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A Model for Interactions of Amino Acid Side Chains with Watson-Crick Base Pair of Guanine and Cytosine. Crystal Structures of 9-(2-Carboxyethyl)guanine and Its Crystalline Complex with 1-Methylcytosine

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A new compound, 9-(2-carboxyethyl)guanine, was successfully synthesized and its crystalline complex with 1-methylcytosine was prepared, in order to investigate the protein-nucleic acid interactions involving guanine base. The crystal structures of 9-(2-carboxyethyl)guanine (cx^9G) and of the complex of cx^9G with 1-methylcytosine ($cx^9G:m^1C$) were determined by the X-ray analysis. Crystal data: cx^9G, $P2_1/c$, $a=12.221(3)$, $b=11.022(2)$, $c=6.961(2)$ Å, $\beta=100.22(2)°$; $cx^9G:m^1C$, $P\bar{1}$, $a=8.932(1)$, $b=12.370(1)$, $c=7.139(1)$ Å, $\alpha=85.01(1)$, $\beta=99.21(1)$, $\gamma=86.64(1)°$. In cx^9G, the carboxyl group is doubly hydrogen-bonded with N(2) and N(3) of the guanine moiety of the adjacent molecule, N(2)-H···O distance being 2.939(5) Å and N(3)···H-O 2.660(5) Å for N···O. In $cx^9G:m^1C$, the guanine moiety and 1-methylcytosine form a Watson-Crick base pair. The carboxyl group takes an O=C-OH antiperiplanar conformation and is hydrogen-bonded with N(7) of guanine in the adjacent base pair. This hydrogen bond distance is very short, 2.634(2) Å, though the unfavorable conformation of the carboxyl group. This may suggest the marked preference of the carboxyl group for N(7) of guanine in the Watson-Crick base pair. On the basis of the geometrical data found in the present crystals, some possible models of interactions were constructed and examined, for example, aspartic or glutamic acid residue in the major groove of double stranded DNA.

In order to understand the mechanism of the specific interactions between nucleic acid and protein, we have been engaged in studying on the elementary binding patterns between their components by X-ray analyses of the model crystals.[1–9)] But most of them are concerned with binary systems.[1–7)] As the structural basis of the interactions between protein and double stranded region of nucleic acid, the systems containing amino acid side chains and Watson-Crick base pairs are important. Two model crystals for the ternary systems of adenine–thymine–carbamoyl group[8)] and of adenine–uracil–carboxyl group[9)] have been reported, but no Watson-Crick base pair has been obtained.

On the other hand, model systems containing guanine base have been little studied because guanine derivatives are poorly soluble for any organic solvent and in addition appropriate guanine derivatives with amino acid side chains are not known. We have succeeded in synthesizing a new compound, 9-(2-carboxyethyl)guanine (cx^9G), which is a starting material to prepare model crystals covalently linked with amino acid and enables us to examine the interactions involving guanine base.

This paper describes the interaction modes between the Watson-Crick base pair of guanine–cytosine and amino acid side chains of glutamic acid and aspartic acid.

Experimental and Structure Determination

Materials. The reaction of 2-*N*-acetylguanine with β-propiolactone in the presence of 4-dimethylaminopyridine resulted in 2-carboxyethylation of the former. After purification on a silica gel column, the product was deacetylated with 6.0 equivalent of NaOH to give 9-(2-carboxyethyl)guanine (cx^9G). Colorless needle-like crystals of cx^9G were obtained from a water–acetic acid (1 : 1) solution. Complex of cx^9G and 1-methylcytosine was prepared in the dimethyl sulfoxide solution containing equimolar amounts of both components. Colorless plate-like crystals were deposited from the solution by the vapor diffusion method with ethyl acetate.

pKa Measurement. A mixture solution of 20.0 cm^3 of cx^9G (0.0050 mol dm^{-3}) and 2.0 cm^3 of NaOH (0.10 mol dm^{-3}) was titrated with HCl (0.10 mol dm^{-3}) and at each step the value of pH was recorded using Toshiba-Beckman pH meter. The p*K*a values were evaluated to be 4.1 for the carboxyl group and 2.5 for the guanine moiety from least-squares fitting.

