scence can be identified. The fact that the vibronic bands are more pronounced in the cationic fluorescence indicates larger reorientation of the ionized substituent group in the excited-state configuration, involving nuclear motion and hence dissipation of energy. However, in the ionic fluorescence spectrum of 1,3-DHN a weak band is found at 410 nm, which probably arises from a separate electronic transition rather than owing to vibrational fine structure. Furthermore, it can be seen that the fluorescence of the cations shows a larger red shift compared to the absorption. This indicates a greater degree of interaction between the ionic substituent group and the aromatic ring in the excited state than in the ground state. In such a case, the energy of vibrational relaxation in the excited state will be greater than that in the ground state. Consequently, the shifting effect of the ionic substituent upon the fluorescence spectrum will be greater than its shifting effect upon the absorption spectrum relative to the spectrum of the parent molecule. In the case of 2,3-DHN and 2,7-DHN one expects intense fluorescence due to strong horizontal polarization of two substituted groups. It is worth noting that the major ionic emission maximum of 2,7-DHN is more redshifted in comparison to that of 2,3-DHN. This difference could be due to the proximity of –OH groups at positions 2 and 3, which could give rise to intramolecular hydrogen bonding.

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Crystal structure of hexanediamine–glutamic acid complex

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Polyamines are some of the most important and ubiquitous small molecules that modulate several functions of plant, animal and bacterial cells. Despite the simplicity of their chemical structure, their specific interactions with other biomolecules cannot be explained solely on the basis of their electrostatic properties. To evolve a structural understanding on the specificity of these interactions it is necessary to determine the structure of complexes of polyamines with other, representative biomolecules. This paper reports the structure of the 1:2 complex of hexanediamine and L-glutamic acid. The complex crystallizes in the monoclinic space group $P2_1$ with $a=5.171(1)$ Å, $b=22.044(2)$ Å, $c=10.481(2)$ Å and $\beta=104.51(1)°$. The structure was refined to an R factor of 6.6%. The structures of these complexes not only suggest the importance of hydrogen-bonding interactions of polyamines but also provide some insight into other complementary interactions probably important for the specificity of biomolecular interactions.

POLYAMINES modulate a variety of cellular functions in plants, animals and bacteria[1]. They are integral components of tRNA and other anionic molecules. They also appear to interact with membrane components in several plant tissues, and such interactions result in modified permeability and delayed senescence of extracted leaves[2]. Considering the simplicity of the chemical structure of polyamines, it is surprising that a clear understanding of their interactions does not exist. Part of the reason is the nonavailability of the molecular structures of the complexes of these amines with other ubiquitous biomolecules. To provide information on these interactions, we have earlier determined and reported structures of complexes of putrescine with glutamic acid[3] and aspartic acid[4]. In this paper we report the structure of hexanediamine–glutamic acid complex, and discuss the nature of the interactions of the longer amine hexanediamine with glutamic acid in the context of the structures reported earlier.

Crystals of 2:1 complex of L-glutamic acid and hexanediamine were obtained by slow diffusion of propanol into an aqueous solution of the complex. On X-ray examination, the crystals were found to be monoclinic $P2_1$ with $a=5.171(1)$ Å, $b=22.044(2)$ Å, $c=10.181(2)$ Å, and $\beta=104.51(1)°$. Two glutamic acid and one hexanediamine molecules, when assumed to be present in the crystal asymmetric unit, give a calculated density of 1.21 g cm^{-3}. This value is less than the density of the crystals of complexes of glutamic and aspartic acid with putrescine.

X-ray diffraction intensities were recorded to 0.84-Å resolution using an Enraf–Nonius 4-circle diffractometer by $w/2\theta$ scan. The X-ray source was a microfocus sealed tube with a molybdenum anode ($\lambda=0.7107$ Å). Reflections with $k\geqslant 0$, $l\geqslant 0$ were recorded, resulting in a total of 2028 unique measurements. The reflection intensities were corrected for Lorentz and polarization factors.

