

# 디아자트리사이클로디온의 X선 결정구조 결정

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## X-Ray Crystal Structure Determination of Diazatricyclodione

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### 요 약

1,3-Diazatricyclo[5.2.1.0<sup>5,10</sup>] decane-2,4-dione, C<sub>8</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>의 단위세포 상수는 a=6.585(7), b=9.089(4), c=12.937(10)Å, β=95.72(5)°, V=770.4Å<sup>3</sup>, Dc=1.43 g/cm<sup>3</sup>, μ=1.0cm<sup>-1</sup>, T=295° K, 공간군은 P2<sub>1</sub>/n이고 단사 정계이며 Z=4이다. λ(Mo Kα)=0.7093Å을 사용한 698개의 회절 반점에 대한 최종 신뢰도 R값은 0.037이다.

본 화합물은 N<sup>1</sup>-(ω-butenyl)uracil의 분자내 [2+2] 광고리화 반응 생성물이며, [5.1.2.0<sup>5,10</sup>] tricyclic 계에 속한다. Inversion symmetry에 의해 관련된 한 쌍의 분자들은 uracil 부분의 O2와 H3 간의 강한 수소 결합을 하고 있다.

### Abstract

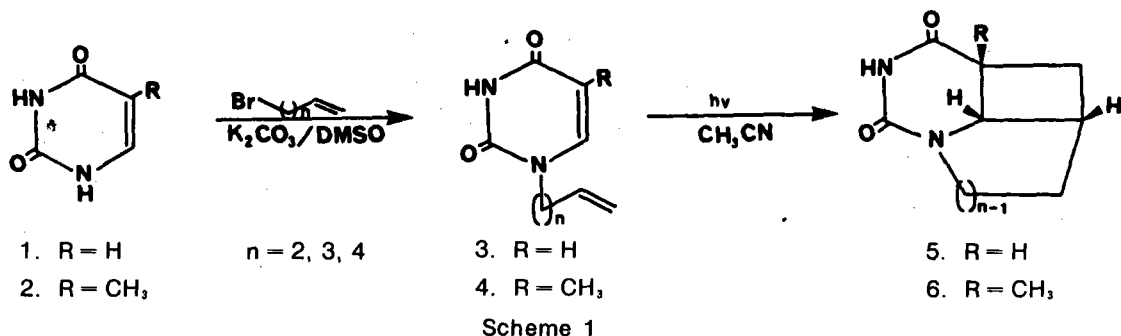
1,3-Diazatricyclo[5.2.1.0<sup>5,10</sup>] decane-2,4-dione, C<sub>8</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>, MW=166.15, Monoclinic, P2<sub>1</sub>/n a=6.585(7), b=9.089(4), c=12.937(10)Å, β=95.72(5)°, V=770.4Å<sup>3</sup>, Z=4, Dc=1.43(4) g/cm<sup>3</sup>, λ(Mo Kα)=0.7093Å, μ=1.0cm<sup>-1</sup>, T=295° K, final R=0.037 for 698 unique observed reflections. The compound is the product of the intramolecular [2+2] photocycloaddition of N<sup>1</sup>-(ω-butenyl)uracil

and belongs to a [5.2.1.0<sup>5,10</sup>] tricyclic system. A pair of molecules related by the inversion symmetry are held together by the strong hydrogen bonding interactions between O2 and H3 of the uracil moiety.

### INTRODUCTION

There are several requirements to meet in designing organic synthesis scheme. The number of reaction steps should be minimized to achieve a high overall yield. In some cases, the critical factor can be the ability to control the regio- and/or stereospecificity of the target compounds. The intramolecular [2+2] photocycloaddition is often used in the syntheses of complex natural compounds because this simple reaction provides good regio- and stereospecificity with relatively high yield.<sup>1-10)</sup>

To exploit this reaction scheme, pyrimidines, especially uracil(1) and thymine(2), were derivatized at their N<sup>1</sup> position with alkenyl, yielding N<sup>1</sup>-(ω-alkenyl) pyrimidines(3 and 4). Subsequent intramolecular cycloaddition by irradiating with a UV source, produced diazatricyclodiones(5 and 6) (Scheme I).