X-Ray Work. Oscillation and Weissenberg photographs showed that the cx^9G crystals were twin in which the c axes of the twin components coincided but their b axes were antiparallel to each other and almost equal quantities of the components were included. Densities of the crystals were measure by the flotation method in a hexane and tetrachloromethane solution. Crystal data are listed in Table 1.

Data collection was carried out for both crystals on a Rigaku four-circle diffractometer with graphite-monochromated Cu $K\alpha$ radiation ($\lambda=1.54184$ Å). Five reference reflections monitored showed no significant intensity deterioration during the data collection. For the crystal of cx^9G, intensities of only one of the twin components were carefully measured; reflections with abnormally high background or unresolved reflections were excluded. Corrections were made for the Lorentz and polarization factors, but not for absorption effects. The standard deviations were estimated by the equation of $\sigma^2(F_o)=\sigma_p^2(F_o)+qF_o^2$, where q was derived from the variation of the monitored reflections and $\sigma_p(F_o)$ was due to counting statistics.[10)] The experimental conditions are summarized in Table 1.

Structure Determination. The structures were solved by the direct method with the program of MULTAN 78[11)] and the atomic parameters were refined by the full-matrix least-squares method. The quantity minimized in the refinement was $\sum\omega(|F_o|-|F_c|)^2$ with $\omega=1/\sigma^2(F_o)$. In the refinement, the zero-reflections with $|F_c|>F_{\rm lim}$ were included by assuming $F_o=F_{\rm lim}$ and $\omega=\omega(F_{\rm lim})$, $F_{\rm lim}$ being the observed threshold value (Table 1). All the hydrogen atoms found on difference maps were included in the refinement. Since the *hk*0 reflections of the crystal of cx^{9}G consist of the contributions from the both twin components, the layer scale of *hk*0 reflections was also refined. Initial value of $1/\sqrt{2}$ was evaluated by assuming 1 : 1 twin and it converged to be 0.6062 in the last some cycles of the refinement.

The space group of the complex was assumed to be $P\bar{1}$, as the normalized structure factor indicated the centrosymmetric distribution. The *R* value and the maximum shift of the parameters are given in Table 1. The final atomic parameters are given in Tables 2 and 3.[12] The atomic scattering factors were taken from Ref. 13.

Results and Discussion

Molecular and Crystal Structure of 9-(2-Carboxyethyl)-guanine. The bond distances and angles are shown in Fig. 1. The guanine moiety is not protonated by the carboxyl group, as expected from the lower dissociation constant of guanine moiety (p*K*a= 2.5). The dimensions of the carboxyl group are typical of the non-dissociated form, and the hydrogen atom of the carboxyl group appears on a difference map. The guanine moiety is planar within 0.020 Å, and its bond distances and angles are similar to those of the guanine derivatives such as 9-ethylguanine[14] and

TABLE 1. CRYSTAL DATA AND DETAILS OF EXPERIMENT AND ANALYSIS

Compound	$C_8H_9N_5O_3$ a)	$C_8H_9N_5O_3$-$C_5H_7N_3O$ b)
Formula weight	223.19	348.32
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	12.221(3)	8.932(1)
b/Å	11.022(2)	12.370(1)
c/Å	6.961(2)	7.139(1)
α/°		85.01(1)
β/°	100.22(2)	99.21(1)
γ/°		84.64(1)
Cell volume/Å^3	922.8(4)	770.9(1)
Z	4	2
D_x/g cm^{-3}	1.606	1.500
D_m/g cm^{-3}	1.56	1.49
Radiation	Cu $K\alpha$	Cu $K\alpha$
μ(calcd)/cm^{-1}	11.0	9.92
Crystal size/mm^3	0.3×0.1×0.05	0.4×0.2×0.1
Scan mode	ω	$\omega/2\theta$
Scan width /°(in ω)	1.6+0.14 tanθ	1.4+0.14 tanθ
Scan speed /°(in ω) min^{-1}	2	2
2θ range/°	3—125	3—127
No. of unique reflections	1409	2202
No. of zero-reflections	247	419
q	2.31×10^{-5}	5.38×10^{-3}
F_{lim}	2.312	0.968
R	0.074	0.044
No. of reflection for R	1126	1979
Maximum shift	0.8σ	0.2σ

a) 9-(2-carboxyethyl)guanine, b) 9-(2-carboxyethyl)-guanine : 1-methylcytosine complex.

