3-N-(2,2-디에토오키시에칠)-2-벤즈-이미다즈오리논의 결정 및 분자구조

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THE CRYSTAL AND MOLECULAR STRUCTURE OF 3-N-(2,2-DIETHOXY-ETHYL)-2-BENZIMIDAZOLINONE.

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요 약

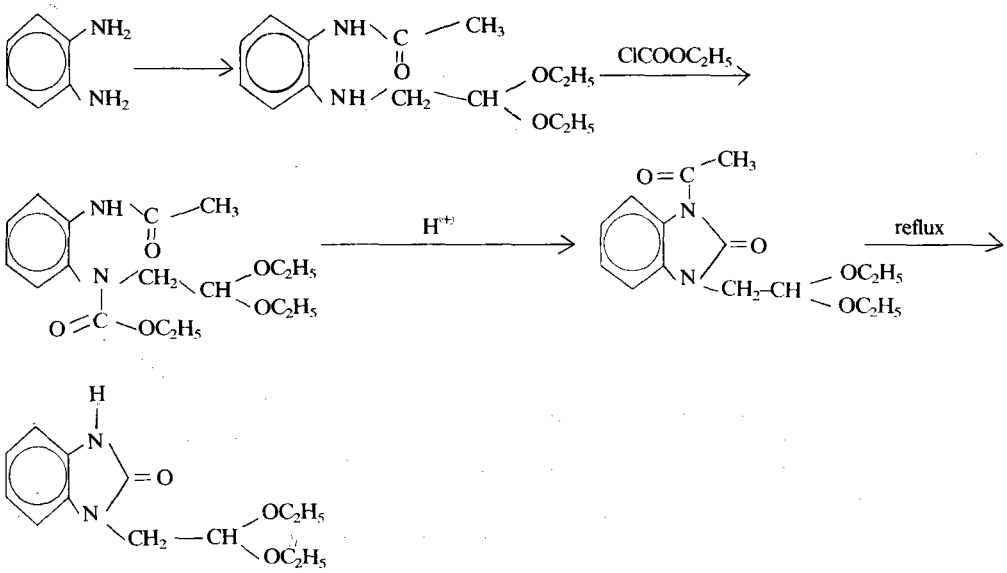
$C_{13}H_{18}N_2O_3$(Mr=250.29)는 단사정계의 $P2_1/a$의 공간군을 갖고 있으며 a=8.765(4), b=17.679(3), c=9.238(4)Å, β=105.6(3)°, z=4, V=1378.53Å^3, λ(Mo Kα)=0.71069Å, μ=0.81cm^{-1}, F(000)=536, T=298 이며 1.0 σ(I)보다 큰 강도를 가진 1783개의 회절반점에 대하여 최종 R값은 0.080이다. 직접법에 의하여 구조를 풀었으며 C-H 결합길이와 메칠기는 길이를 고정시켜 이상적인 기하학적 구조에 맞추어 계단식 대각최소자승법에 의하여 정밀화하였다. 두 에토오키시기중의 하나는 다른 기에 비해 100° 나 더 기울어져있다. 결정격자내에 한개의 N-H···O(2.798Å)수소결합이 있어 두 분자를 연결하면서 b-축에 따라 쌓여져 있다.

Abstract

$C_{13}H_{18}N_2O_3$, Mr=250.29, is monoclinic, space group $P2_1/a$ with a=8.765(4), b=17.679(3), c=9.238(4) Å, b=105.6(3)°, Z=4, V=1378.53 Å^3, λ(Mo Kα)=0.71069 Å, μ=0.81cm^{-1}, F(000)=536, T=298, R=0.080 for 1783 unique observed reflections with I > 1.0 σ(I). The structure was solved by direct methods and refined by cascade diagonal least-squares refinement. The C-H bond lengths and methyl groups were fixed and refined as their ideal geometry. One of two ethoxy groups is more twisted by 100° as compared with another. There is one hydrogen bond in the crystal lattice, N-H···O= 2.789 Å, forming a molecular pair packing along the b-axis.

