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X-ray Studies on Crystalline Complexes Involving Amino Acids and Peptides. XXIII. Variability in Ionization State, Conformation and Molecular Aggregation in the Complexes of Succinic Acid with DL- and L-Lysine

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Abstract

Crystalline complexes of succinic acid with DL- and L-lysine have been prepared and analysed by X-ray diffraction. DL-Lysine complex: $C_6H_{15}N_2O_2^+.\frac{1}{2}C_4H_4O_4^{2-}.\frac{1}{2}C_4H_6O_4$, $M_r = 264{\cdot}2$, $P\bar{1}$, $a = 5{\cdot}506\ (4)$, $b = 8{\cdot}070\ (2)$, $c = 14{\cdot}089\ (2)$ Å, $\alpha = 92{\cdot}02\ (1)$, $\beta = 100{\cdot}69\ (3)$, $\gamma = 95{\cdot}85\ (3)^\circ$, $Z = 2$, $D_x = 1{\cdot}44$ g cm^{-3}, $R = 0{\cdot}059$ for 2546 observed reflections. Form I of the L-lysine complex: $C_6H_{15}N_2O_2^+.C_4H_5O_4^-$, $M_r = 264{\cdot}2$, $P1$, $a = 5{\cdot}125\ (2)$, $b = 8{\cdot}087\ (1)$, $c = 8{\cdot}689\ (1)$ Å, $\alpha = 112{\cdot}06\ (1)$, $\beta = 99{\cdot}08\ (2)$, $\gamma = 93{\cdot}77\ (2)^\circ$, $Z = 1$, $D_m = 1{\cdot}34\ (3)$, $D_x = 1{\cdot}34$ g cm^{-3}, $R = 0{\cdot}033$ for 1475 observed reflections. Form II of the L-lysine complex: $C_6H_{15}N_2O_2^+.\frac{1}{4}C_4H_4O_4^{2-}.\frac{1}{4}C_4H_6O_4.\frac{1}{4}(C_4H_5O_4\cdots H\cdots C_4H_4O_4)^2$, $M_r = 264{\cdot}2$, $P1$, $a = 10{\cdot}143\ (4)$, $b = 10{\cdot}256\ (2)$, $c = 12{\cdot}916\ (3)$ Å, $\alpha = 105{\cdot}00\ (2)$, $\beta = 99{\cdot}09\ (3)$, $\gamma = 92{\cdot}78\ (3)^\circ$, $Z = 4$, $D_m = 1{\cdot}37\ (4)$, $D_x = 1{\cdot}38$ g cm^{-3}, $R = 0{\cdot}067$ for 2809 observed reflections. The succinic acid molecules in the structures exhibit a variety of ionization states. Two of the lysine conformations found in the complexes have been observed for the first time in crystals containing lysine. Form II of the L-lysine complex is highly pseudosymmetric. In all the complexes, unlike molecules aggregate into separate alternating layers. The basic element of aggregation in the lysine layer in the complexes is an *S*2-type head-to-tail sequence. This element combines in different ways in the three structures. The basic element

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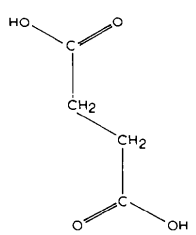
of aggregation in the succinic acid layer in the complexes is a hydrogen-bonded ribbon. The ribbons are interconnected indirectly through amino groups in the lysine layer.

Introduction

We have been pursuing a programme of X-ray studies on crystalline complexes involving amino acids and peptides in order to explore, at atomic resolution, the geometrical features of biologically significant interactions (Vijayan, 1983, 1988). The aggregation and the interaction patterns elucidated during the course of these investigations have been found to be relevant to chemical evolution with particular reference to prebiotic polymerization and chiral effects (Vijayan, 1980, 1988; Suresh & Vijayan, 1983, 1985; Vijayan & Suresh, 1985; Suresh, Ramaswamy & Vijayan, 1986; Soman, Ramakrishnan, Row & Vijayan, 1990). The current focus of the programme involves complexes between amino acids and simple organic molecules that are believed to have existed in the prebiotic milieu (Soman, Rao, Radhakrishnan & Vijayan, 1989; Prasad & Vijayan, 1990). The aggregation and the interaction patterns observed in such complexes could contribute to the understanding of the self-assembly processes that might have led to the emergence of the primitive multi-molecular systems. Succinic acid (1) is among the organic compounds found almost invariably in simulated prebiotic experiments (Miller & Orgel, 1974) and in carbonaceous chondrites (Kvenvolden, Lawless & Ponnamperuma, 1971). Here we report the crystal structures of the complexes of this compound with DL- and L-lysine.



(1)

Experimental

Crystals of the complexes were grown by diffusion of ethanol into aqueous solutions of succinic acid and the amino acid in 2:1 molar proportion. The complex involving DL-lysine was highly hygroscopic and hence the crystals were mounted in thin-walled glass capillaries for X-ray work; the density of these crystals could not be measured. Two forms of the L-lysine complex were obtained depending upon the concentration of the solutions used. The densities of the crystals were measured using flotation in a mixture of benzene and carbon tetrachloride. The space group and the unit-cell dimensions were determined from oscillation and Weissenberg photographs. The unit-cell parameters were subsequently refined on a CAD-4 diffractometer. Details of data collection from the crystals are given in Table 1 along with the refinement parameters.