TABLE 2. FRACTIONAL COORDINATES AND ISOTROPIC TEMPERATURE FACTORS OF 9-(2-CARBOXYETHYL)GUANINE

The *B* values accompanied by ⟨ ⟩ are the equivalent isotropic temperature factors calculated from anisotropic thermal parameters using the equation, $B=8\pi^2(U_1+U_2+U_3)/3$, where U_1, U_2, and U_3 are principal components of mean square displacement matrix $\boldsymbol{U}$. Values in ⟨ ⟩ are anisotropicity defined by $(\sum(B-8\pi^2U_i)^2/3)^{1/2}$ and those in ( ) are e.s.d.'s; they refer to last decimal places.

Atom	x	y	z	B/Å^2
N(1)	0.9363(2)	0.2522(3)	0.6940(5)	2.0<12>
C(2)	0.8321(3)	0.2237(3)	0.5951(6)	2.2<7>
N(2)	0.8054(3)	0.1057(2)	0.5719(5)	2.5<11>
N(3)	0.7563(2)	0.3070(3)	0.5235(5)	2.3<8>
C(4)	0.7966(3)	0.4222(3)	0.5518(7)	2.2<9>
C(5)	0.8993(3)	0.4578(3)	0.6507(7)	2.1<8>
C(6)	0.9773(3)	0.3690(3)	0.7305(7)	2.5<6>
O(6)	1.0718(2)	0.3848(2)	0.8249(4)	2.9<17>
N(7)	0.9081(2)	0.5822(3)	0.6503(6)	2.7<11>
C(8)	0.8116(3)	0.6220(3)	0.5571(7)	2.6<9>
N(9)	0.7400(2)	0.5271(3)	0.4898(5)	2.3<10>
C(10)	0.6234(3)	0.5362(3)	0.3912(8)	3.2<22>
C(11)	0.6042(3)	0.6359(4)	0.2432(7)	3.0<16>
C(12)	0.4828(3)	0.6463(3)	0.1552(7)	2.7<11>
O(13)	0.4582(2)	0.7516(3)	0.0716(5)	3.7<26>
O(14)	0.4163(2)	0.5660(2)	0.1616(5)	3.3<21>
H(1)	0.987(3)	0.182(3)	0.743(6)	1.5(10)
H(2A)	0.857(3)	0.045(3)	0.601(6)	1.3(10)
H(2B)	0.746(3)	0.069(3)	0.511(7)	3.1(12)
H(8)	0.792(3)	0.716(3)	0.522(6)	1.1(10)
H(10A)	0.595(3)	0.456(3)	0.312(7)	2.6(11)
H(10B)	0.572(3)	0.552(3)	0.506(7)	4.3(13)
H(11A)	0.646(3)	0.627(3)	0.144(6)	1.4(10)
H(11B)	0.635(3)	0.710(3)	0.293(6)	2.0(11)
H(13)	0.386(3)	0.758(4)	0.045(7)	5.1(13)

TABLE 3. FRACTIONAL COORDINATES AND ISOTROPIC TEMPERATURE FACTORS OF 9-(2-CARBOXYETHYL)GUANINE: 1-METHYLCYTOSINE COMPLEX

The *B* values accompanied by ⟨ ⟩ are the equivalent isotropic temperature factors. Details are given in Table 2.