The structure was solved by direct methods using the program MULTAN[5]. After initial refinement of C, N and O atoms of the complex, using a block-diagonal structure factor least-squares program originally written

by R. Shiano, examination of the difference fourier map suggested the presence of two water molecules in the asymmetric unit. Re-examination of the E-maps obtained by direct methods also revealed peaks indicating water molecules. The density of the crystal including the water molecules is 1.37 g cm^{-3}, which agrees favourably with the density of the other two complexes. The refinement converged to an R index of 6.6% for the 1143 reflections with $F_0 > 3\sigma|F_0|$. The final refinement included the positional and anisotropic thermal parameters of C, N and O atoms and the positional and isotropic thermal parameters of H atoms.

The crystal asymmetric unit consists of two glutamic acid, one hexanediamine and two water molecules. The two glutamic acid molecules have different conformations. Table 1 gives the coordinates and equivalent temperature factors of all the non-hydrogen atoms at the end of refinement; Tables 2 and 3 give the bond lengths and bond angles of the two glutamic acid molecules; Table 4 gives the bond lengths and bond angles of hexanediamine; Table 5 gives the hydrogen-bonding pattern observed in the structure; Table 6 gives the torsion angles of hexanediamine; and Table 7 gives a comparison of torsion angles of the two different glutamic acid molecules in the present structure with those of the unprotonated α (ref. 6) and β (ref. 7) forms,

Table 1. Positional parameters (× 10,000) and equivalent temperature factors of non-hydrogen atoms. The estimated standard deviations (for parameters refined) are given in parentheses

Atom	X	Y	Z	Equivalent B
N1	−472(22)	−175	−1938(10)	2.4(3)
O1	5554(18)	−925(5)	−1396(10)	3.4(3)
O2	1562(19)	−1331(5)	−1592(12)	3.8(3)
C1	3148(25)	−900(6)	−1332(14)	2.4(4)
C2	2192(24)	−264(7)	−952(14)	2.5(4)
C3	1653(28)	−300(7)	440(13)	3.1(4)
C4	4117(29)	−433(6)	1607(13)	2.6(4)
C5	6222(28)	73(6)	1956(14)	2.6(4)
O6	8373(17)	−55(5)	2764(9)	3.1(3)
O7	5558(20)	590(5)	1463(10)	3.8(3)
N11	2004(21)	850(5)	3459(11)	2.6(3)
O11	4459(17)	1899(5)	3416(10)	3.2(3)
O12	1061(19)	2448(4)	3737(11)	3.3(3)
C11	2246(25)	1962(6)	3659(12)	2.3(4)
C12	711(23)	1385(7)	3890(13)	2.3(4)
C13	525(24)	1329(7)	5357(15)	2.8(4)
C14	3038(27)	1405(7)	6441(14)	2.9(4)
C15	5065(27)	905(7)	6748(13)	2.7(4)
O16	4765(21)	456(5)	5947(10)	3.9(3)
O17	6999(19)	947(5)	7788(10)	3.8(3)
N21	3914(21)	3481(5)	3804(12)	2.9(3)
C22	6781(27)	3419(7)	4627(14)	3.0(4)
C23	6894(25)	3170(7)	5996(15)	2.7(4)
C24	9783(28)	3127(8)	6875(14)	3.6(5)
C25	10011(29)	2852(7)	8260(14)	3.2(4)
C26	12873(28)	2797(7)	9107(15)	3.1(4)
C27	13022(26)	2577(7)	10531(13)	2.4(4)
N28	15854(20)	2513(5)	11319(11)	2.0(3)
O31	7838(22)	1485(5)	305(10)	4.0(3)
O32	2203(19)	4574(5)	4794(10)	3.4(3)

Table 2. Bond lengths (Å) of glutamic acid molecules in hexanediamine–glutamic acid complex

Bond	Glu I	Glu II
N1–C2	1.50(01)	1.47(01)
O1–C1	1.26(01)	1.23(02)
O2–C1	1.23(01)	1.25(02)
C1–C2	1.53(02)	1.54(02)
C2–C3	1.51(01)	1.52(02)
C3–C4	1.53(02)	1.48(01)
C4–C5	1.53(02)	1.50(02)
C5–O6	1.24(01)	1.26(02)
C5–O7	1.27(01)	1.26(01)

