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Bull. Chem. Soc. Jpn., 57, 275—276 (1984)

The Crystal Structure of 4-Cyanoimino-3-methoxymethyl-perhydro-1,3,5-oxadiazine

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(Received May 4, 1983)

Synopsis. The structure of 4-cyanoimino-3-methoxymethylperhydro-1,3,5-oxadiazine in the crystalline state was determined by X-ray crystal analysis. The crystal is triclinic, space group $P\bar{1}$, a=10.307(3), b=8.166(2), c=5.082(1) Å, α=97.34(2), β=91.98(2), γ=107.13(2)°, Z=2. The final R value was 0.061 for 1651 reflections.

In the reaction of cyanoguanidine (CG) with formaldehyde, only two hydroxymethylated CG have been isolated;[1] mono- and 1,3-bis(hydroxymethyl)-2-cyanoguanidine (CG-1F and CG-2F). No adducts of 3 mol or more of formaldehyde per mole of CG have been isolated. As reported in the previous paper,[2] the exhaustive hydroxymethylation of 1,3-bis(methoxymethyl)-2-cyanoguanidine (CG-2M), prepared by the methoxylation of CG-2F, was examined and two new products were isolated. They had the structure of a cyclic ether of perhydro-1,3,5-oxadiazine. One was assigned as 4-cyanoimino-3-methoxymethylperhydro-1,3,5-oxadiazine (CG-1Mcyc2F), an adduct of 3 mol of formaldehyde per mole of CG, and the other as 3,5-bis(methoxymethyl)-4-methoxymethyl (carbamoylimino)perhydro-1,3,5-oxadiazine (AU-3Mcyc2F) by the elemental analysis, FD-MS and ^{1}H- and ^{13}C-NMR spectrometry. The latter product was derived from the hydration of the cyano group in the former and further addition of 2 mol of formaldehyde, one by one, to the imino group and to the newly formed amino group. The former product was derived by the dehydration from two newly introduced hydroxymethyl groups in methoxylated CG-1F or by the MeOH elimination between a newly introduced hydroxymethyl group in one imino group and the methoxymethyl group in the other imino group in CG-2M.

In order to confirm the cyclic nature of CG-1Mcyc2F and to elucidate its structural characteristic, the crystal structure of CG-1Mcyc2F has been determined by the X-ray method. Intensity data were collected on a Rigaku automated four-circule diffractometer using Mo $K\alpha$ radiation (λ=0.7107 Å).

Results and Discussion

Crystal Data. $C_6H_{10}N_4O_2$, M.W.=170.17, triclinic, space group $P\bar{1}$, a=10.307(3), b=8.166(2), c=5.082(1) Å, α=97.34(2), β=91.98(2), γ=107.13(2)° U=404.3 Å^3, Z=2, D_C=1.40 g cm^{-3}, μ(Mo $K\alpha$)=1.0 cm^{-1}. The structure of CG-1Mcyc2F was solved by direct methods and refined to a final R value of 0.061 for 1651 unique reflections. All the scattering factors were taken from the International Tables for X-Ray Crystallography.[3] The final atomic parameters are listed in Table 1. The complete table of observed and calculated structure factors is kept as Document No. 8403 at the Office of the Editor of the Bulletin of the Chemical Society of Japan. A perspective drawing of the molecular structure of CG-1Mcyc2F is shown in Fig. 1, which is a view perpendicular to the plane of the guanidine moiety. The structure agrees with that deduced from the spectroscopic data.[2] The underscored numbers in Fig. 1 give the heights of the atoms above or below the plane in Å. The interatomic distances and bond angles are listed in Table 2. Figure 1 shows a plane char-

TABLE 1. FINAL ATOMIC PARAMETERS (POSITIONAL $\times 10^4$, FOR H $\times 10^3$) AND THERMAL PARAMETERS (B_{eq} FOR NON-H $\times 10$, B_{iso} FOR H $\times 10$), WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	$B_{eq}(B_{iso})$/Å^2
C_1	3342(3)	1736(3)	6160(5)	32(1)
C_2	2311(3)	-1156(4)	3771(7)	51(1)
C_3	1553(3)	1027(4)	2513(6)	43(1)
C_4	4894(3)	2402(3)	9690(6)	37(1)
C_5	2801(3)	4101(3)	4248(6)	38(1)
C_6	1286(3)	4629(4)	7441(7)	49(1)
N_1	3198(2)	42(3)	5908(5)	39(1)
N_2	2577(2)	2262(3)	4445(4)	35(1)
N_3	4164(2)	2912(3)	7997(5)	40(1)
N_4	5560(3)	2089(3)	11281(5)	48(1)
O_1	1171(2)	- 598(3)	3318(5)	56(1)
O_2	1602(2)	4547(2)	4719(4)	43(1)
H_1	199(4)	- 232(5)	424(7)	43(9)
H_2	273(4)	- 89(5)	189(8)	61(10)
H_3	72(3)	146(4)	249(7)	33(8)
H_4	199(4)	86(5)	75(7)	48(9)
H_5	363(3)	484(4)	559(6)	29(7)
H_6	301(3)	431(4)	233(6)	27(7)
H_7	108(3)	343(4)	797(7)	35(8)
H_8	210(4)	551(4)	861(7)	40(9)
H_9	48(4)	502(5)	780(8)	52(10)
H_{10}	364(3)	38(4)	705(6)	26(7)