Table 1. *Details of data collection and refinement parameters*

	DL-Lysine complex	L-Lysine complex form I	L-Lysine complex form II
Radiation used	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (cm $^{-1}$)	7·6	7·1	7·3
Crystal size (mm)	0·30 × 0·35 × 0·60	0·14 × 0·20 × 0·32	0·10 × 0·10 × 0·37
Method of measuring intensities	ω–2θ	ω–2θ	ω–2θ
Number and θ range ( ) of reflections used for refining lattice parameters	25 12 19	25 8 22	25 6 18
Maximum Bragg angle ( )	30	28	24
Ranges of			
h	0 to 7	0 to 6	0 to 11
k	−11 to 11	−10 to 10	−11 to 11
l	−19 to 19	−11 to 11	−14 to 14
ΔI for standard reflections (%)	1·5	0·7	2·4
Number of reflections measured	2978	1862	4572
Number of unique reflections with $I > 2\sigma(I)$	2546	1475	2809
R_{int}	0·016	0·008	0·012
R [reflections with $I > 2\sigma(I)$]	0·059	0·033	0·067
wR [reflections with $I > 2\sigma(I)$]	0·069	0·039	0·070
$(\Delta/\sigma)_{max}$	0·050	0·311	0·496
$\Delta\rho_{max}$ (e Å $^{-3}$)	0·35	0·16	0·39
$\Delta\rho_{min}$ (e Å $^{-3}$)	−0·52	−0·18	−0·33
Weighting function	$[\sigma^2(F_o) + 0{\cdot}005129F_o^2]^{-1}$	$[\sigma^2(F_o) + 0{\cdot}001580F_o^2]^{-1}$	$[\sigma^2(F_o) + 0{\cdot}000534F_o^2]^{-1}$
Number of parameters refined	243	240	646

The DL-lysine complex and form I of the L-lysine complex were solved using the program *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1984) whereas the program *SHELX*86 (Sheldrick, 1986) was used to solve form II of the L-lysine complex. The refinements, using *SHELX*400, of the first two structures were uneventful. The non-H atoms were refined anisotropically and the H atoms, located from difference Fourier maps using geometrical considerations, isotropically. During the refinement of form II of the L-lysine complex, the bond lengths in the side chain of one of the four crystallographically independent molecules deviated from standard values. Although difference Fourier maps, including those with the relevant atoms omitted from phasing, were carefully examined, distinct multiple conformations could not be assigned to the side chain. Disorder, which presumably exists, probably involves small differences in atomic positions within the same unique conformation. Therefore, these bond lengths, four in number, were restrained during the refinement. The H atoms were fixed geo-

Table 2. *Positional parameters* (× 10^4) *and equivalent isotropic temperature factors of non-*H *atoms in the* DL-*lysine complex*

Estimated standard deviations are given in parentheses.

	x	y	z	B_{eq}(Å^2)
N(1)	7686 (4)	5651 (3)	8784 (2)	1·90 (5)
O(1)	2762 (3)	5548 (3)	8788 (2)	2·77 (5)
O(2)	3478 (4)	7148 (3)	10147 (1)	2·66 (5)
C(1)	4122 (4)	6537 (3)	9424 (2)	1·84 (6)
C(2)	6780 (4)	7049 (3)	9284 (2)	1·77 (5)
C(3)	6837 (5)	8628 (3)	8715 (2)	2·19 (6)
C(4)	9419 (5)	9334 (3)	8564 (2)	2·23 (6)
C(5)	9275 (5)	10955 (3)	8047 (2)	2·28 (6)
C(6)	11732 (5)	11623 (3)	7796 (2)	2·19 (6)
N(7)	11435 (5)	13067 (3)	7174 (2)	2·51 (6)
O(11)	5870 (4)	4253 (3)	6738 (2)	3·67 (6)
O(12)	8958 (5)	6149 (3)	6728 (2)	4·03 (7)
C(13)	7026 (5)	5279 (3)	6292 (2)	2·25 (6)
C(14)	6272 (5)	5442 (4)	5220 (2)	2·20 (6)
O(21)	985 (4)	8139 (3)	4759 (2)	3·47 (6)
O(22)	2232 (5)	8209 (3)	6351 (2)	4·18 (7)
C(23)	2462 (5)	8646 (3)	5482 (2)	2·49 (7)
C(24)	4759 (6)	9830 (4)	5498 (2)	2·60 (7)

Table 3. *Positional parameters* (× 10^4) *and equivalent isotropic temperature factors of non-*H *atoms in form* I *of the* L-*lysine complex*

Estimated standard deviations are given in parentheses.