Atom	x	y	z	B/Å^2
C(1')	1.0048(5)	0.8948(3)	0.2296(5)	4.9<8>
N(1')	0.9994(2)	0.8192(2)	0.3984(3)	3.7<8>
C(2')	0.9113(3)	0.7329(2)	0.3757(4)	3.6<9>
O(2')	0.8399(2)	0.7251(2)	0.2156(3)	4.7<23>
N(3')	0.9059(3)	0.6611(2)	0.5284(3)	3.7<12>
C(4')	0.9862(3)	0.6738(2)	0.6980(4)	4.1<13>
N(4')	0.9770(4)	0.6016(3)	0.8447(4)	5.8<30>
C(5')	1.0781(4)	0.7604(3)	0.7250(4)	4.7<18>
C(6')	1.0820(4)	0.8304(3)	0.5726(4)	4.5<15>
N(1)	0.7208(2)	0.4788(2)	0.4697(3)	3.1<10>
C(2)	0.6357(3)	0.4783(2)	0.2906(3)	2.9<8>
N(2)	0.6497(3)	0.5590(2)	0.1607(3)	3.8<21>
N(3)	0.5436(2)	0.4032(2)	0.2449(2)	2.83<90>
C(4)	0.5480(3)	0.3255(2)	0.3922(3)	2.8<5>
C(5)	0.6313(3)	0.3177(2)	0.5740(3)	2.9<9>
C(6)	0.7258(3)	0.3997(2)	0.6232(3)	3.1<11>
O(6)	0.8085(2)	0.4077(2)	0.7773(2)	4.3<21>
N(7)	0.6068(3)	0.2222(2)	0.6764(3)	3.5<12>
C(8)	0.5109(3)	0.1761(2)	0.5584(3)	3.7<12>
N(9)	0.4704(2)	0.2354(2)	0.3838(3)	3.0<9>
C(10)	0.3749(3)	0.2005(2)	0.2177(4)	3.4<7>
C(11)	0.4639(3)	0.1796(2)	0.0594(3)	2.9<7>
C(12)	0.5972(3)	0.0936(2)	0.1129(3)	2.8<10>
O(13)	0.6197(2)	0.0310(1)	0.2572(2)	3.82<147>
O(14)	0.6940(2)	0.0888(2)	-0.0086(3)	3.9<14>
H(1A')	1.074(5)	0.952(3)	0.261(5)	6.2(11)
H(1B')	0.906(4)	0.938(3)	0.182(5)	4.9(10)
H(1C')	1.036(4)	0.852(3)	0.127(6)	5.6(11)
H(4A')	1.028(4)	0.611(3)	0.952(6)	4.9(10)
H(4B')	0.914(5)	0.536(3)	0.821(5)	6.1(11)
H(5')	1.138(4)	0.765(2)	0.848(5)	4.0(8)
H(6')	1.145(4)	0.897(3)	0.570(4)	3.6(8)
H(1)	0.783(3)	0.537(2)	0.490(3)	1.0(5)
H(2A)	0.718(3)	0.609(2)	0.183(4)	1.4(6)
H(2B)	0.594(3)	0.564(2)	0.035(4)	2.9(7)
H(8)	0.464(3)	0.107(2)	0.582(4)	2.2(6)
H(10A)	0.333(3)	0.132(2)	0.263(4)	1.7(6)
H(10B)	0.289(3)	0.258(2)	0.176(4)	1.6(6)
H(11A)	0.396(3)	0.155(2)	-0.048(4)	2.3(6)
H(11B)	0.506(3)	0.248(2)	0.013(3)	1.0(5)
H(14)	0.661(4)	0.148(3)	-0.120(5)	5.3(9)