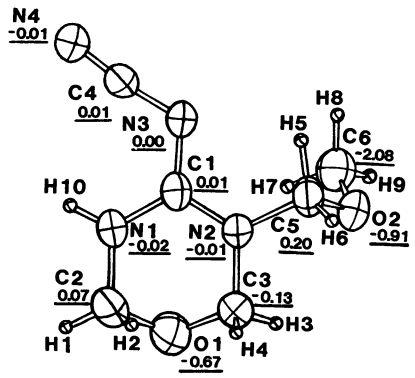

Fig. 1. The structure of CG-1Mcyc2F projected on the plane of the guanidine moiety composed of C_1, N_1, N_2, and N_3. Underscored numbers are heights in Å of the atoms above or below the plane.

acteristic of the structure which is composed of four nitrogen atoms (N_1, N_2, N_3, and N_4) and two carbon atoms (C_1 and C_4). Furthermore, two carbon atoms (C_2 and C_3) and one hydrogen atom (H_{10}) are placed near the plane. This planar structure is due to the triple bond character of the cyano group and to the resonated structure of the guanidine moiety and is similar to the molecular structure of CG.[4] The observed atomic distances for the cyanoimino group (1.308 Å (C_4–N_3) and 1.144 Å (C_4–N_4)) are in fair agreement with the previously predicted values,[5] 1.32 and 1.20 Å, but differ from those for the cyanoimino group in CG,[4] 1.28 and 1.22 Å. This difference in the atomic distances for the cyanoimino group between CG and CG-1Mcyc2F is probably due to the presence and absence of hydrogen bonds in CG and CG-1Mcyc2F, respectively. In CG, the terminal nitrogen of the cyanoimino group was reported to have three hydrogen bonds directed towards three amino groups in two adjacent molecules, while in CG-1Mcyc2F, most of the hydrogen atoms in the amino groups have already been substituted and the residual one hydrogen atom of H_{10} in the imino group is placed near the plane. The intra- and intermolecular distances and the bond angle of N_1–H_{10}– –X in CG-1Mcyc2F clearly indicate that there are no hydrogen bonds.

Table 2. Interatomic distances and angles for CG-1Mcyc2F

Bond distance	l/Å	Bond angle	ϕ/°	Bond angle	ϕ/°
C_1 N_1	1.336(5)	N_1-C_1-N_2	117.3(10)	O_2-C_6-H_7	109.1(21)
C_1-N_2	1.346(13)	N_1-C_1-N_3	124.4(8)	O_2-C_6-H_8	109.1(22)
C_1-N_3	1.323(20)	N_2-C_1-N_3	118.4(6)	O_2-C_6-H_9	113.9(25)
C_2-N_1	1.451(22)	N_1-C_2-O_1	108.5(8)	H_7-C_6-H_8	111.6(30)
C_2-O_1	1.402(9)	N_1-C_2-H_1	111.4(22)	H_7-C_6-H_9	106.6(32)
C_2-H_1	0.971(37)	N_1-C_2-H_2	108.9(19)	H_8-C_6-H_9	106.5(30)
C_2-H_2	1.085(41)	O_1-C_2-H_1	107.8(24)	C_1-N_1-C_2	120.9(8)
C_3-N_2	1.465(22)	O_1-C_2-H_2	95.3(26)	C_1-N_1-H_{10}	120.8(20)
C_3-O_1	1.388(10)	H_1-C_2-H_2	123.1(31)	C_2-N_1-H_{10}	118.3(19)
C_3-H_3	1.017(39)	N_2-C_3-O_1	110.4(8)	C_1-N_2-C_3	121.7(6)
C_3-H_4	1.026(39)	N_2-C_3-H_3	106.6(18)	C_1-N_2-C_5	122.0(10)
C_4-N_3	1.308(12)	N_2-C_3-H_4	108.8(19)	C_3-N_2-C_5	116.1(9)
C_4-N_4	1.144(11)	O_1-C_3-H_3	108.1(20)	C_1-N_3-C_4	118.5(6)
C_5-N_2	1.467(5)	O_1-C_3-H_4	104.6(23)	C_2-O_1-C_3	110.9(9)
C_5-O_2	1.407(8)	H_3-C_3-H_4	118.2(31)	C_5-O_2-C_6	113.8(10)
C_5-H_5	1.051(32)	N_3-C_4-N_4	174.5(3)		
C_5-H_6	1.029(33)	N_2-C_5-O_2	110.2(10)		
C_6-O_2	1.430(8)	N_2-C_5-H_5	108.7(22)		
C_6-H_7	1.010(36)	N_2-C_5-H_6	108.9(20)		
C_6-H_8	1.034(34)	O_2-C_5-H_5	112.4(21)		
C_6-H_9	0.987(44)	O_2-C_5-H_6	106.2(22)		
N_1-H_{10}	0.883(36)	H_5-C_5-H_6	110.4(25)		

The authors wish to express their hearty thanks to Professor Hayao Kobayashi of Toho University, for his kind support in the data collection on the Rigaku automated four-circle diffractometer at Toho University and computation.

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