In order to confirm the structures of these products, NMR spectroscopic method was applied. The 500MHz spectrum was very complicated and difficult to interpret due to long range coupling effect common to bi- or tricyclic compounds.<sup>11-12)</sup> Here we report the X-ray crystallographic structure determination of the diazatricyclodione compound (5(n=2)). In the literature, crystal structures of several tricyclic compounds have been reported.<sup>13-16)</sup> To our knowledge, this is the first structure determination of a [5.2.1.0<sup>5,10</sup>] tricyclic system. Since this is the first publication of the crystal structure determination using our X-ray diffraction facility, a rather detailed procedure and strategy of the technique used will be described.

#### DATA COLLECTION AND REDUCTION

A white plate-like crystal of dimensions 0.8×0.8×0.2mm was scrubbed off the reaction flask, and glued at the tip of a glass fiber. The crystal was then transferred to an Enraf-Nonius CAD4 diffractometer and optically aligned. The X-ray generator was operated at 50kv and 20mA with a 2kW Mo sealed tube.

The diffractometer was equipped with a graphite crystal monochromator ( $\lambda = 0.7093\text{\AA}$ ). A 10min. rotation photograph was taken on a polaroid film. The picture revealed that the crystal was of good quality and had reasonable diffracting power to a high reaction.

From the picture, 15 reflections well-separated in space within  $8 \leq \theta \leq 12^\circ$  were selected and their angular positions were carefully centered. Angular positions of 10 more reflections within  $10 \leq \theta \leq 12^\circ$  were centered using a "blind" search procedure.

Using the positions of these 25 reflections, an auto indexing procedure was applied, yielding a monoclinic type unit cell ( $a=6.585(7)$ ,  $b=9.089(4)$ ,  $c=12.937(10)\text{\AA}$ ,  $\beta=95.72(5)^\circ$ ).

On the basis of the symmetry of  $I(hkl)=I(h\bar{k}l)$  evaluated from a trial data collection run of 1k2 ( $-8 \leq k \leq 8$ ) reflections, the crystal system was presumed to be monoclinic and confirmed later by the successful structural solution. All the reflections in the  $hk\pm 1$  octant within the sphere of  $\theta \leq 20^\circ$  were collected using an  $\omega$ -scan method with the scan width of  $\Delta\omega = 1.0 + 0.35 \tan \theta$  (estimated from a  $\omega$ - $\theta$  plot).

Moving-crystal moving-counter background counts were made by scanning an additional 25% above and below this range. The counter aperture was also adjusted as a function of  $\theta$ , the horizontal aperture width ranging from 1.5 to 1.6mm, while the vertical one set at 4mm. For very strong or unobserved reflections, a fast scan speed of  $7^\circ/\text{min.}$  was used. For other reflections, a variable speed of  $2-7^\circ/\text{min.}$  was chosen to assure  $I \geq \sigma$ .

Intensities of three strong reflections were repeatedly monitored every 2hr. during the data collection and did not show any significant variation. All reflections were corrected for Lorentz and polarization effect, but not for the absorption ( $\mu = 1.0\text{cm}^{-1}$ ).

Intensities of 0k1 reflections were averaged with  $R_{\text{sym}}=1.5\%$  (for 151 observed reflections), yielding 718 unique reflections which were used in the subsequent structure determination.

From the systematic absences of  $h+1=2n+1$  for  $h01$  and  $k=2n+1$  for  $0k0$  reflections, the space group was determined as  $P2_1/n$ .

### STRUCTURE SOLUTION AND REFINEMENT

Assuming one molecule per asymmetric unit (F.W. = 166.15), the calculated crystal density is 1.43 g/cm<sup>3</sup>, a reasonable packing for an organic molecule. The structure was solved by direct method.

Using 176 reflections ( $E \geq 1.2$ ) and 2067 triplet relationships, a total of 16 phase sets were produced. All 12 non-hydrogen atoms were located from an E-map prepared from the phase set with the best figure of merits. After a few cycles of the structure factor calculation and least-squares refinement employing initially isotropic and later anisotropic temperature factors, a difference electron density map was calculated and all 10 hydrogen atoms were located from the map. All the positional and thermal parameters – anisotropic non-hydrogen atoms and isotropic hydrogen atoms – were refined using a full-matrix least-squares refinement procedure by minimizing  $\sum (|F_o| - |F_c|)^2$ . After all the parameters were converged, the  $|F_o| - |F_c|$  values were examined for systematic errors. For the strong low-angle reflections,  $|F_o|$  were systematically less than  $|F_c|$ . In the subsequent refinement cycles, the secondary extinction effect was included in the least-squares refinement procedure, according to the method of Coppens and Hamilton's.<sup>17)</sup> The final secondary extinction coefficient was  $2.36 \times 10^{-7}$ . The final residual indices were  $R = \sum (|F_o| - |F_c|) / \sum |F_o| = 3.7\%$  and  $R_w = [\sum (|F_o| - |F_c|)^2 / \sum |F_o|]^2 = 3.4\%$  against 698 reflection with  $I \geq \sigma_I$  ( $R = 3.8\%$  against all 718 reflections). The final difference electron density map was featureless.