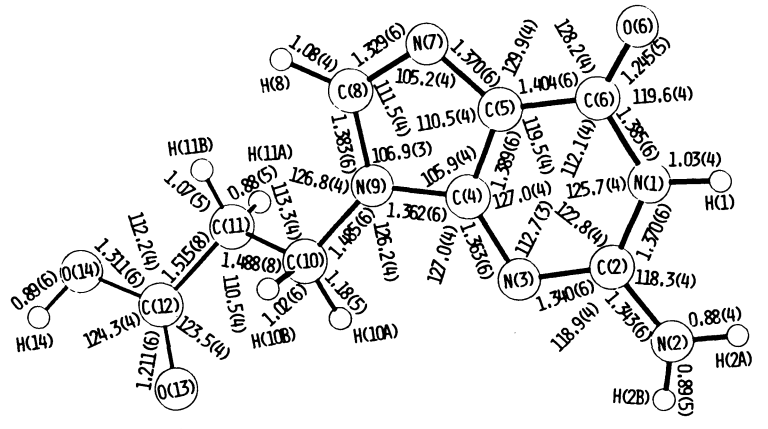

Fig. 1. Bond distances (l/Å) and angles (ϕ/°) in 9-(2-carboxyethyl) guanine. E.s.d.'s are shown in parentheses.

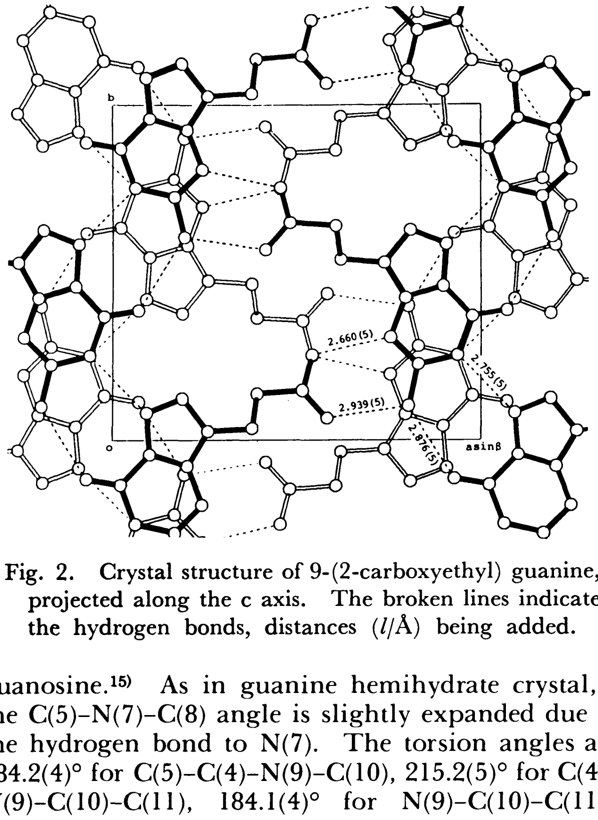

Fig. 2. Crystal structure of 9-(2-carboxyethyl) guanine, projected along the c axis. The broken lines indicate the hydrogen bonds, distances (l/Å) being added.

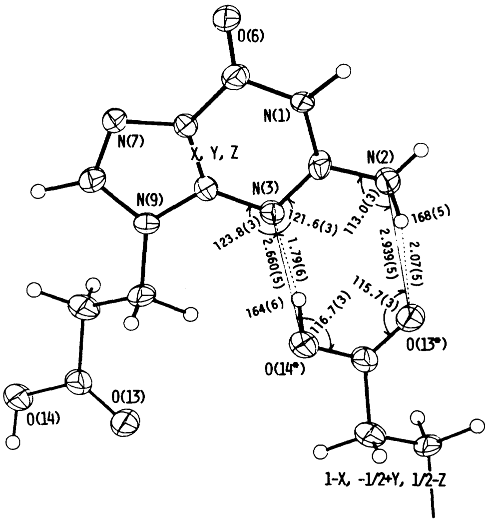

Fig. 3. A projective view of binding mode of the carboxyl group to the guanine moiety. Hydrogen bond distances (l/Å) and angles (ϕ/°) are shown with e.s.d.'s in parentheses. Thermal ellipsoids are drawn at 50% probability level.

guanosine.[15] As in guanine hemihydrate crystal,[16] the C(5)-N(7)-C(8) angle is slightly expanded due to the hydrogen bond to N(7). The torsion angles are 184.2(4)° for C(5)-C(4)-N(9)-C(10), 215.2(5)° for C(4)-N(9)-C(10)-C(11), 184.1(4)° for N(9)-C(10)-C(11)-C(12), and 162.4(4)° for C(10)-C(11)-C(12)-O(14).

