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, $c=10.181(2)$ Å and $\beta=104.51(1)^\circ$. 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 $\beta=104.51(1)^\circ$. 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 $k\geq 0$, $l\geq 0$ 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