INTRODUCTION

Title compound has been synthesized as a by-product in the reaction associated with the intramolecular cyclization of acetal compounds, and the three-dimensional structure determination by X-ray diffraction methods has been completed in order to clarify some aspects of its mechanism of action that it might have as an insecticide. The reactions for synthesis are as follows :



EXPERIMENTAL

Single crystals of the title compound[1,2,3] were grown from slow evaporation in acetone solvent. Crystal sizes were 0.30×0.26×0.33㎜.

Accurate lattice parameters were calculated by least squares refinement of the diffractometer settings for 25 reflections within $25^{\circ}<2\theta<35^{\circ}$, measured with graphite monochromatized Mo K_{α} radiation(λ = 0.71069 Å) on the Nicolet R3m/E diffractometer. Data collections were performed by $\theta-2\theta$ scan technique at variable rates 4.9 to 29.3°/min, with $2\theta_{max}=45^{\circ}$ for the ranges $-9\leq h\leq 9$, $0\leq k\leq 20$, $0\leq 1\leq 9$. Three standard reflections monitered every 97 reflections during collections. Only small random fluctuations of these check reflections were noted. Of the 2059 measured reflections, the 1555 unique observed reflections gave $R_{int}=0.023$ and 1783 data with $I>1.0\sigma(I)$ were used in the refinement. Lorentz-polarization corrections were applied to the intensity data, while no absorption or extinction was not used.

Structure was solved by direct methods using 200 reflections with $E>1.26$. All the non-hydrogen atoms were identified in the E map. The further difference Fourier synthesis were done, fixing all C-H bond lengths at 0.96 Å, and refining the methyl groups as rigid groups with ideal geometry. The refinements, anisotropically for the non-hydrogen atoms and isotropically for the hydrogen atoms, carried out by cascade block-diagonal least-squares on F with the maximum $\sin\theta/\lambda=0.253$ $Å^{-1}$. The final cycles of least squares with 167 parameters converged to the maximum shift/e.s.d=0.01, R=0.080 and wR=0.1078, where $w=1/(\sigma^2(F)+0.0004\,F^2)$; $\sigma^2(F)$ from statistics of counting ; goodness of fit=3.691. The maximum and minimum peaks were 0.292 and 0.332 $Å^{-3}$, respectively.

All atomic scattering factors used were from the "International Tables for X-ray Crystallography[4]" and all calculations were performed on a Data General Eclips S140 computer using the SHELXTL 5.1 program package[5](Nicolet Instrument Company).

Crystal data of 3-N-(2, 2-diethoxyethyle)-2-benzimidazolinone are summerized in Table 1.

RESULT AND DISCUSSION

The molecular conformation with the thermal ellipsoids and atomic labelling scheme are shown in Fig. 1. The final fractional atomic coordinates and anisot-

Table 1. Crystal data

Chemical formula	$C_{13}H_{18}N_2O_3$
Molecular weight	250.29
Crystal system	monoclinic
Space group	$P2_1/a$
Unit cell parameters	a=8.765(4) Å b=17.679(3) c=9.238(4) z=4 v=1378.53 Å^3 β=105.6(3)°
Dencity	d_c=1.205 g cm^{-3} μ=0.81cm^{-1} F(000)=536
Systematic absences	h 0 l ; h=2n h 0 0 ; h=2n 0 k 0 ; l=2n