Table 3. Bond angles (deg) of glutamic acid molecules in hexanediamine–glutamic acid complex

Angle	Glu I	Glu II
O2–C1–O1	124.2	127.0
O2–C1–C2	119.8	114.7
O1–C1–C2	115.9	118.3
N1 C2–C3	106.0	111.7
N1–C2–C1	105.9	108.8
C1–C2–C3	111.3	112.0
C2–C3–C4	114.6	117.3
C3–C4–C5	116.2	120.5
O6–C5–C4	116.9	118.2
O7–C5–C4	117.3	119.0
O6–C5–O7	125.5	122.7

Errors in bond angles are approximately one degree

Table 4. Bond lengths and bond angles of hexanediamine.

Bond	Bond length (Å)
N21–C22	1.51(01)
C22–C23	1.48(02)
C23–C24	1.53(02)
C24–C25	1.51(02)
C25–C26	1.52(01)
C26–C27	1.51(02)
C27–N28	1.49(01)
Angle	**Angle (deg)**
N21–C22 C23	110.7
C22 C23–C24	111.9
C23–C24 C25	113.8
C24–C25 C26	113.5
C25–C26 C27	112.2
C26–C27–N28	110.7

Errors in angles are approximately one degree

that of the protonated[8] form, and that of glutamic acid complexed to putrescine.

Hexanediamine is in its most favourable *trans* conformation. The only other two aliphatic primary diamine structures reported so far are those of the inorganic salts of putrescine[9,10] and 1,3-diaminopropane[11]. In crystal structures of the chloride salts, these molecules occupy special positions and have completely extended conformations. The special position constrains only the central bond to have a strict *trans* geometry,

Table 5. Hydrogen-bonding pattern in hexanediamine–glutamic acid complex.

Atoms A	Atoms B	A–B length (Å)	H——A–B angle	Symmetry
N1	O17	2.77	15.4	$X-1,Y,Z-1$
N1	O1	2.80	3.0	$X-1,Y,Z$
N1	OW2	2.87	20.0	$-X,Y-0\,5,-Z$
N11	O6	2.70	15.5	$X-1,Y,Z$
N11	O7	3.11	30 0	X,Y,Z
N11	O16	2.71	26.8	X,Y,Z
N21	O12	2.70	10.1	X,Y,Z
N21	OW2	2.84	10.0	X,Y,Z
N21	O1	2.85	5.0	$-X+1,0.5+Y,-Z$
N28	O11	2.77	16.7	$1+X,Y,1+Z$
N28	O2	2 86	8.1	$-2+X,0.5+Y,1-Z$
N28	OW1	2.79	12.3	$1+X,Y,1+Z$
OW1	O7	2.71	----	X,Y,Z
OW1	O17	2.75	----	$X,Y,Z-1$
OW2	O6	2.70	----	$-X+1,0.5+Y,-Z+1,$
OW2	O16	2.72	----	$-X+1,0.5+Y,-Z+1$

Table 6. Torsion angles of hexanediamine.

Torsion angle	Angle (degrees)
N21–C22–C23–C24	−177
C22–C23–C24–C25	−177
C23–C24–C25–C26	178
C24–C25–C26–C27	175
C25–C26–C27–N28	178

although all the bonds are found to have *trans* configuration. The only exception is that of putrescine phosphate[10], in which putrescine has *trans-gauche* conformation. However, in this structure, putrescine occupies a crystallographic centre of symmetry, leading to *trans* geometry for the central bond. All protons of the primary amines in the three structures are involved in hydrogen bonds. These observations suggest that the most favourable conformation of the aliphatic primary amines is the extended one. All-*trans* conformation is favoured owing to both steric factors and electrostatic repulsion between the protonated amino groups. As the length of the aliphatic backbone increases, the electrostatic repulsion probably plays a less important role. The energy required for a *trans–gauche* conformational change is only of the order of hydrogen-bonding or crystal-packing energy. It might be anticipated that *trans–gauche* conformational change is energetically less expensive in longer amines compared to that in the shorter animals.