	x	y	z	B_{eq}(Å^2)
N(1)	− 155	877	− 137	2·16 (4)
O(1)	2388 (5)	470 (5)	2688 (4)	4·38 (8)
O(2)	6305 (5)	871 (4)	2003 (4)	3·44 (6)
C(1)	3836 (6)	945 (4)	1894 (4)	2·23 (5)
C(2)	2612 (5)	1793 (4)	680 (3)	1·89 (5)
C(3)	2593 (5)	3801 (4)	1589 (4)	2·40 (5)
C(4)	5406 (6)	4832 (4)	2283 (4)	2·72 (6)
C(5)	5431 (6)	6863 (4)	2993 (4)	2·52 (5)
C(6)	8230 (5)	7836 (4)	3765 (4)	2·62 (6)
N(7)	8286 (5)	9809 (3)	4491 (3)	2·45 (5)
O(11)	7120 (5)	2722 (4)	8007 (4)	3·63 (6)
O(12)	3287 (5)	977 (3)	6713 (3)	3·13 (5)
C(13)	4768 (5)	2478 (4)	7287 (3)	2·11 (5)
C(14)	3466 (6)	4023 (4)	7053 (4)	2·68 (6)
C(15)	5305 (7)	5764 (4)	7700 (6)	3·87 (9)
C(16)	3917 (6)	7316 (4)	7590 (4)	2·54 (6)
O(17)	1683 (5)	7508 (4)	7830 (5)	4·62 (8)
O(18)	5395 (5)	8451 (3)	7240 (3)	2·91 (5)

metrically. Only one H atom belonging to the carboxyl group of the succinic acid molecule could be located from difference Fourier maps. These H atoms were included in structure-factor calculations but the parameters were not refined. They were assigned the equivalent isotropic temperature factors (Hamilton, 1959) of the heavier atoms to which they were attached. The form factors given in the program were used in the refinement calculations. The final coordinates and equivalent isotropic temperature factors of the non-H atoms are given in Tables 2, 3 and 4 respectively.* The origins in the two L-lysine complexes were fixed by holding the coordinates of one atom in each structure constant.

* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving non-H atoms and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54211 (54 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Positional parameters* (× 10^4) *and equivalent isotropic temperature factors of non-*H *atoms in form* II *of the* L-*lysine complex*

Estimated standard deviations are given in parentheses.

