Studies on the Polymerization of Acrolein Oxime. XIV.† The Structure of 2,4,7-Trimethylperhydroisoxazolo-[2,3-*a*]pyridine-2,7-dicarbaldehyde Dioxime

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The thermal oligomerization of methacrylaldehyde oxime leads preferentially to two 2,4,7-trimethylperhydroisoxazolo[2,3-*a*]pyridine-2,7-dicarbaldehyde dioximes, which are comformationally isomeric with each other. The crystal structure of the α-form has been determined by means of X-ray diffraction. It is monoclinic, with the space group $P2_1/a$. The cell dimensions are $a=7.858(3)$, $b=13.186(6)$, $c=17.259(6)$ Å, $\beta=130.38(3)°$, and $Z=4$. The molecules are linked by OH···O and OH···N intermolecular hydrogen bonds, with the O···O and O···N distances of 2.794(6) and 2.760(5) Å respectively. Since attempts of the crystallization of the β-form have been unsuccessful, the determination of its chemical structure was attempted by means of ^{13}C-NMR spectroscopy and gas chromatography-mass spectrometry. The β-form is, at any rate, different from the α-form.

Methacrylaldehyde oxime undergoes spontaneous polymerization on heating to give, though in a very low yield, oligomers which consist of several products, including isomeric bicyclic trimers. A previous paper has shown that the recrystallization of the oligomers from methanol gives colorless, needle-like crystals, which are identified as 2,4,7-trimethylperhydroisoxazolo[2,3-*a*]pyridine-2,7-dicarbaldehyde dioxime(**1**).[1] The present paper will be concerned with the structure determination of two isomers (α- and β-forms) of **1**. In order to obtain detailed information on the molecular structure of the α-form, the X-ray crystal structure analysis has been carried out. Since the crystallization of the β-form has been unsuccessful, the spectroscopic determination of the chemical structure was attempted.

Experimental

Oligomerization of Methacrylaldehyde Oxime. The thermal oligomerization of methacrylaldehyde oxime was carried out at 60—90 °C for 10 h in an ampoule. The unreacted monomer was removed in a stream of nitrogen under reduced pressure, the residue was placed in a large amount of ether, and then the oligomer was precipitated. Three crystallizations from methanol gave colorless needle crystals of **1** (α-form). After the removal of these crystals, the mother liquor was condensed, and then an isomeric trimer of **1** (β-form) was fractionated by gas chromatography, silicon OV-17 (5%) supported on Gaschrom Q being used as the stationary phase.

Mass and NMR Spectroscopy. The mass spectra were measured on a Shimadzu LKB-9000 mass spectrometer, equipped with a gas-chromatographic inlet system. The ionizing potential was 70 eV, and the ionizing current was 60 μA. The ^{13}C-NMR spectra were obtained with a Hitachi R-42 FT apparatus (22.6 MHz), using DMSO-d_6 as the solvent and the internal standard.

X-Ray Diffraction. An α-form crystal, with approximate dimensions of $0.5\times0.5\times0.8$ mm, was mounted on a Syntex R_3 automated four-circle diffractometer. The unit-cell dimensions were precisely determined by the least-square method, using 11 reflections measured on the diffractometer with graphite-monochromatized Mo K_α radiation (collimator size, 1.5 mm). The crystal data are summarized in Table 1.

The intensity data were collected on the diffractometer with the same radiation, using the ω scan mode ($2\theta\leqq50°$) at a variable scan speed. Reflections with intensities below the minimum intensity (150) were collected at the minimum scan speed (3 ° min^{-1}); those with intensities above the maximum intensity (2500) were collected at the maximum scan speed (30 ° min^{-1}). Medium-range intensities were collected at a scan speed on a linear scale between the minimum and maximum speeds. The intensities of the reference reflections were measured periodically; they showed no significant fluctuation during the course of data collection. Background counts were accumulated in each 1-scan range (in degree) before and after each scan and at the same scan speed. A total of 2409 independent reflections were collected, among which 1699 ($I\geqq1.96\ \sigma\ (I)$) were classed as observed. These intensity data were corrected for Lorentz and polarization effects, but not for absorption [μ(Mo K_α)= 1.0 cm^{-1}].

Structure Determination and Refinement

The structure was solved by the direct method (MULTAN program package[2]). The atomic parameters were then refined by the block-diagonal least-squares method, using anisotropic temperature factors for all the non-hydrogen atoms and isotropic ones for hydrogen atoms. The final value of R was 0.078 for non-zero reflections. In the least-squares procedure, the function minimized was $\Sigma(|F_o|-|F_c|)^2$.

