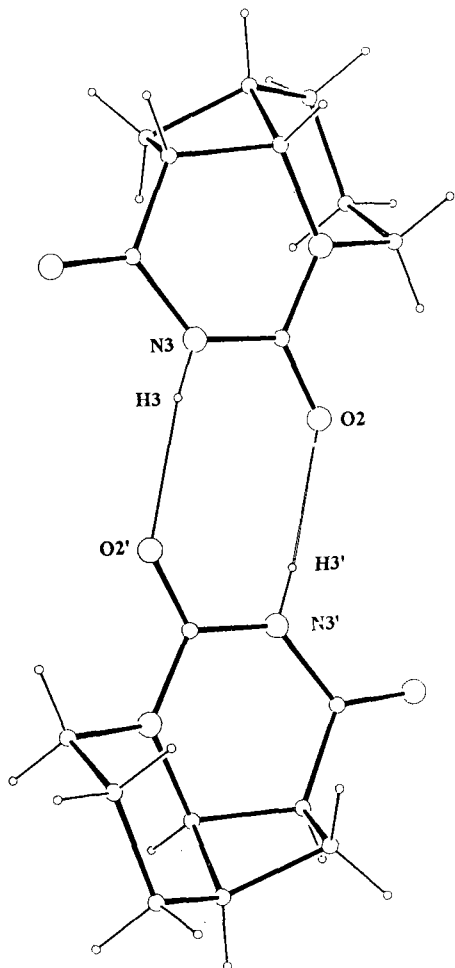| atom	distance
*C6	0.000
*C10	0.000
*C5	0.000
C11	-0.578(7)

* Indicates atom used to define planes

Fig. 2. Hydrogen bonding interactions between two molecules.

O2 by an inversion center(Fig. 2).

Acknowledgments

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