Table 1. Positional parameters and isotropic equivalents of thermal parameters.

Atom	x	y	z	B(A <sup>2</sup> )
O2	0.4913(3)	0.3069(2)	0.4830(2)	4.06(5)
O4	0.0281(3)	0.6245(2)	0.3407(2)	4.55(5)
N1	0.1757(3)	0.2140(3)	0.4426(2)	3.21(6)
C2	0.3102(4)	0.3251(3)	0.4560(2)	3.12(7)
N3	0.2317(3)	0.4663(3)	0.4368(2)	3.19(6)
C4	0.0609(4)	0.4999(3)	0.3706(2)	3.22(7)
C5	-0.0754(4)	0.3703(3)	0.3432(2)	3.42(7)
C6	-0.0410(5)	0.2687(4)	0.2509(2)	4.42(8)
C7	-0.0814(5)	0.1352(4)	0.3194(2)	3.79(7)
C8	0.0714(5)	0.0096(4)	0.3343(3)	4.34(8)
C9	0.2438(5)	0.0663(4)	0.4122(3)	4.32(8)
C10	-0.0447(4)	0.2372(3)	0.4139(2)	3.13(7)
H3	0.322(4)	0.539(3)	0.453(2)	1.1(6)*
H5	-0.211(4)	0.403(3)	0.337(2)	0.5(6)*
H6A	0.117(4)	0.263(3)	0.238(2)	0.6(6)*
H6B	-0.132(4)	0.284(3)	0.194(2)	2.7(7)*
H7	-0.218(4)	0.100(3)	0.307(2)	1.2(6)*
H8A	0.009(4)	-0.080(3)	0.360(2)	2.5(7)*
H8B	0.123(5)	-0.023(4)	0.271(2)	3.7(8)*
H9A	0.368(5)	0.077(4)	0.377(2)	3.1(8)*
H9B	0.263(4)	0.009(3)	0.471(2)	1.8(7)*
H10	-0.131(4)	0.229(3)	0.478(2)	0.3(5)*

Starred atoms are refined isotropically.

Anisotropically refined atoms are given the form of the isotropic equivalent displacement parameter defined as:  $(4/3) \times [a^2 B(1,1) + b^2 B(2,2) + c^2 B(3,3) + a^* b^* (\cos \gamma) B(1,2) + a^* c^* (\cos \beta) B(1,3) + b^* c^* (\cos \alpha) B(2,3)]$ .

Plots of  $\langle \omega (|F_o| - |F_c|)^2 \rangle$  versus  $|F_o|$  and  $\sin \theta / \lambda$  showed no unusual trends. Thus, the structure determination was complete. All calculations

Table 2. Anisotropic thermal parameters for non-hydrogen atoms

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)	Beqv
O2	2.52(8)	3.30(9)	6.0(1)	-0.05(8)	-1.38(8)	-0.27(9)	4.06(5)
O4	4.9(1)	2.45(9)	5.9(1)	0.18(9)	-1.5(1)	0.53(9)	4.55(5)
N1	2.8(1)	2.4(1)	4.2(1)	-0.1(1)	-0.7(1)	0.0(1)	3.21(6)
C2	3.2(1)	2.6(1)	3.3(1)	-0.3(1)	-0.7(1)	-0.3(1)	3.12(7)
N3	2.8(1)	2.0(1)	4.5(1)	-0.33(9)	-1.2(1)	-0.2(1)	3.19(6)
C4	3.2(1)	2.7(1)	3.8(1)	0.1(1)	-0.5(1)	-0.3(1)	3.22(7)
C5	2.7(1)	3.1(1)	4.2(1)	0.4(1)	-1.2(1)	-0.1(1)	3.42(7)
C6	5.3(2)	4.2(2)	3.5(1)	-0.3(2)	-1.0(1)	-0.1(1)	4.42(8)
C7	3.5(1)	3.2(1)	4.4(1)	-0.8(1)	-1.1(1)	-0.5(1)	3.79(7)
C8	4.4(2)	2.9(1)	5.5(2)	-0.2(1)	-0.5(1)	-0.9(1)	4.34(8)
C9	4.0(2)	2.4(1)	6.4(2)	0.1(1)	-0.6(1)	-0.0(1)	4.32(8)
C10	2.6(1)	2.7(1)	3.9(1)	-0.2(1)	-0.3(1)	-0.3(1)	3.13(7)