Table 1. Crystal data

$C_{12}H_{21}N_3O_3$, M.W.=255.32	
Space group $P2_1/a$ (systematic absence of reflections, $h0l$: $h=2n+1$, $0k0$: $k=2n+1$)	
a/Å 7.858(3)	Z, 4
b/Å 13.186(6)	D_x/g cm^{-3} 1.243
c/Å 17.259(6)	D_m/g cm^{-3} 1.239 (flotation
β/° 130.38(3)	in C_6H_6-CCl_4 solution, 25 °C)
U/Å^3 1362	

† Part XIII: T. Ota, Y. Mori, M. Tanaka, H. Tamai, and S. Masuda, *Polymer J.*, **12**, 751 (1980).

TABLE 2. ATOMIC CO-ORDINATES, MULTIPLIED BY 10^4 FOR NON-HYDROGEN ATOMS AND BY 10^3 FOR HYDROGEN ATOMS, AND THERMAL PARAMETERS, MULTIPLIED BY 10^2

The anisotropic temperature factors are in this form:
$\exp[-(1/4)(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)]$.

Atoms	x	y	z	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	5254(5)	3716(3)	4179(3)	27(2)	36(2)	30(2)	10(2)	23(2)	7(1)
O(14)	12511(5)	3187(3)	7371(2)	17(2)	36(2)	20(1)	6(1)	6(1)	−2(1)
O(18)	−909(6)	5348(3)	2073(3)	23(2)	37(2)	36(2)	7(2)	13(2)	−2(2)
N(8)	6157(6)	2878(3)	3990(3)	19(2)	30(2)	23(2)	1(2)	13(2)	−1(2)
N(13)	11221(6)	2521(3)	6537(3)	18(2)	32(2)	16(2)	−1(2)	8(2)	−3(2)
N(17)	1460(7)	5401(3)	2853(3)	25(2)	34(2)	31(2)	4(2)	16(2)	2(2)
C(2)	4866(8)	4567(4)	3534(4)	26(2)	28(3)	24(2)	2(2)	16(2)	3(2)
C(3)	5844(9)	4210(4)	3038(4)	32(3)	36(3)	35(3)	7(2)	25(2)	4(2)
C(4)	8233(10)	2572(5)	3425(4)	48(3)	48(3)	50(3)	11(3)	41(3)	6(3)
C(5)	9733(9)	1845(5)	4333(4)	37(3)	53(4)	33(3)	15(3)	24(3)	−4(3)
C(6)	8516(9)	1421(4)	4675(4)	37(3)	35(3)	29(3)	8(2)	17(2)	−2(2)
C(7)	7548(8)	2237(4)	4922(4)	23(2)	31(3)	21(2)	2(2)	11(2)	1(2)
C(9)	7506(8)	3401(4)	3787(4)	22(2)	41(3)	29(2)	−1(2)	20(2)	1(2)
C(10)	9563(11)	3028(5)	3153(5)	62(4)	57(4)	59(4)	1(3)	47(4)	3(3)
C(11)	5982(9)	1765(5)	5073(4)	29(3)	45(3)	33(3)	−5(3)	18(2)	9(2)
C(12)	9266(8)	2863(4)	5847(3)	23(2)	36(3)	19(2)	1(2)	15(2)	−4(2)
C(15)	6075(9)	5467(5)	4234(4)	30(3)	43(3)	41(3)	−8(2)	21(3)	−6(3)
C(16)	2368(8)	4683(4)	2771(4)	26(2)	30(3)	24(2)	4(2)	15(2)	1(2)
HO(14)	1354(7)	283(3)	779(3)	50(11)					
HO(18)	−129(7)	592(3)	220(3)	60(10)					
H(31)	648(7)	478(3)	297(3)	48(10)					
H(32)	460(7)	388(3)	234(3)	50(10)					
H(4)	662(5)	222(3)	258(2)	74(8)					
H(51)	1119(7)	220(3)	494(3)	45(10)					
H(52)	997(7)	127(3)	410(3)	46(10)					
H(61)	713(7)	98(3)	404(3)	45(10)					
H(62)	964(7)	98(3)	538(3)	40(10)					
H(9)	896(7)	374(3)	452(3)	19(10)					
H(101)	828(7)	350(3)	249(3)	65(10)					
H(102)	1103(6)	344(3)	387(3)	87(10)					
H(103)	959(6)	235(3)	270(3)	74(10)					
H(111)	690(6)	123(3)	566(3)	30(10)					
H(112)	479(6)	137(3)	443(3)	46(10)					
H(113)	552(6)	237(3)	535(3)	68(10)					
H(12)	880(6)	345(3)	600(3)	79(10)					
H(151)	756(6)	535(3)	467(3)	51(9)					
H(152)	577(6)	604(3)	383(3)	47(9)					
H(153)	567(6)	559(3)	463(3)	53(9)					
H(16)	153(6)	418(3)	217(3)	37(9)					