	x	y	z	B_{eq}(Å^2)
Lys 1				
N(1)	7991	9861	8964	2·5 (2)
O(1)	7529 (6)	10061 (7)	11019 (5)	3·2 (2)
O(2)	5333 (6)	9643 (7)	10431 (5)	3·9 (2)
C(1)	6536 (8)	9686 (8)	10293 (7)	2·3 (2)
C(2)	6741 (9)	9093 (9)	9126 (7)	2·5 (2)
C(3)	6999 (8)	7602 (8)	8929 (7)	2·7 (2)
C(4)	5693 (9)	6690 (9)	8785 (8)	3·2 (3)
C(5)	5960 (8)	5220 (9)	8698 (8)	3·0 (3)
C(6)	4682 (10)	4307 (9)	8417 (8)	3·6 (3)
N(7)	4912 (8)	2917 (7)	8489 (6)	3·1 (2)
Lys 2				
N(11)	3084 (7)	10047 (7)	9066 (6)	2·4 (2)
O(11)	2507 (6)	10351 (6)	11082 (5)	3·3 (2)
O(12)	336 (6)	9862 (7)	10447 (5)	3·2 (2)
C(11)	1540 (9)	9891 (8)	10338 (7)	2·5 (3)
C(12)	1831 (9)	9317 (9)	9186 (7)	2·2 (2)
C(13)	2053 (9)	7819 (9)	8991 (7)	2·7 (2)
C(14)	772 (11)	6887 (9)	8804 (8)	3·5 (3)
C(15)	1095 (10)	5449 (9)	8755 (8)	3·7 (3)
C(16)	− 199 (10)	4506 (9)	8475 (8)	3·4 (3)
N(17)	55 (8)	3129 (7)	8591 (5)	2·9 (2)
Lys 3				
N(21)	9322 (8)	2533 (7)	1890 (5)	2·7 (2)
O(21)	7931 (6)	2599 (6)	− 38 (5)	3·0 (2)
O(22)	6076 (6)	3175 (7)	624 (5)	3·4 (2)
C(21)	7297 (8)	2965 (8)	718 (7)	2·3 (2)
C(22)	8046 (9)	3213 (9)	1879 (7)	2·8 (3)
C(23)	8278 (10)	4697 (10)	2496 (7)	3·3 (3)
C(24)	8963 (10)	5550 (10)	1905 (9)	4·0 (3)
C(25)	9259 (10)	7055 (10)	2561 (8)	3·6 (3)
C(26)	9764 (11)	7831 (9)	1859 (8)	4·0 (3)
N(27)	10078 (9)	9339 (7)	2412 (6)	3·3 (2)
Lys 4				
N(31)	4304 (7)	2742 (7)	1974 (5)	2·4 (2)
O(31)	2910 (6)	2825 (6)	19 (4)	2·5 (2)
O(32)	1127 (6)	3468 (7)	753 (5)	3·2 (2)
C(31)	2351 (9)	3242 (9)	803 (7)	2·7 (3)
C(32)	3195 (10)	3689 (10)	1947 (7)	3·4 (3)
C(33)	3853 (15)	5151 (11)	2177 (15)	14·4 (8)
C(34)	3061 (19)	6329 (16)	2073 (20)	22·2 (18)
C(35)	3815 (17)	7510 (16)	1818 (14)	9·5 (7)
C(36)	5009 (16)	8186 (14)	2680 (16)	9·6 (7)
N(37)	5273 (8)	9541 (7)	2557 (6)	3·0 (2)
Succ 1				
O(41)	8002 (7)	222 (7)	3584 (5)	4·1 (2)
O(42)	9397 (7)	2044 (7)	3989 (5)	3·9 (2)
C(43)	8500 (11)	1327 (10)	4223 (7)	3·3 (3)
C(44)	8131 (11)	1790 (9)	5336 (8)	3·8 (3)
C(45)	7113 (10)	882 (9)	5597 (8)	3·5 (3)
C(46)	6822 (11)	1315 (10)	6725 (7)	3·5 (3)
O(47)	7421 (8)	2352 (9)	7373 (6)	5·7 (3)
O(48)	5927 (8)	609 (8)	7017 (6)	5·1 (2)
Succ 2				
O(51)	2668 (7)	− 117 (7)	3633 (5)	4·1 (2)
O(52)	4084 (7)	1700 (7)	4019 (5)	4·0 (2)
C(53)	3216 (9)	954 (10)	4254 (8)	3·1 (3)
C(54)	2864 (10)	1462 (10)	5400 (7)	3·5 (3)
C(55)	1770 (10)	557 (9)	5606 (7)	2·8 (2)
C(56)	1481 (9)	1017 (9)	6771 (7)	2·8 (3)
O(57)	2147 (7)	1983 (7)	7441 (6)	4·4 (2)
O(58)	544 (8)	325 (7)	7004 (5)	4·0 (2)
Succ 3				
O(61)	6094 (7)	4103 (7)	3999 (5)	4·5 (2)
O(62)	5155 (8)	3814 (7)	5367 (6)	4·7 (2)
C(63)	5973 (9)	4436 (10)	4944 (8)	3·1 (3)
C(64)	6976 (11)	5647 (10)	5739 (8)	3·7 (3)
C(65)	7716 (12)	6441 (11)	5254 (8)	4·5 (3)
C(66)	8485 (10)	7650 (9)	6043 (7)	3·0 (3)
O(67)	8262 (8)	8118 (8)	6944 (6)	5·6 (3)
O(68)	9428 (8)	8234 (7)	5677 (6)	4·9 (2)

Table 4 (*cont.*)

	x	*y*	*z*	B_{eq}(Å^2)
Succ 4				
O(71)	1351 (8)	4507 (8)	4007 (6)	5·6 (3)
O(72)	536 (10)	4174 (8)	5384 (6)	6·3 (3)
C(73)	1313 (11)	4827 (11)	4961 (9)	4·0 (3)
C(74)	2116 (13)	6040 (12)	5788 (9)	5·2 (4)
C(75)	3051 (12)	6810 (11)	5288 (9)	4·3 (3)
C(76)	3836 (11)	8008 (10)	6092 (8)	3·8 (3)
O(77)	3623 (8)	8477 (8)	7016 (6)	4·9 (2)
O(78)	4810 (8)	8526 (8)	5717 (6)	5·4 (3)

Discussion

Stoichiometry and ionization state

All the lysine molecules in the three complexes are zwitterionic and positively charged. The unit cell of the DL-lysine complex contains two lysine molecules, one doubly negatively charged succinate ion and one neutral succinic acid molecule. The succinate ions and the succinic acid molecules are located on inversion centres so that the asymmetric unit of the crystal contains one lysine molecule, half a succinate ion and half a succinic acid molecule, and the complex may be described as DL-lysine hemisuccinate hemisuccinic acid. Form I of the L-lysine complex contains one lysine molecule and one partially ionized singly negatively charged succinic acid molecule in the unit cell and the complex may be described as L-lysine semisuccinate.

The relative inaccuracy of the structure, presumably caused by pseudosymmetry and disorder, and the inability to locate the relevant H atoms from difference Fourier maps made the assignments of ionization states in form II of the L-lysine complex rather difficult. However, a careful examination of bond lengths and angles and the hydrogen-bonding pattern indicated that one (Succ 2) of the four succinic acid molecules in the structure is completely ionized and doubly negatively charged while another (Succ 3) is neutral. The bond lengths and angles in the remaining two are given in Fig. 1 which also illustrates two hydrogen bonds between them. The carboxyl group involving O(41) and O(42) is clearly deprotonated while that involving O(71) and O(72) is neutral. O(48) and O(78) are connected to each other by a hydrogen bond with a length of 2·44 (1) Å which is appropriate for a symmetrical O···O hydrogen bond (Vinogradov, 1979). The two atoms thus presumably share a proton and the carboxyl groups concerned carry partial negative charges.