The form of the anisotropic displacement parameter is:  $\exp [-0.25 [h^2 a^* 2B(1,1) + k^2 b^* 2B(2,2) + l^2 c^* 2B(3,3) + 2hka^* b^* B(1,2) + 2hla^* c^* B(1,3)]]$  where  $a^*$ ,  $b^*$ , and  $c^*$  are reciprocal lattice constants.

were performed on a VAX computer using the SDP program package.<sup>18)</sup> The final positional and anisotropic thermal parameters are listed in Table 1 and 2, respectively.

## RESULTS AND DISCUSSION

A stereoview of the molecule with labelling is shown in Figure. 1. All bond distances and angles are listed in Table 3 and 4, respectively. The intramolecular [2+2] photocycloaddition of  $N^1 - (\omega\text{-butenyl})\text{uracil}$  produces a [5.2.1.0<sup>5,10</sup>] tricyclic system.

In this tricyclic system, the three rings (4,5 and 6-membered) are fused by the N1-C10, C5-C10, and C7-C10 bonds.

The cyclobutane moiety is nearly planar (max. dev.  $\leq 0.12\text{\AA}$ , see Table 5) with the bond angles close to  $90^\circ$  (Table 4).

The torsional angles around this four membered ring are all only  $17^\circ$  (Table 6). In other related tricyclic

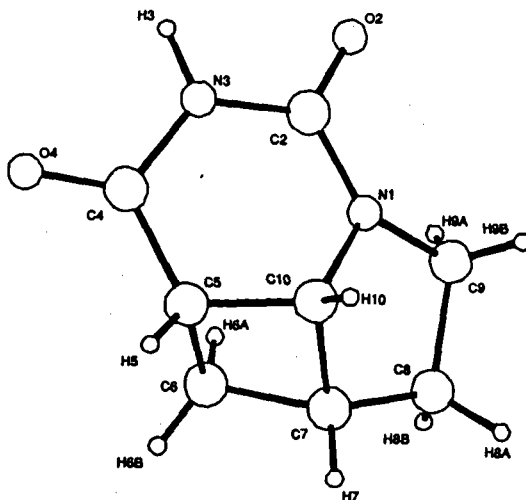


Fig 1. A molecular drawing of 1,3-diazatricyclo[5.2.1.0<sup>5,10</sup>]-decane-2,4-dione with atom labelling.

compounds, the ring often adapts to "butterfly" conformation with two bond angles near  $80^\circ$ <sup>13-16</sup>. The four carbon atoms in the pyrrolidine moiety also form a plane (max. dev.  $\leq 0.12\text{\AA}$ ), while the N1 atom deviates by  $0.32\text{\AA}$  from the least-squares plane. The uracil moiety is also planar except for C10 which de-

Table 3. Bond distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
O2	C2	1.220(3)	C6	C7	1.542(5)
O4	C4	1.209(4)	C6	H6A	1.07(2)
N1	C2	1.343(4)	C6	H6B	0.92(3)
N1	C9	1.481(4)	C7	C8	1.521(4)
N1	C10	1.477(4)	C7	C10	1.534(4)
C2	N3	1.397(4)	C7	H7	0.95(3)
N3	C4	1.378(4)	C8	C9	1.530(5)
N3	H3	0.90(3)	C8	H8A	0.99(3)
C4	C5	1.502(4)	C8	H8B	0.96(3)
C5	C6	1.544(5)	C9	H9A	0.98(3)
C5	C10	1.518(4)	C9	H9B	0.92(3)
C5	H5	0.94(2)	C10	H10	1.06(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 4. Bond Angles in Degrees