The computer programs used were the Syntex R_3 package.*** The atomic-scattering factors were taken from "International Tables for X-Ray Crystallography," Vol IV.[3] All the calculations were carried out on the NOVA 3 belonging to the diffractometer. The atomic parameters are given in Table 2.****

Results and Discussion

Molecular Structure. Figure 1 shows the molecular structure, while the bond distances and bond angles are given in Tables 3 and 4 respectively. The six-membered ring (piperidine ring) of the α-form has a chair comformation, and the five-membered ring, which is in a half-chair form, is joined to the piperidine ring through two equatorial-type bonds (N(8)–O(1) and C(9)–C(3)). The two rings are approximately coplanar to each other. The methyl groups at the C(4) and C(7) carbons are equatorial, while the oxime group at the C(7) carbon is axial. In addition, the oxime and methyl groups at the C(2) carbon are on the same side of the average coplane of the rings, and on the opposite side, with the methyl group at the C(7) carbon, respectively. The bond distances

*** The MULTAN program is modified for the Syntex R_3 diffractometer.

**** The observed and calculated structure factors are kept as Document No. 8033 at the Chemical Society of Japan.

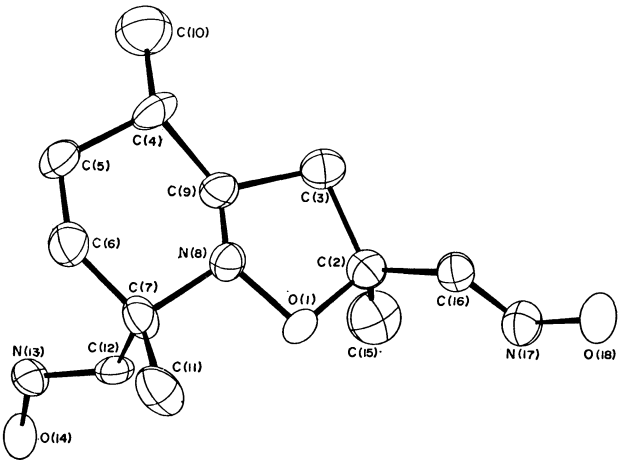

Fig. 1. A perspective view of the α-form molecule. Thermal ellipsoids of non-hydrogen atoms were drawn, at 50% probability level, by *ORTEP*.[4]

Table 3. Bond distances

Bond	Distance (*l*/Å)	Bond	Distance (*l*/Å)
O(1)-N(8)	1.460(6)	O(1)-C(2)	1.467(6)
O(14)-N(13)	1.408(5)	O(18)-N(17)	1.426(7)
N(8)-C(9)	1.484(9)	N(8)-C(7)	1.490(6)
N(13)-C(12)	1.269(7)	N(17)-C(16)	1.247(8)
C(2)-C(3)	1.548(10)	C(2)-C(15)	1.512(8)
C(2)-C(16)	1.504(9)	C(3)-C(9)	1.526(8)
C(4)-C(9)	1.541(10)	C(4)-C(5)	1.540(8)
C(4)-C(10)	1.519(13)	C(5)-C(6)	1.519(11)
C(6)-C(7)	1.529(9)	C(7)-C(11)	1.544(11)
C(7)-C(12)	1.502(7)		
O(14)-HO(14)	0.81(5)	O(18)-HO(18)	0.88(5)
C(3)-H(31)	0.95(5)	C(3)-H(32)	1.04(4)
C(4)-H(4)	1.25(3)	C(5)-H(51)	1.04(5)
C(5)-H(52)	0.94(5)	C(6)-H(61)	1.09(4)
C(6)-H(62)	1.10(4)	C(9)-H(9)	1.11(4)
C(10)-H(101)	1.11(4)	C(10)-H(102)	1.15(4)
C(10)-H(103)	1.20(5)	C(11)-H(111)	1.04(4)
C(11)-H(112)	1.02(4)	C(11)-H(113)	1.10(5)
C(12)-H(12)	0.96(5)	C(15)-H(151)	0.90(5)
C(15)-H(152)	0.94(4)	C(15)-H(153)	0.93(5)
C(16)-H(16)	1.03(4)		