The crystal structure and the hydrogen bond geometry are shown in Figs. 2 and 3. The carboxyl group of the adjacent molecule interacts with N(2) and N(3) of the guanine moiety through O···H-N and O-H···N hydrogen bonds. The dihedral angle between the least-squares planes of the purine ring and carboxyl group is 24.6(2)°. The guanine ring related by the 2_1 screw symmetry are linked by hydrogen bonds between N(1) and N(7) and between N(2) and O(6). These hydrogen bonds form a sheet parallel to the ab plane. There is no hydrogen bonds between the sheets.

Molecular and Crystal Structure of the Complex of 9-(2-Carboxyethyl)guanine and 1-Methylcytosine. The bond distances and angles are shown in Fig. 4. The carboxyl group takes an antiperiplanar O=C-O-H conformation.[17] This conformation is less stable by 2—4 kcal mol^{-1} than the synperiplanar form[18] and is usually found when the hydroxyl group participates in the intramolecular hydrogen bond.[19] The present crystal is a rare case where the hydroxyl group is hydrogen-bonded to the adjacent molecule. The bond distances of C=O and C-O of the carboxyl group are significantly different. The O=C-O angle is slightly contracted and the C-C-O angle is slightly expanded, in contrast to the synperiplanar O=C-O-H form. The geometry may be typical of the antiperiplanar carboxyl group without constrain of intramolecular hydrogen bonding.

The purine ring is planar within 0.030 Å. The bond distances and angles of the guanine moiety are similar to those of cx^{9}G in the preceding section. The torsion angles are 185.2(2)° for C(5)-C(4)-N(9)-C(10), 60.4(3)° for C(4)-N(9)-C(10)-C(11), 59.4(2)° for N(9)-C(10)-C(11)-C(12) and 12.7(3)° for C(10)-C(11)-C(12)-O(14).

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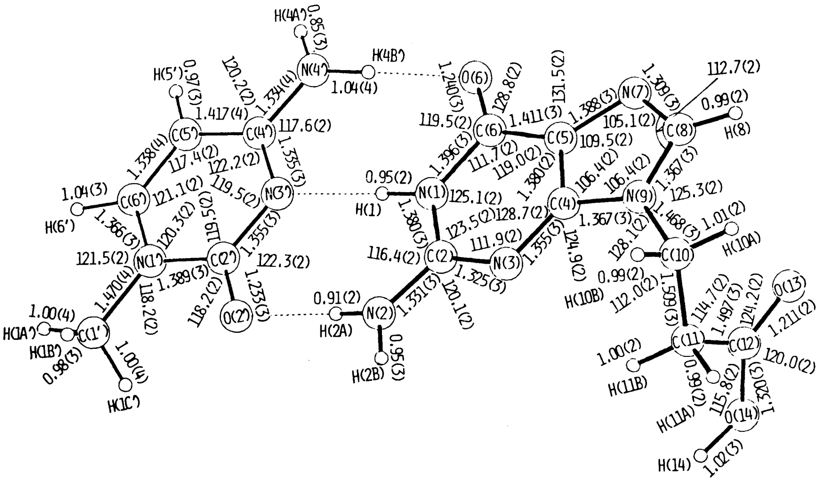

Fig. 4. Bond distances (l/Å) and angles (ϕ/°) in 9-(2-carboxyethyl)guanine : 1-methylcytosine complex. E.s.d.'s are shown in parentheses.