A	B	C	Angle	A	B	C	Angle
C2	N1	C9	120.2(2)	C6	C7	C8	120.9(3)
C2	N1	C10	123.0(2)	C6	C7	C10	87.7(2)
C9	N1	C10	112.2(2)	C6	C7	H7	112.(2)
O2	C2	N1	123.3(3)	C8	C7	C10	107.6(2)
O2	C2	N3	120.6(3)	C8	C7	H7	112.(2)
N1	C2	N3	116.1(3)	C10	C7	H7	114.(2)
C2	N3	C4	125.4(3)	C7	C8	C9	105.6(3)
C2	N3	H3	114.(2)	C7	C8	H8A	112.(2)
C4	N3	H3	118.(2)	C7	C8	H8B	114.(2)
O4	C4	N3	121.0(2)	C9	C8	H8A	111.(2)
O4	C4	C5	125.1(3)	C9	C8	H8B	111.(2)
N3	C4	C5	113.8(3)	H8A	C8	H8B	103.(3)
C4	C5	C6	121.4(3)	N1	C9	C8	104.8(2)
C4	C5	C10	116.3(2)	N1	C9	H9A	109.(2)
C4	C5	H6	108.(2)	N1	C9	H9B	108.(2)
C6	C5	C10	88.2(2)	C8	C9	H9A	109.(2)
C6	C5	H5	110.(1)	C8	C9	H9B	113.(2)
C10	C5	H5	112.(2)	H9A	C9	H9B	113.(2)
C5	C6	C7	88.8(3)	N1	C10	C5	109.5(2)
C5	C6	H6A	111.(1)	N1	C10	C7	100.8(3)
C5	C6	H6B	114.(2)	N1	C10	H10	112.(1)
C7	C6	H6A	106.(1)	C5	C10	C7	90.0(3)
C7	C6	H6B	117.(2)	C5	C10	H10	119.(1)
H6A	C6	H6B	117.(2)	C7	C10	H10	122.(1)

Numbers in parentheses are estimated standard deviations in the least significant digits.

viates by 0.53Å from the least-squares plane defined by N1, C2, N3, C4 and C5. As shown in Figure 2, the two molecules related by the inversion symmetry pair together by the hydrogen bonding interaction formed between O2 and H3 ( $O2+ - H3 = 1.99(3)\text{\AA}$ ,  $N3 - H3 - - - O2+ = 169(2)^\circ$ ), where O2+ is related to O2 by inversion.

Table 5. Least-squares Planes

## Crystallographic Equation of Plane No. 1

3.4768 X	+ 1.1597 Y	-11.4883 Z	+4.6544=0
Atom	Distance	Atom	Distance
N1	-0.0682	C2	0.1178
N3	-0.098 <sup>c</sup>	C4	0.0286
C5	0.0202	O2*	0.4572
O4*	0.1133	C10*	-0.5314
H3*	-0.0566		

## Crystallographic Equation of Plane No. 2

3.4737 X	+5.0907 Y	-8.9021 Z	+2.5586=0
Atom	Distance	Atom	Distance
C7	0.1209	C8	-0.1202
C9	0.0735	C10	-0.0742
N1*	0.3177		

## Crystallographic Equation of Plane No. 3

-6.5435 X	+ 0.1833 Y	-0.1308 Z	-0.3996=0
Atom	Distance	Atom	Distance
C5	0.1169	C6	-0.1151
C7	0.1157	C10	-0.1175