Table 4. Bond angles

Bond	Angle (ϕ/°)	Bond	Angle (ϕ/°)
N(8)-O(1)-C(2)	107.5(4)	O(1)-N(8)-C(9)	103.1(4)
O(1)-N(8)-C(7)	108.1(4)	C(9)-N(8)-C(7)	112.5(4)
O(14)-N(13)-C(12)	111.7(5)	O(18)-N(17)-C(16)	110.4(5)
O(1)-C(2)-C(3)	104.7(5)	O(1)-C(2)-C(15)	106.2(5)
O(1)-C(2)-C(16)	104.7(5)	C(3)-C(2)-C(15)	113.7(5)
C(3)-C(2)-C(16)	112.4(5)	C(15)-C(2)-C(16)	114.1(5)
C(2)-C(3)-C(9)	101.8(5)	C(9)-C(4)-C(5)	105.6(5)
C(9)-C(4)-C(10)	110.8(6)	C(5)-C(4)-C(10)	109.6(6)
C(4)-C(5)-C(6)	111.5(6)	C(5)-C(6)-C(7)	113.6(5)
N(8)-C(7)-C(6)	104.3(5)	N(8)-C(7)-C(11)	107.7(5)
N(8)-C(7)-C(12)	111.2(5)	C(6)-C(7)-C(11)	110.9(5)
C(6)-C(7)-C(12)	114.5(5)	C(11)-C(7)-C(12)	108.0(5)
C(8)-C(9)-C(3)	100.0(5)	N(8)-C(9)-C(4)	106.0(5)
C(3)-C(9)-C(4)	119.4(5)	N(13)-C(12)-C(7)	120.7(5)
N(17)-C(16)-C(2)	119.8(5)		
N(8)-O(14)-HO(14)	101(4)	N(17)-O(18)-HO(18)	100(3)
C(2)-C(3)-H(31)	108(3)	C(2)-C(3)-H(32)	110(3)
C(9)-C(3)-H(31)	115(3)	C(9)-C(3)-H(32)	109(3)
H(31)-C(3)-H(32)	112(4)	C(9)-C(4)-H(4)	112(2)
C(5)-C(4)-H(4)	119(2)	C(10)-C(4)-H(4)	100(2)
C(4)-C(5)-H(51)	111(3)	C(4)-C(5)-H(52)	108(3)
C(6)-C(5)-H(51)	110(3)	C(6)-C(5)-H(52)	102(3)
H(51)-C(5)-H(52)	114(4)	C(5)-C(6)-H(61)	106(3)
C(5)-C(6)-H(62)	111(3)	C(7)-C(6)-H(61)	108(3)
C(7)-C(6)-H(62)	105(3)	H(61)-C(6)-H(62)	113(4)
N(8)-C(9)-H(9)	106(3)	C(3)-C(9)-H(9)	112(3)
C(4)-C(9)-H(9)	112(3)	C(4)-C(10)-H(101)	101(3)
C(4)-C(10)-H(102)	105(2)	C(4)-C(10)-H(103)	102(2)
H(101)-C(10)-H(102)	117(4)	H(101)-C(10)-H(103)	98(3)
H(102)-C(10)-H(103)	130(3)	C(7)-C(11)-H(111)	108(3)
C(7)-C(11)-H(112)	107(3)	C(7)-C(11)-H(113)	108(3)
H(111)-C(11)-H(112)	107(4)	H(111)-C(11)-H(113)	106(4)
H(112)-C(11)-H(113)	121(4)	N(13)-C(12)-H(12)	118(3)
C(7)-C(12)-H(12)	119(3)	C(2)-C(15)-H(151)	109(3)
C(2)-C(15)-H(152)	108(3)	C(2)-C(15)-H(153)	113(3)
H(151)-C(15)-H(152)	109(4)	H(151)-C(15)-H(153)	107(4)
H(152)-C(15)-H(153)	111(4)	N(17)-C(16)-H(16)	124(3)
C(2)-C(16)-H(16)	116(3)		

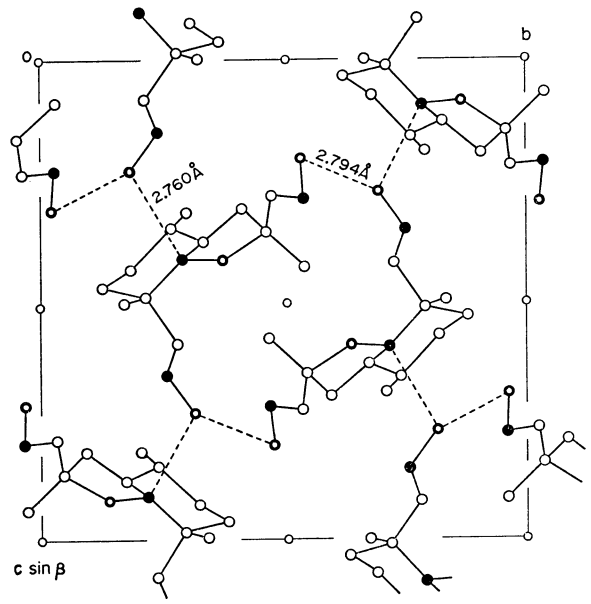

Fig. 2. Orthogonal projection of the crystal structure viewed along the a-axis.
Dashed lines exhibit hydrogen bonds.

