The Reaction of *N″*-Cyanoguanidine with Formaldehyde. II. Bis(*N″*-carbamoylguanidino)methane or *N,N′*-Methylenebis[*N′*-(diaminomethylene)urea]

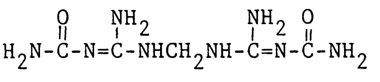
Ryuichi Shiba,* Miyuki Takahashi, Toichi Ebisuno,† and Michiaki Takimoto†
Department of Applied Science, Faculty of Technology, Tokyo Denki University, Kanda, Chiyoda-ku, Tokyo 101
†Department of Chemistry, Faculty of Science, Toho University, Miyama 2-2-1, Funabashi, Chiba 274

(Received August 6, 1987)

Synopsis. The condensation product in the reaction of *N″*-cyanoguanidine with paraformaldehyde under strongly acidic conditions was identified as *N,N′*-methylenebis[*N′*-(diaminomethylene)urea] by X-ray analysis. This structure agreed with that estimated from the ¹H NMR data.

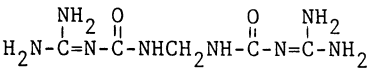
The resinous products from *N″*-cyanoguanidine (CG) and formaldehyde are useful as modifiers for urea- and melamine-formaldehyde resins,[1] sticking agents for dyes,[2] and commercial flocculants.[3] The reaction of CG with formaldehyde is, however, complicated under acidic conditions because of the simultanious structural conversion of CG into diaminomethyleneaminourea (DU).[4]

Spiethoff[5] has prepared a condensate of CG with paraformaldehyde in the presence of 30% hydrochloric acid and identified it as bis(*N″*-carbamoylguanidino)methane (**1**) on the basis of the infrared absorption bands at 1680 and 1740 cm^{-1}, which have been considered to be characteristic of the primary carbamoyl group:



$$\mathrm{H_2N-\overset{\overset{O}{\|}}{C}-N=\overset{\overset{NH_2}{|}}{C}-NHCH_2NH-\overset{\overset{NH_2}{|}}{C}=N-\overset{\overset{O}{\|}}{C}-NH_2}$$

(1)



$$\mathrm{H_2N-\overset{\overset{NH_2}{|}}{C}=N-\overset{\overset{O}{\|}}{C}-NHCH_2NH-\overset{\overset{O}{\|}}{C}-N=\overset{\overset{NH_2}{|}}{C}-NH_2}$$

(2)

The hydrochloride of the condensate was prepared according to the procedure of Spiethoff.[5] Elemental analysis: Found, C, 20.68; H, 4.92; N, 38.88; Cl, 24.22%: Calcd for $C_5H_{12}N_8O_2\cdot 2HCl$, C, 20.77; H, 4.88; N, 38.76; Cl, 24.52%. It showed the same melting point (230—232 °C) as has previously reported. Its infrared spectrum in the KBr pellet exhibited the same absorption bands at 1680 and 1740 cm^{-1}. The ¹H NMR spectrum of the free base of the condensate was measured in a DMSO-d_6 solution, with TMS as the internal standard, at 90 MHz on a JEOL FX90Q instrument. In addition to the signal of methylene protons (δ=4.30, t, 2H), two signals (δ=6.57, s, 8H, -N$\underline{\mathrm{H}}_2$; 6.18, t, 2H, -N$\underline{\mathrm{H}}$-) were observed. This observation was conflict with Spiethoff's identification and suggested that the condensate was not **1** but *N,N′*-methylenebis[*N′*-(diaminomethylene)urea] (**2**).

X-Ray analysis was employed in order to confirm the structure of **2**. As crystals of dihydrochloride of **2** were twinned, a crystal of the free base was prepared by passing it through a Dowex SBR column, followed by extraction with acetone and the cooling of the acetone solution.

The unit-cell parameters and intensity data for a single crystal (ca. 0.1×0.2×0.2 mm³) were measured on a Rigaku four-circle diffractometer AFC-6S with graphite-monochromatized Mo *K*α radiation (λ=0.7107 Å). Systematic absences led to the space group $P2_1/c$.

Crystal Data: $C_5H_{12}N_8O_2$, M.W.=216.21, monoclinic, space group $P2_1/c$, a=7.954(3), b=9.553(6), c=14.963(7) Å, β=123.76(3)°, V=945.2(9) Å³, D_c=1.52 g·cm^{-3}, Z=4 and μ(Mo *K*α)=1.1 cm^{-1}.

The intensity data were collected by the ω-2θ scan technique up to 2θ=60° with a scan rate of 4° min^{-1}. The intensity data were corrected to the F_o data in the usual manner. Absorption corrections were not applied. Reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the structure determination. The structure was solved by the direct method and refined by a block-diagonal least-squares procedure. All the calculations were carried out on a HITAC M-680H computer at the Computer Center of The University of Tokyo, using the local version of UNICS III.[6] All the scattering factors were taken from the International Tables for X-Ray Crystallography.[7] The final residual values for 1862 reflections were R=0.068 and R_w=0.075.