It is clear from the above discussion that the seven succinic acid molecules (ions) exist in widely different ionization states. Two are neutral, two doubly negatively charged and one singly charged with one of the two carboxyl groups deprotonated. One of the remaining two appears to carry one and a half negative charges while the other half a negative charge. It is also interesting to note that different ionization states of the molecule are found in the same crystal structure. Thus, the succinic acid molecule can adopt one or another of a number of possible ionization states in response to slight environmental changes. The implication of this capability in the prebiotic scenario, especially in terms of catalysis, deserves further exploration.

Molecular dimensions

The bond lengths and angles in the structures are normal within experimental error and do not merit comment. The three complexes, among them, contain six crystallographically independent lysine molecules. The torsion angles that define their conformations (IUPAC–IUB Commission on Biochemical Nomenclature, 1970) are listed in Table 5. Those in other crystal structures containing lysine are also given in the table for comparison. Each of the torsion angles can assume values around 60, 180 or −60° corresponding to the three possible staggered conformations about a single bond. Therefore the lysine molecule can assume a large number of unique conformations although some combinations of the favoured values of the four torsion angles are likely to be disallowed. Five unique conformations have

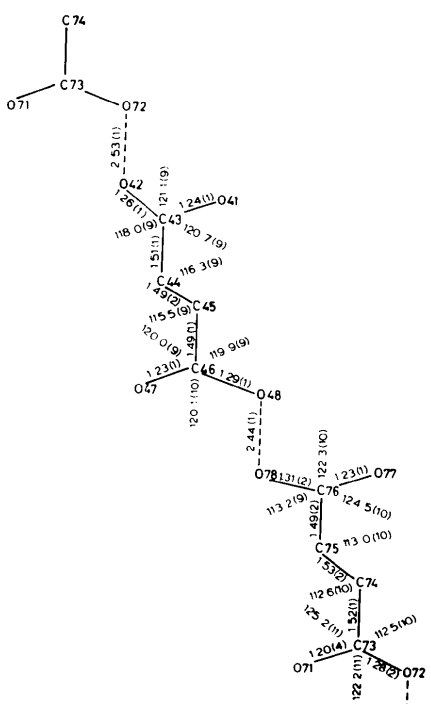


Fig. 1. Bond lengths (Å) and angles (°) in two partially ionized succinic acid molecules in form II of the L-lysine complex. The lengths of the hydrogen bonds between them, indicated here and in the subsequent figures by dotted lines, are also given. See text for details.

Table 5. *Torsion angles (°) that define the side-chain conformation of lysine molecules*

Estimated standard deviations are given in parentheses.

Compound/complex	χ^1	χ^2	χ^3	χ^4	Ref.
DL-Lysine complex*	-61·3 (3)	-176·5 (2)	174·6 (2)	172·1 (2)	(1)
L-Lysine complex (form I)	-173·7 (2)	172·5 (3)	176·5 (3)	-178·9 (3)	(1)
L-Lysine complex (form II)					
Lys 1	165·6 (6)	-174·4 (7)	-172·8 (8)	171·6 (8)	(1)
Lys 2	-165·5 (7)	-173·1 (8)	-175·4 (8)	-170·8 (8)	(1)
Lys 3	72·2 (10)	-177·4 (8)	-172·8 (8)	-179·3 (8)	(1)
Lys 4	172·0 (14)	-153·4 (14)	-61·5 (21)	158·0 (14)	(1)
L-Lysine monohydrochloride dihydrate	-56·4 (2)	176·0 (1)	-171·1 (2)	-179·2 (2)	(2)
DL-Lysine hydrochloride	170·5 (7)	-177·0 (8)	76·9 (10)	170·5 (7)	(3)
L-Lysine L-aspartate	-67·7 (7)	179·6 (6)	165·5 (7)	161·2 (6)	(4)
L-Lysine pantothenate	-79·0 (3)	-175·1 (2)	-175·1 (2)	-179·9 (2)	(5)
L-Lysine D-aspartate	-62·8 (3)	175·2 (3)	168·5 (3)	173·2 (3)	(6)
L-Lysine D-glutamate					
Lys 1	63 (2)	-152 (2)	170 (2)	170 (2)	(6)
Lys 2	68 (2)	-157 (1)	-176 (1)	-172 (1)	(6)
L-Lysine acetate	-63·9 (2)	178·2 (2)	167·4 (2)	175·3 (2)	(7)
DL-Lysine acetate	58·5 (10)	177·2 (8)	-177·1 (8)	177·5 (8)	(8)
L-Lysine sulfate	53·6 (7)	-179·6 (9)	176·3 (9)	-73·3 (8)	(9)
$PtCl_4$, L-lysine	-179·1 (20)	168·1 (20)	172·2 (22)	-73·1 (18)	(10)

Notes: (1) present study; (2) Koetzle, Lehmann, Verbist & Hamilton (1972); (3) Bhaduri & Saha (1979); (4) Bhat & Vijayan (1976); (5) Salunke & Vijayan (1984); (6) Soman, Suresh & Vijayan (1988); (7) Suresh & Vijayan (1983); (8) Soman, Rao, Radhakrishnan & Vijayan (1989); (9) Capasso, Mattia, Mazzarella & Zagari (1983); (10) L'Haridon, Lang, Patuszak & Dobrowolski (1978).