ropic temperature factors for non-hydrogen atoms of 3-N-(2, 2-diethoxyethyle)-2-benzimidazolinone are listed in Table 2. Table 3 gives the fractional hydrogen coordinates with equivalent isotropic thermal parameters. Bond lengths and bond angles for non-hydrogen atoms are given in Table 4. In the bicyclic[6,7,8,9] ring, average bond length and bond angle for the benzene ring are 1.383(6) Å and 120(4)°, and for the pentagonal ring[6] being 1.383(5) Å and 108.0(3)°, respectively. From the torsion angles in Table 5, it can be seen that the bicyclic ring is coplanar with the biggest deviation of the C(3) atom -0.014 Å from its plane. The C(7)-O(1) that is a carbonyl group has 1.221(5) Å of a double bond length. The skeletons of two ethoxy groups are zigzag forms with the angles of 110.3(.4)°-116.9(.3)°, and with the bond lengths ; 1.498(7) Å of CH_3-CH_2-, 1.379(8)-1.397(5) Å of -CH_2-O and 1.379(4)-1.393(5) Å of -O-C(9). The C(9) atom connecting two ethoxy groups in which have the hybrid angle of 111.7(3)°(O(2)-C(9)-O(3)) makes a V like-shape with the angle 113.1(3)° at the fold of the C(8) atom against the N(2) atom. From the values of torsion angles in Table 5, N(2)-C(8)-C(9)-O(2)=65.1(.4) and N(2)-C(8)-C(9)-O(3)=174.9(.3), two ethoxy groups give a twisted conformation about the N(2) atom.

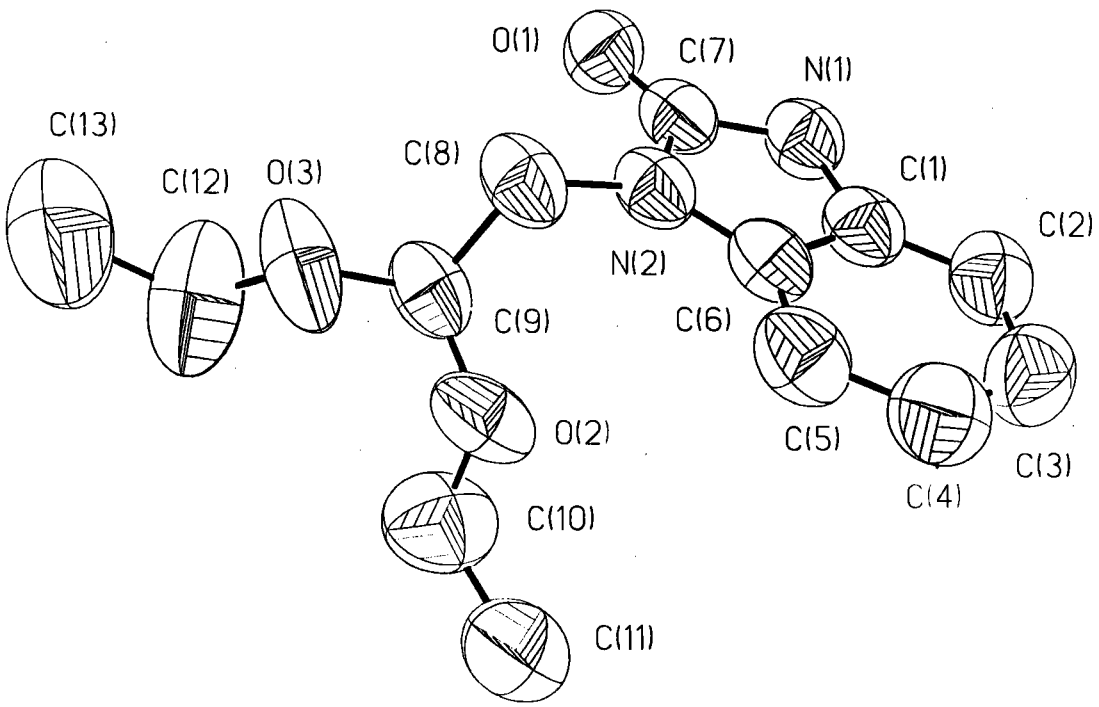


Fig 1. A molecular conformation with the thermal ellipsoids and atomic labelling scheme for 3-N-(2,2-diethoxyethyl) -2-benzimidazolinone.

Table 2. Fractional atomic coordinates(x 10^4) and anisotropic temperature factors ($Å^2 \times 10^3$) for the non-H atoms of 3-N-(2,2-diethoxyethyl) -2-benzimidazolinone. The estimated standard deviations are in parentheses.