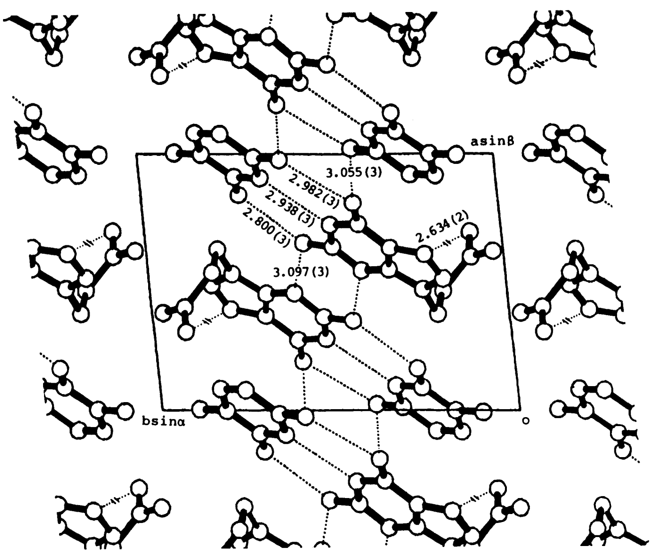

Fig. 5. Crystal structure of 9-(2-carboxyethyl) guanine: 1-methylcytosine complex projected along the c axis. Hydrogen bond distances (l/Å) are indicated.

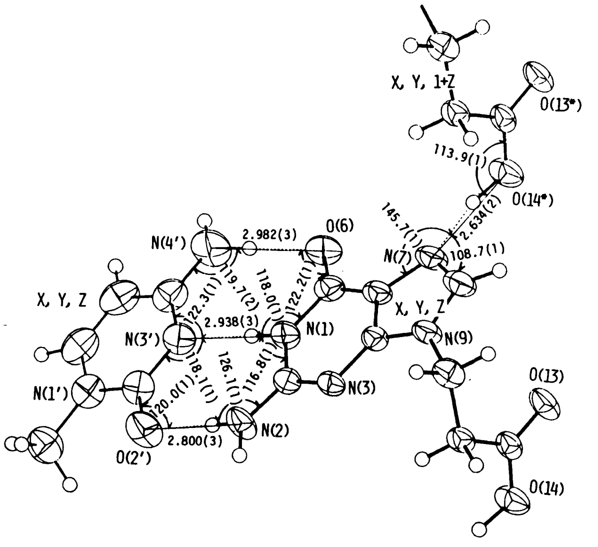

Fig. 6. A projective view of binding mode of the carboxyl group to the guanine-cytosine Watson-Crick base pair. Hydrogen bond distances (l/Å) and angles (ϕ/°) are shown with e.s.d.'s in parentheses. Thermal ellipsoids are drawn at 50% probability level.

The methylene chain is folded in contrast to that of cx^{9}G.

The bond distances and angles of 1-methylcytosine in the present complex are in good agreement with those of 1-methylcytosine[20] and cytidine.[21] The pyrimidine ring is essentially planar.

The crystal structure and hydrogen bond geometry are shown in Figs. 5 and 6. The guanine moiety and 1-methylcytosine form a Watson-Crick base pair through N(2)-H···O(2′), N(1)-H···N(3′), and O(6)···H-N(4′) hydrogen bonds. The hydrogen bond distances are similar to those found in the complexes of 9-ethylguanine: 1-methylcytosine,[22] 9-ethylguanine: 1-methyl-5-fluorocytosine,[22] 9-ethylguanine: 1-methyl-5-bromocytosine,[23] deoxyguanosine: 5-bromocytidine,[24] and some salts of guaninyl-3′,5′-cytidine.[25] The carboxyl group of the adjacent molecule interacts with N(7) of guanine in the Watson-Crick pair by O-H···N hydrogen bond. The hydrogen bond distance is very short, although the carboxyl group takes an unfavorable conformaion. This suggests that there is a marked preference between the carboxyl group and N(7) of guanine.

The carbonyl oxygen O(13) does not participate in any hydrogen bond; the closest contact 2.23(3) Å is observed with H(8) of the guanine moiety at ($-x$, $-y$, $1-z$). The base pairs form a ribbon extending along the [102] axis by the hydrogen bonds N(2)-H···N(3) and N(4′)-H···O(6) around inversion centers at (1/2, 1/2, 0) and (1, 1/2, 1). The O(2′) atom of 1-methylcytosine points to C(11) at ($1-x$, $1-y$, $-z$), the distance being 3.147(4) Å.