* The torsional angles correspond to the L isomer.

already been observed in the other structures. The molecule in form I, and Lys 1 and Lys 2 in form II of the L-lysine complex, represent a unique conformation not previously observed. Lys 4 in form II shows yet another unique conformation.

The crystal structures listed in Table 5 contain 17 crystallographically independent lysine molecules, including the six in the complexes reported here. In 13 of these, the side chain is all *trans* and thus fully extended with values of χ^2, χ^3 and χ^4 close to 180°. This indeed is presumably the most favourable conformation for the side chain of lysine. The orientation of the side chain with respect to the rest of the molecule is described by χ^1. In seven molecules χ^1 has, sterically, the most favourable value around $-60°$ with the side chain *trans* to the α-carboxylate group while in six it has the second most favourable value in the neighbourhood of 180° with the side chain *trans* to the α-amino group. In the remaining four the side chain is staggered between the α-carboxylate and the α-amino groups with $\chi^1 \sim 60°$. Thus, although the distribution follows the expected pattern, the discrimination between the three allowed orientations is not very striking.

The succinic acid molecule (ion) consists of two CCOOH ($CCOO^-$) groups connected by a C—C single bond. As in the case of other relevant structures (Leviel & Auvert, 1981; Huang, Leiserowitz & Schmit, 1973; Prasad & Vijayan, 1990), all the molecules (ions) adopt *trans* conformation about the central bond so that the two carboxyl (carboxylate) groups are as far apart as possible. The succinic acid molecules and the succinate ions in the DL-lysine complex are located at crystallographic inversion centres and are planar. Succ 1 and Succ 2 in form II of the L-lysine complex are also very nearly centrosymmetric and planar. These features are also approximately shown by Succ 3 and Succ 4, which have one of their two carboxyl groups twisted by about 10° with respect to the rest of the molecule. This twist is as much as 36° in the semisuccinate ion in form I and consequently the centre of symmetry and planarity in it are only very approximate. Another relevant feature of the succinic acid conformation pertains to the position of the carboxyl hydrogen. In the crystal structures of succinic acid (Leviel & Auvert, 1981) and its complex with benzamide (Huang, Leiserowitz & Schmit, 1973), the H atom is *cis* with respect to the O atom double bonded to the central C atom in the carboxyl group whereas it is *trans* in L-arginine hemisuccinate hemisuccinic acid monohydrate (Prasad & Vijayan, 1990). It is *cis* in the carboxyl groups in the DL-lysine complex, form I of the L-lysine complex and in the one carboxyl group in which the H atom could be located in form II of the L-lysine complex.

Pseudosymmetry

The crystal structures of the three complexes are shown in Figs. 2, 3 and 4. Form II of the L-lysine complex, with four sets of crystallographically independent molecules, is highly pseudosymmetric. One half of the structure is related to the other by a pseudo $a/2$ translation. The pseudo translation between Lys 1 and Lys 2 is almost exact while that between Lys 3 and Lys 4 is only approximate as the two molecules have different side-chain conformations. The pseudo translational symmetry involving succinic acid molecules (ions) (Succ 1 and Succ 2, and Succ 3 and Succ 4) is also almost exact. The main-chain atoms in Lys 1 and Lys 2 are related to those in Lys 3 and Lys 4 respectively by a pseudo twofold axis parallel to a located approximately at $y = 0{\cdot}65$ and $z = 0{\cdot}55$. The additional presence of a pseudo translation $a/2$ in the structure leads to a pseudo 2_1 screw axis coincident with the pseudo twofold axis relating these atoms. As indicated earlier each of the succinic acid molecules (ions) has a pseudo inversion centre. They are located at 0·77, 0·13, 0·55; 0·23, 0·10, 0·55; 0·72, 0·61, 0·55; and 0·26, 0·64, 0·55.

Hydrogen bonding and molecular aggregation

The parameters of the hydrogen bonds that stabilize the structures are listed in Tables 6, 7 and 8. Those in the N—H···O hydrogen bonds are normal (Mitra & Ramkrishnan, 1977, 1981) except for the three large H—N···O angles observed in the DL-lysine complex. Altogether there are six O—H···O hydrogen bonds in the complex, all between succinic acid molecules or ions. Five of them have parameters comparable to those observed in other structures involving succinic acid molecules or succinate ions (Leviel & Auvert, 1981; Huang, Leiserowitz & Schmit, 1973; Prasad & Vijayan, 1990). The shortness of the O···O distance and the information presented in Fig. 1 appear to suggest that the sixth one, O(48)···O(78) in form II of the L-lysine complex, is a symmetrical hydrogen bond.