Comparison of the torsion angles of the two glutamic acid molecules in this structure with those in the putrescine–glutamic acid complex reveals some interesting differences. In the complex with putrescine[3], the two crystallographically independent glutamic acid molecules have nearly identical backbone structure, while the orientations of the carboxyl groups are different. The changes in the conformation probably result from asymmetric crystal-packing forces on the two molecules. In the present case the Cα–Cβ–Cγ–Cδ torsion angle of one of the glutamic acids has a *gauche* conformation (70.6°). This is not observed in the protonated form of glutamic acid or in the two glutamic acid molecules in the asymmetric unit of the complex with putrescine. However, the α-form of glutamic acid[6] has a similar *gauche* conformation. Another novel feature of the glutamic acid molecules of this complex, which is distinct from the earlier structures, is the presence of an intramolecular hydrogen bond between the α-amino group and the side-chain carboxyl group.

All the amino groups make three hydrogen bonds as in the case of the other two structures. The presence of two water molecules has increased the number of hydrogen bonds contributing to crystal stability. The hydrogen atoms associated with the water molecules could not be located in the difference fourier map and hence were not considered in deducing hydrogen-bonding patterns. The hydrogen bonds involving water-oxygen atoms were inferred on the basis of a limiting donor–acceptor distance of $\leqslant 3.2$ Å. Water molecules participate both as donors and acceptors of hydrogen bonds, leading to both N–H . . . O- and O–H . . . O-type hydrogen bonds. There is, however, no water–water hydrogen bonding observed, and both the water oxygens make at least one hydrogen bond with the hexanediamine.

The crystal structure of putrescine–glutamic acid complex does not have water molecules. The hydrogen-bonding requirements of the amino group are satisfied by the acceptor groups of glutamic acid. The similar molecular dimensions of putrescine and glutamic acid

Table 7. Comparison of torsion angles (deg) of different glutamic acid forms.

Torsion angle	α-Form	β-Form	Protonated	Complex-I Glu-I	Complex-I Glu-II	Present structure Glu-I	Present structure Glu-II
N C C O(1)	−50	−42	161	168	156	134	−12
N C C O(2)	130	141	−21	−11	−24	−43	166
N C C C	178	−51	−69	65	63	178	73
Cα–Cβ Cγ–Cδ	68	−73	−173	−179	175	71	−178
C C C O(6)	74	19	15	9	−53	−171	10
C C C O(7)	−105	−161	−167	176	128	14	−170

Errors in angles are of the order of one degree.
Complex-I: Putrescine glutamic acid complex.

allow formation of these hydrogen bonds without distortions requiring large energy changes. In contrast, owing to the greater length of hexanediamine, it is unlikely that a similar hydrogen-bonding pattern could be formed without excessive distortion of hexanediamine. Perhaps for this reason, the hydrogen-bonding requirement of the primary amines is satisfied by the inclusion of water molecules.

Examination of the crystal packing (Figure 1) suggests channels for water molecules along the *a*-axis. Hexanediamine molecules form a sheet parallel to the *ab* plane. Between two such layers related by the screw symmetry parallel to the *b*-axis, two distinct sheets of glutamic acid molecules are stacked such that the polar groups of glutamic acid as well as the amine groups cluster around the water molecules. The apolar neutral carbon atoms of hexanediamine molecules make van der Waals contacts with layers of glutamic acid on either side, thus contributing to the stability of the crystal packing.

In the putrescine–aspartic acid structure, the packing diagrams indicated layers of hydrophobic and hydrophilic groups. This feature is absent in both the putrescine–glutamic acid structure and the present structure. The same number of carbon atoms separate the carboxyl oxygens in aspartic acid and the amino groups in putrescine. However, in glutamic acid the carboxyl oxygens are separated by five carbon atoms, while the amino groups in putrescine and hexanediamine are separated by four and six carbon atoms respectively. It is likely that the layered structure provides the most efficient packing only when the dimensions of the two molecular species of the complex are similar. Hence it might be anticipated that the crystal structure of cadaverine–glutamic acid complex will exhibit a layered structure similar to that of putrescine–aspartic acid complex. The structure of these complexes appears to suggest the subtle mechanisms by which specificity of recognition is achieved in interactions between biomolecules.