\*Atoms not included in the plane definition

## Dihedral Angles Between Planes:

Plane No.	Plane No.	Dihedral Angle
1	2	41.98
1	3	115.80
2	3	116.29

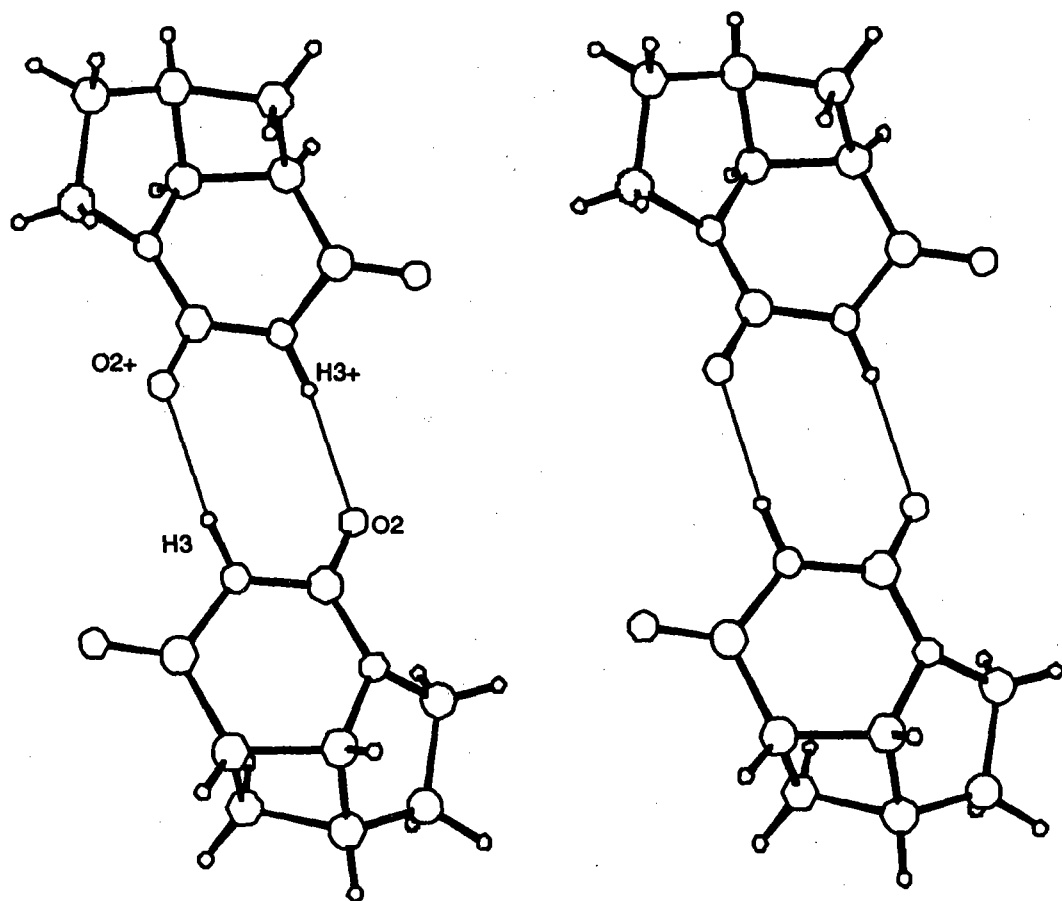


Fig 2. A stereoview showing hydrogen bonding interaction (thin line) between two molecules related by the inversion symmetry. O2+ and H3+ are related to O2 and H3 by inversion symmetry, respectively.

$O2^+ \cdots H3^+ = 1.99(3)\text{\AA}$ ,  $N3 - H3 \cdots O2^+ = 169(2)^\circ$ .

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Table 6. Torsion Angles

A	B	C	D	angle
C9	N1	C2	O2	-28.6(4)
C9	N1	C2	N3	151.3(3)
C10	N1	C2	O2	177.5(3)
C10	N1	C2	N3	-2.6(4)
C2	N1	C9	C8	-140.6(3)
C10	N1	C9	C8	16.0(3)
C2	N1	C10	C5	33.8(4)
C2	N1	C10	C7	127.7(3)
C9	N1	C10	C5	-121.9(3)
C9	N1	C10	C7	-28.0(3)
O2	C2	N3	C4	153.4(3)
N1	C2	N3	C4	-26.5(4)
C2	N3	C4	C4	-163.6(3)
C2	N3	C4	C5	17.6(4)
O4	C4	C5	C6	93.9(4)
O4	C4	C5	C10	-161.0(3)
N3	C4	C5	C6	-87.3(3)
N3	C4	C5	C10	17.8(4)
C4	C5	C6	C7	137.2(3)
C10	C5	C6	C7	17.2(2)
C4	C5	C10	N1	-40.4(3)
C4	C5	C10	C7	-141.8(3)
C6	C5	C10	N1	84.1(3)
C6	C5	C10	C7	17.3(2)
C5	C6	C7	C8	-126.3(3)
C5	C6	C7	C10	-17.1(2)
C6	C7	C8	C9	77.2(4)
C10	C7	C8	C9	-21.0(3)
C6	C7	C10	N1	-92.5(2)
C6	C7	C10	C5	17.4(2)
C8	C7	C10	N1	29.3(3)
C8	C7	C10	C5	139.2(3)
C7	C8	C9	N1	3.7(3)

Numbers in parentheses are estimated standard deviations in the least significant digits.

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