The final atomic parameters are listed in Table 1. The equivalent isotropic temperature parameters were defined by Hamilton.[8] The coordinate and isotropic temperature factors of hydrogen atoms, the anisotropic thermal parameters of the non-hydrogen atoms, and

Table 1. Final Atomatic Parameters (Positional ×10⁴) and Equivalent Isotropic Temperature Parameters (B_{eq}×10), with Their Estimated Standard Deviations in Parentheses

Atom	*x*	*y*	*z*	B_{eq}/Å²
O(1)	7204(4)	9549(3)	5855(2)	32(1)
O(2)	6661(4)	5605(3)	4907(2)	27(1)
N(1)	10222(4)	9014(3)	6141(2)	26(1)
N(2)	8699(5)	7186(4)	4853(3)	32(1)
N(3)	9685(4)	11271(3)	6354(2)	24(1)
N(4)	6688(5)	5921(4)	3365(3)	28(1)
N(5)	4675(6)	4815(4)	1754(3)	41(1)
N(6)	4376(7)	4151(5)	3136(3)	36(1)
N(7)	6442(5)	12304(4)	5611(3)	36(1)
N(8)	9451(3)	13603(3)	6531(3)	30(1)
C(1)	9793(6)	7540(4)	5985(3)	28(1)
C(2)	7306(5)	6175(4)	4400(3)	23(1)
C(3)	8902(5)	9948(4)	6097(3)	23(1)
C(4)	5279(5)	4949(4)	2795(3)	30(1)
C(5)	8465(5)	12356(4)	6163(3)	23(1)

Table 2. Selected Intermolecular Bond Lengths and Bond Angles, with Their Estimated Standard Deviations in Parentheses

Bond length	l/Å	Bond angle	ϕ/°
O(1)-C(3)	1.247(6)	C(1)-N(1)-C(3)	122.1(5)
O(2)-C(2)	1.253(6)	C(1)-N(2)-C(2)	123.4(14)
N(1)-C(1)	1.437(5)	C(3)-N(3)-C(5)	119.5(9)
N(1)-C(3)	1.352(5)	C(2)-N(4)-C(4)	119.6(15)
N(2)-C(1)	1.450(6)	N(1)-C(1)-N(2)	110.6(4)
N(2)-C(2)	1.336(6)	O(2)-C(2)-N(2)	120.9(9)
N(3)-C(3)	1.366(6)	O(2)-C(2)-N(4)	127.0(8)
N(3)-C(5)	1.338(8)	N(2)-C(2)-N(4)	112.3(16)
N(4)-C(2)	1.361(5)	O(1)-C(3)-N(1)	119.9(4)
N(4)-C(4)	1.335(5)	O(1)-C(3)-N(3)	128.0(5)
N(5)-C(4)	1.358(5)	N(1)-C(3)-N(3)	112.1(7)
N(6)-C(4)	1.328(8)	N(4)-C(4)-N(5)	115.7(16)
N(7)-C(5)	1.339(7)	N(4)-C(4)-N(6)	126.5(6)
N(8)-C(5)	1.338(5)	N(5)-C(4)-N(6)	117.7(12)
		N(3)-C(5)-N(7)	125.7(5)
		N(3)-C(5)-N(8)	116.5(12)
		N(7)-C(5)-N(8)	117.7(8)

the F_o-F_c tables have been deposited as Document No. 8799 at the Office of the Editor of the Bulletin of the Chemical Society of Japan. Selected bond lengths and bond angles are listed in Table 2, while a perspective drawing of the molecular structure of the condensate is shown in Fig. 1. The structure agrees with that estimated from the ^{1}H NMR data. These results clearly show that the structure of the condensate is not **1** but **2**.

Although dihydrochloride of **2** has absorption bands at 1680 and 1740 cm^{-1} in the infrared region, these are not necessarily assigned to the primary carbamoyl group, but perhaps to the stretching of the C=N and C=O of **2**. Under strongly acidic conditions, CG can be expected to be converted into DU by the hydration of the cyano group, and the resulting DU can be estimated to be hydroxymethylated with formaldehyde selectively on the amino group in the carbamoyl group, but not on the amino group in the diaminomethyleneamino group probably because of the protonated amino group in the diaminomethyleneamino group is less active with the protonated formaldehyde ($^+CH_2OH$) than that in the carbamoyl group.

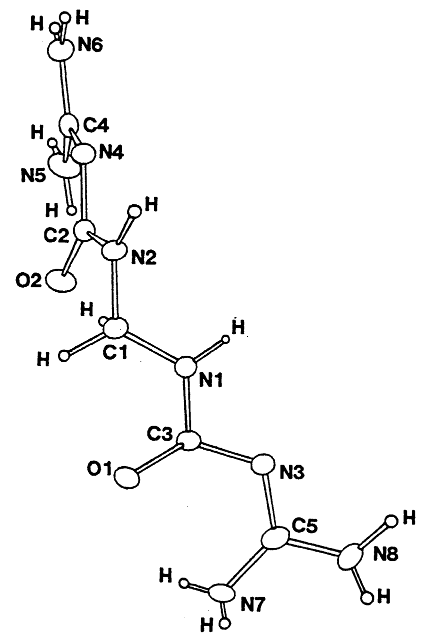


Fig. 1. A perspective drawing of the molecular structure of the condensate from N''-cyanoguanidine and paraformaldehyde projected on the plane at right angles to bc plane.

The authors wish to express their deep gratitude to Professor Hayao Kobayashi of Toho University for his kind support in the data collection and the computation.

References

1) K. Ripper, U. S. Patent 2286228 (1942); *Chem. Abstr.*, **36**, 7189^5 (1942).

2) L. Sellet and W. O. Dawson, U. S. Patent 2690434 (1954); *Chem. Abstr.*, **49**, 1370a (1955).

3) S. Sakai, *Kobunshi*, **8**, 612 (1959).

4) E. Yamada, *Kogyo Kagaku Zasshi*, **62**, 1161 (1959).

5) W.-D. Spiethoff, *Chem. Ber.*, **100**, 4050 (1967).

6) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, **55**, 69 (1979).

7) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV.

8) W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).