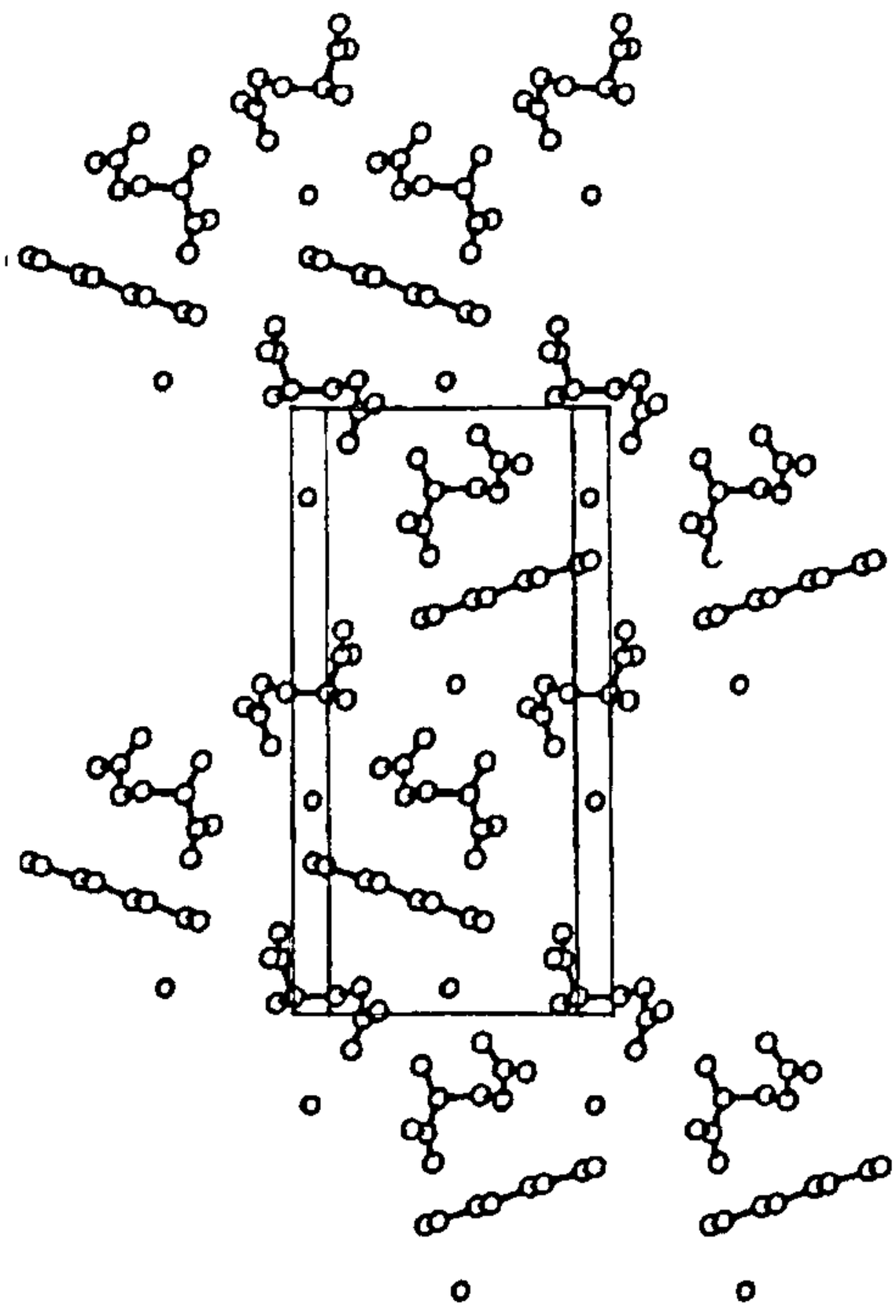

Figure 1. Packing diagram of hexanediamine–glutamic acid complex as viewed down the *a*-axis.

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