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	2232(4)	9772(2)	2897(4)	70(2)	58(2)	81(2)	−2(2)	12(2)	−11(1)
C(2)	1956(5)	9993(2)	1417(4)	85(2)	83(2)	85(2)	−7(2)	11(2)	−13(2)
C(3)	3034(6)	9739(3)	649(5)	118(3)	100(3)	88(2)	2(2)	32(3)	−25(3)
C(4)	4329(6)	9321(2)	1363(5)	113(3)	91(3)	117(3)	0(2)	57(3)	−10(3)
C(5)	4616(4)	9105(2)	2853(4)	81(2)	74(2)	111(3)	8(2)	35(2)	1(2)
C(6)	3546(4)	9342(2)	3609(4)	69(2)	54(2)	88(2)	2(2)	21(2)	−5(1)
C(7)	2145(4)	9582(2)	5293(4)	68(2)	56(2)	81(2)	−1(2)	11(2)	3(2)
C(8)	4610(4)	8858(2)	6299(4)	64(2)	62(2)	102(2)	10(2)	7(2)	3(2)
C(9)	4313(4)	8027(2)	6373(4)	61(2)	68(2)	105(3)	17(2)	16(2)	8(2)
C(10)	3834(7)	6995(3)	4683(5)	131(4)	103(3)	138(4)	−17(2)	44(3)	−31(3)
C(11)	3997(7)	6755(3)	3176(5)	178(5)	100(3)	132(4)	−6(3)	18(4)	17(3)
C(12)	4911(7)	7166(4)	8385(6)	153(5)	212(7)	132(4)	68(4)	23(4)	−6(4)
C(13)	5934(9)	7057(4)	9955(6)	261(9)	172(6)	172(6)	61(5)	49(6)	43(6)
N(1)	1402(3)	9926(1)	3947(3)	67(2)	67(2)	82(2)	4(1)	14(1)	8(1)
N(2)	3464(3)	9235(1)	5077(3)	63(2)	57(1)	82(2)	3(1)	11(1)	6(1)
O(1)	1715(3)	9579(1)	6445(3)	81(2)	85(2)	78(1)	3(1)	18(1)	16(1)
O(2)	4539(3)	7701(1)	5073(3)	103(2)	58(1)	138(2)	0(1)	55(2)	−2(1)
O(3)	5392(3)	7760(4)	7647(4)	101(2)	93(2)	147(2)	58(2)	3(2)	1(2)