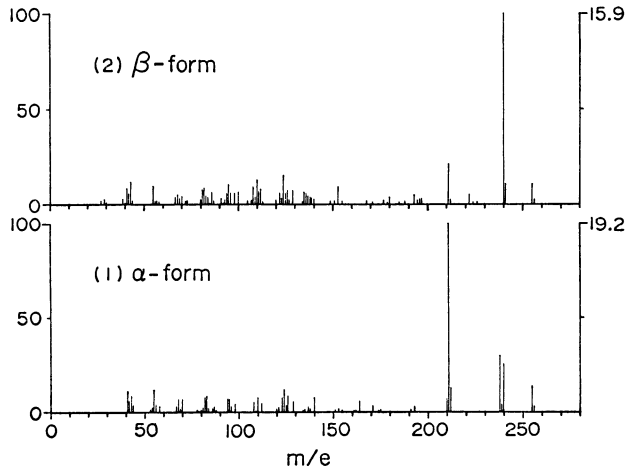

Fig. 3. Mass spectra of (1) α- and (2) β-forms.

between the skeleton atoms are in the range of 1.548 to 1.460 Å; they seem to be reasonable. The deviation of the N(8)–C(3)–C(9) angle from the tetrahedral angle corresponding to the sp^3 hybrid orbital is obviously to be ascribed to the highly-strained ring system caused by the heterobicyclic compound. On the whole, the values of the bond distances and angles shown in the tables are reasonable except that the C(4)–H(4) distance is too long.

Crystal Structure. The crystal structure is shown in Fig. 2. Both oxygen and nitrogen atoms participate in the hydrogen bond. The molecules related by a center of symmetry form a cyclic aggregate by means of O(18)–H···O(14) hydrogen bonds, 2.794(6) Å. The aggregates are linked by O(14)–H···N(8) hydrogen bonds, 2.760(5) Å, to make a three-dimensional network.

Characterization of the β-form. Since the attempts of crystallization of the β-form has been unsuccessful, the determination of the chemical structure was attempted by ^{13}C-NMR and mass spectrometric methods.

Table 5. Assignment of ^{13}C-NMR peaks of **1**

Structure	Peak position/ppm from TMS	
	α-form	β-form
$-CH_3$	18.79 24.42 27.42	10.86 12.59 24.38
$\backslash CH_2 /$	30.16 35.28 44.41	27.15 30.78 41.75
$\backslash -CH /$	36.44	30.47
$\backslash CH\text{-}N /$	65.99	59.13
$\backslash -C\text{-}N /$	60.75	61.41
$\backslash -C\text{-}O- /$	77.62	77.16
$-CH{=}N-$	150.40 154.44	154.41 156.48

As is shown in Fig. 3, the mass spectra of both α- and β-forms have a molecular ion peak at *m/e* 255, and they give similar fragmentation patterns except for the base ion peaks, which appear at *m/e* 211 (the lost of the oxime radical) for the former and at *m/e* 240 (the lost of the methyl radical) for the latter.

The NMR peak assignments are shown in Table 5, together with those of the α-form. The peak positions for the α-form were assigned by using the off-resonance technique and on the basis of the molecular structure determined by means of X-ray diffraction. The assignments for the β-form were made by comparison with those for the α-form. Carbon atoms of the β-form, particularly C(4), C(9), C(10), and C(11), resonate at a higher magnetic field compared with those of the α-form; that is due to a steric compression effect. These data reveal that the β-form is a geometrical isomer of the α-form, 2,4,7-trimethylperhydroisoxazolo[2,3-*a*]pyridine-2,7-dicarbaldehyde dioxime. The most plausible structure of the β-form is as follows. In the five-membered ring fused to the piperidine ring, the O(1) atom remains equatorial, but the C(3) atom goes to the axial position, the two rings being neither coplanar nor perpendicular to each other. Further, it can also be concluded that the methyl and oxime groups at the C(7) atom are axial and equatorial respectively, contrary to those of the α-form, because the C(11) and C(12) atoms of the β-form resonate 12 ppm higher and 4 ppm lower respectively than those of the α-form.

References

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