As in many other complexes involving amino acids (Vijayan, 1988; Soman & Vijayan, 1989), the dissimilar molecules aggregate into separate alternating layers in the complexes (see Figs. 2, 3 and 4). However, while in most other complexes of lysine the amino-acid layer is stabilized exclusively or primarily by interactions involving α-amino and α-carboxylate groups (Bhat & Vijayan, 1976; Salunke & Vijayan, 1984; Soman, Suresh & Vijayan, 1988; Suresh & Vijayan, 1983; Soman, Rao, Radhakrishnan & Vijayan, 1989), interactions involving side-chain amino groups also play an important role, as can be seen from Fig. 5. In all three complexes, the layer is parallel to the *ab* plane. The pattern of molecular aggregation in the layer is perhaps simplest in form I of the L-lysine complex (Fig. 5*b*). The molecules form *S*2-type head-to-tail sequences (Suresh & Vijayan,

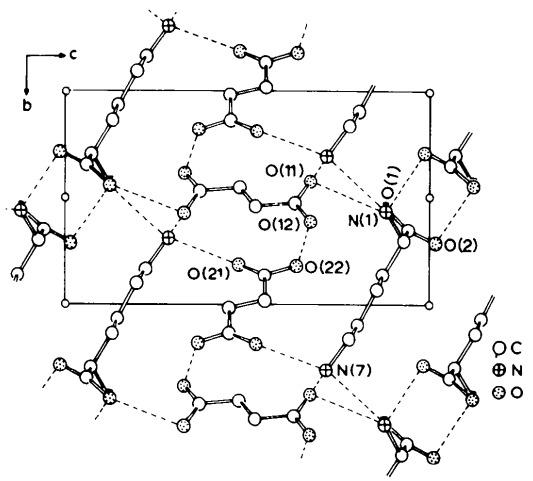


Fig. 2. The crystal structure of the DL-lysine complex. In this and and in the subsequent figures, only O and N atoms are numbered.

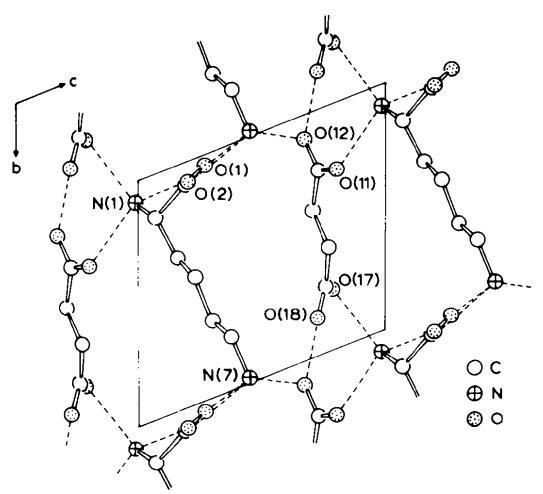


Fig. 3. The crystal structure of form I of the L-lysine complex.

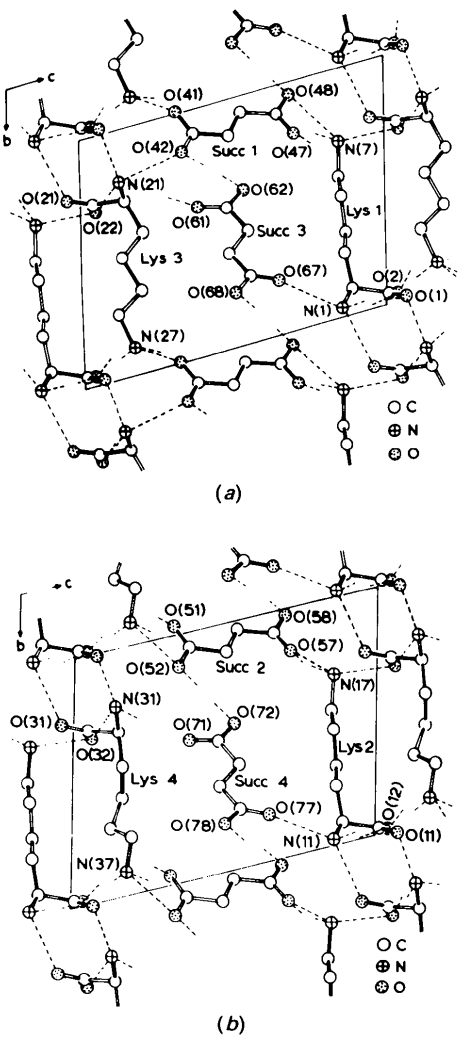


Fig. 4. Atoms in the unit cell of form II of the L-lysine complex, with x coordinates between (*a*) 0 to 0·5 and (*b*) 0·5 to 1·0.

Table 6. *Hydrogen-bond parameters in the* DL-*lysine complex*

Estimated standard deviations are given in parentheses.