Hydrogen Bonding between the Watson-Crick Base Pair and Acidic Side Chain of Amino Acid. The present X-ray analyses of the model crystals are the first study on the interaction of amino acid side chain with guanine base, especially with guanine-cytosine Watson-

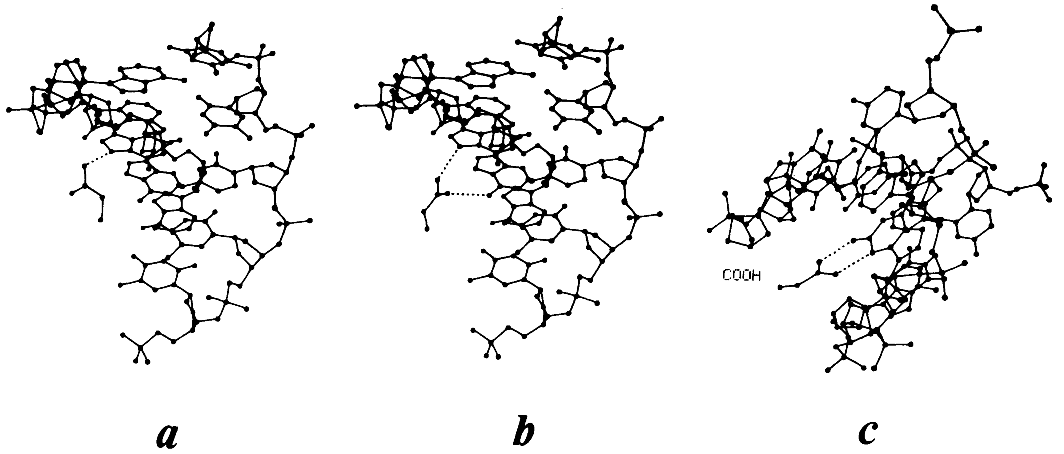

Fig. 7. Possible model fitting for the binding of the carboxyl group with guanine in the major and minor grooves of B-DNA. a) The carboxyl group takes an antiperiplanar conformation in the major groove, b) it is hydrogen-bonded with two adjacent base pairs in the major groove, and c) it is doubly hydrogen-bonded with guanine in the minor groove.

Crick pair. The model compound cx^{9}G contains the guanine moiety (pKa=2.5) and propionic acid moiety (pKa=4.1), the dissociation constants of which are comparable to those of guanosine nucleotide derivatives[26] and acidic side chains in the derivatives of amino acid or peptide,[27] respectively. So, the chemical behavior of each part of the present model compound is similar to that of the corresponding derivatives. Thus, the interaction found in this study may be realized in the protein-nucleic acid interactions.

The specificity in protein-nucleic acid interactions would arise from suitable combination of preferred hydrogen bonds between their components which are supported by the three-dimensional structure of macromolecules. It is important to examine if the hydrogen bonding found in the model crystals could be permitted for the bases in the particular secondary or tertiary structure of nucleic acids.

The carboxyl group was inserted in the major groove of B-DNA using the interaction geometry found here. Model fitting has been done successfully with the antiperiplanar O=C–O–H conformation (Fig. 7a). By the rotation of the carboxyl group around the O–C bond followed by slight translation, the other oxygen atom can form a hydrogen bond with the adjacent base in the same strand, as shown in Fig. 7b where adenine amino group is a binding site. Thus, the present hydrogen bond geometry may be an interaction model of guanine–cytosine base pair in the major groove with acidic side chain of proteins.

As the model for binding of the carboxyl group in the minor groove, the double hydrogen bonds with N(2) and N(3) of guanine, found in the crystal of cx^{9}G, might be useful, because the formation energy of this type is greater than any other double hydrogen bonds ($\Delta H_f = -15.0$ kcal mol^{-1} calculated by the CNDO/2 method[28] while that for the Watson-Crick pairing is -18.2 kcal mol^{-1}). Although this groove is rather tight, the model fitting was also successful with slight changes of the binding geometry, as shown in Fig. 7c. As any double hydrogen bonds of carboxyl group in the minor groove can not be set up for the other nucleic acid bases, the present model could take a part in recognition of particular base sequences.

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