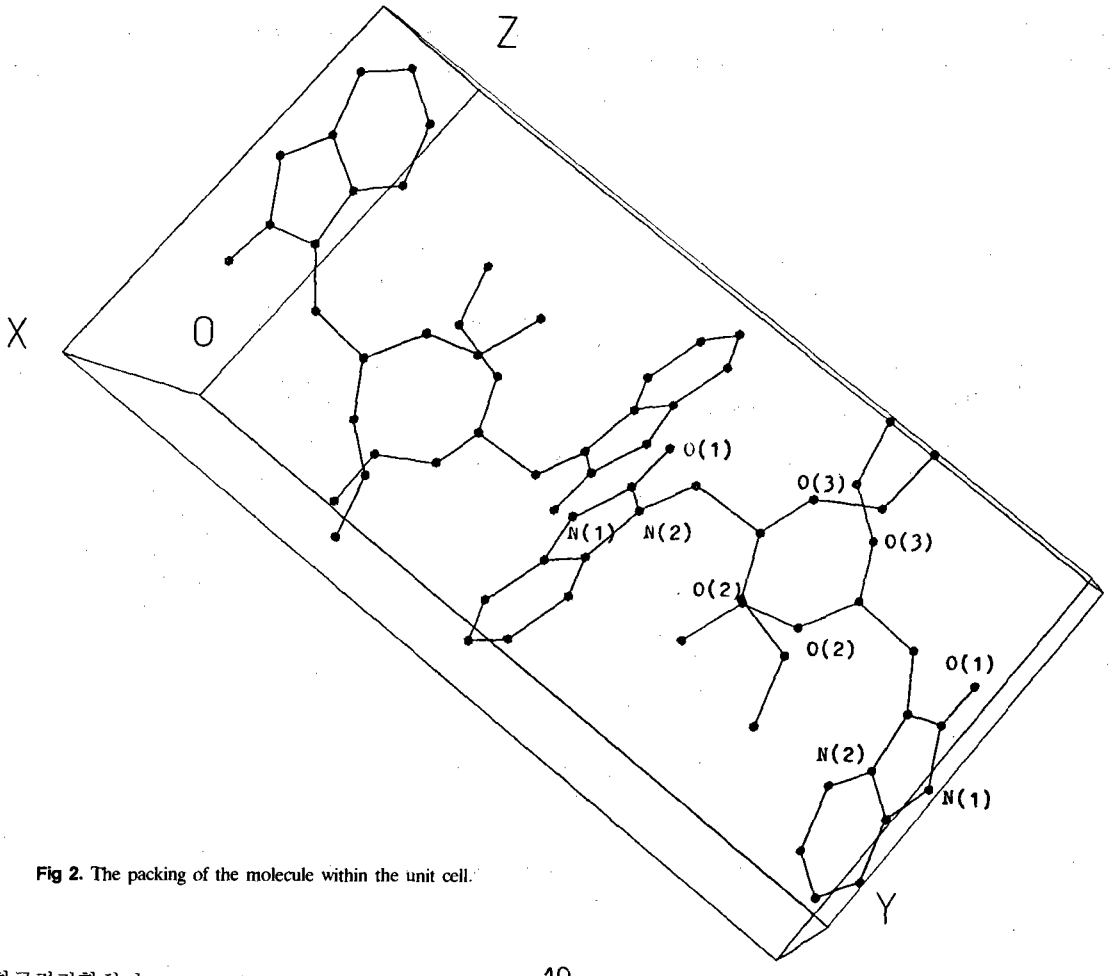


Fig 2. The packing of the molecule within the unit cell.

Table 3. Fractional hydrogen coordinates(x 10^4) and temperature factors ($Å^2 \times 10^3$) for 3-N-(2,2-diethoxyethyl) -2-benzimidazolinone.

atom	x	y	z	U*
H(2)	1069	10306	938	104
H(3)	2860	9860	-396	120
H(4)	5066	9172	813	126
H(5)	5522	8804	3338	106
H(8a)	5648	8930	6163	97
H(8b)	4563	9084	7232	97
H(9)	3260	7909	6427	98
H(10a)	4342	6629	5424	147
H(10b)	2731	7026	4646	147
H(11a)	3513	6268	2923	172
H(11b)	5099	6725	3209	172
H(11c)	3483	7118	2431	172
H(12a)	3846	7260	8427	200
H(12b)	4938	6710	7825	200
H(13a)	5543	6638	10410	236
H(13b)	5911	7507	10531	236
H(13c)	7003	6956	9929	236
H	314	10095	3829	82

* Equivalent isotropic U defined as one third of the trace of the orthogonalized tensor.

Table 4. Bond lengths(Å) and bond angles (°) for 3-N-(2,2-diethoxyethyl) -2-benzimidazolinone.

(1) Bond lengths(Å)

C(1)-C(2)	1.379(5)	C(1)-C(6)	1.389(4)
C(1)-N(1)	1.386(5)	C(2)-C(3)	1.399(7)
C(3)-C(4)	1.367(6)	C(4)-C(5)	1.385(6)
C(5)-C(6)	1.377(6)	C(6)-N(2)	1.390(5)
C(7)-N(1)	1.379(4)	C(7)-N(2)	1.370(5)
C(7)-O(1)	1.221(5)	C(8)-C(9)	1.479(5)
C(8)-N(2)	1.456(4)	C(9)-O(2)	1.393(5)
C(9)-O(3)	1.379(4)	C(10)-C(11)	1.498(7)
C(10)-O(2)	1.397(5)	C(12)-C(13)	1.498(7)
C(12)-O(3)	1.379(8)		

(2) Bond angles(°)

C(2)-C(1)-C(6)	121.7(4)	C(2)-C(1)-N(1)	130.8(3)
C(6)-C(1)-N(1)	107.5(3)	C(1)-C(2)-C(3)	116.8(3)
C(2)-C(3)-C(4)	121.0(4)	C(3)-C(4)-C(5)	122.3(5)
C(4)-C(5)-C(6)	117.0(4)	C(1)-C(6)-C(5)	121.2(3)
C(1)-C(6)-N(2)	106.4(3)	C(5)-C(6)-N(2)	132.4(3)
N(1)-C(7)-N(2)	106.1(3)	N(1)-C(7)-O(1)	127.3(3)
N(2)-C(7)-O(1)	126.6(3)	C(9)-C(8)-N(2)	113.1(3)
C(8)-C(9)-O(2)	107.4(3)	C(8)-C(9)-O(3)	106.7(3)
O(2)-C(9)-O(3)	111.7(3)	C(11)-C(10)-O(2)	110.3(4)
C(13)-C(12)-O(3)	113.2(5)	C(1)-N(1)-C(7)	109.6(3)
C(6)-N(2)-C(7)	110.4(3)	C(6)-N(2)-C(8)	127.8(3)
C(7)-N(2)-C(8)	121.7(3)	C(9)-O(2)-C(10)	115.8(3)
C(9)-O(3)-C(12)	116.9(3)		

Table 5. Torsion angles(°) in 3-N-(2,2-diethoxyethyl) -2-benzimidazolinone.

C(6)-C(1)-C(2)-C(3)	2.3(.5)
N(1)-C(1)-C(2)-C(3)	180.0(.3)
C(2)-C(1)-C(6)-C(5)	-1.2(.5)
C(2)-C(1)-C(6)-N(2)	179.0(.3)
N(1)-C(1)-C(6)-C(5)	-179.4(.3)
N(1)-C(1)-C(6)-N(2)	0.9(.3)
C(2)-C(1)-N(1)-C(7)	-179.6(.3)
C(6)-C(1)-N(1)-C(7)	-1.7(.3)
C(1)-C(2)-C(3)-C(4)	-2.8(.6)
C(2)-C(3)-C(4)-C(5)	2.3(.7)
C(3)-C(4)-C(5)-C(6)	-1.1(.6)
C(4)-C(5)-C(6)-C(1)	0.5(.5)
C(4)-C(5)-C(6)-N(2)	-179.8(.3)
C(1)-C(6)-N(2)-C(7)	0.2(.3)
C(1)-C(6)-N(2)-C(8)	-176.2(.3)
C(5)-C(6)-N(2)-C(7)	-179.5(.3)
C(5)-C(6)-N(2)-C(8)	4.1(.5)
N(2)-C(7)-N(1)-C(1)	1.7(.3)
O(1)-C(7)-N(1)-C(1)	-177.6(.3)
N(1)-C(7)-N(2)-C(6)	-1.2(.3)
N(1)-C(7)-N(2)-C(8)	175.5(.3)
O(1)-C(7)-N(2)-C(6)	178.2(.3)
O(1)-C(7)-N(2)-C(8)	-5.2(.5)
N(2)-C(8)-C(9)-O(2)	65.1(.4)
N(2)-C(8)-C(9)-O(3)	-174.9(.3)
C(9)-C(8)-N(2)-C(6)	-89.4(.4)
C(9)-C(8)-N(2)-C(7)	94.6(.4)
C(8)-C(9)-O(2)-C(10)	-159.8(.3)
O(3)-C(9)-O(2)-C(10)	83.6(.4)
C(8)-C(9)-O(3)-C(12)	147.5(.4)
O(2)-C(9)-O(3)-C(12)	-95.4(.5)
C(11)-C(10)-O(2)-C(9)	173.0(.4)
C(13)-C(12)-O(3)-C(9)	-163.5(.5)

Crystal packing is given in Fig. 2. There is one hydrogen bond in the crystal lattice [N(1)-H···O(1)(x, 1-y, -z)=2.798(3), N(1)-H=0.98, H···O(1)=1.871 Å, N(1)-H···O(1)=156.7(4)°]. This hydrogen bond forms a molecular pair packing along the b-axis.

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