A—H···*B*	*A*···*B* (Å)	H—*A*···*B* ( )
N1— H1N1···O11^{a}	3·013 (4)	14 (3)
N1—H2N1···O2^{b}	2·835 (4)	6 (2)
N1—H3N1···O1^{c}	2·804 (3)	4 (2)
N7—H1N7···O1^{d}	2·909 (4)	40 (2)
N7—H2N7···O21^{e}	2·892 (4)	36 (3)
N7—H3N7···O11^{d}	2·714 (4)	39 (2)
O22—HO22···O12^{f}	2·465 (4)	22 (7)

Symmetry code: (*a*) *x*, *y*, *z*; (*b*) $-x+1$, $-y+1$, $-z+2$; (*c*) $x+1$, *y*, *z*; (*d*) $x+1$, $y+1$, *z*; (*e*) $-x+1$, $y+2$, $-z+1$; (*f*) $x-1$, *y*, *z*.

Table 7. *Hydrogen-bond parameters in form* I *of the* L-*lysine complex*

Estimated standard deviations are given in parentheses.

A—H···*B*	*A*···*B* (Å)	H—*A*···*B* ( )
N1—N1H1···O2^{a}	2·797 (3)	8 (2)
N1—H2N1···O17^{b}	2·946 (3)	18 (3)
N1···H3N1···O11^{c}	2·854 (4)	4 (3)
N7—H1N7···O1^{d}	2·946 (5)	22 (3)
N7—H2N7···O2^{e}	2·694 (5)	5 (3)
N7—H3N7···O12^{d}	2·818 (3)	14 (3)
O18—HO18···O12^{c}	2·527 (4)	10 (3)

Symmetry code: (*a*) $x-1$, *y*, *z*; (*b*) *x*, $y-1$, $z-1$; (*c*) $x-1$, *y*, $z-1$; (*d*) $x+1$, $y+1$, *z*; (*e*) *x*, $y+1$, *z*.

1983) along the *a* direction. The sequences are interconnected through interactions between the side-chain amino group in one sequence and the α-carboxylate oxygen in the neighbouring sequence. In the DL-lysine complex (Fig. 5*a*), two *S*2 type head-to-tail sequences along the *a* direction interact across

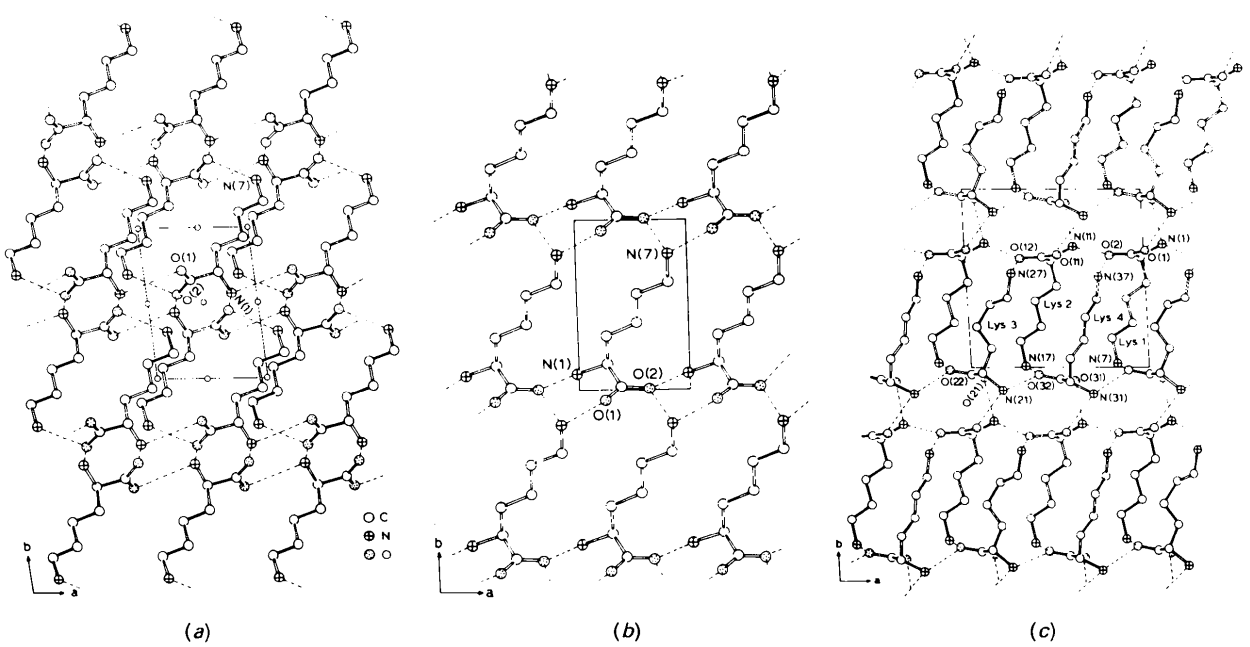
Table 8. *Hydrogen-bond parameters in form* II *of the* L-*lysine complex*

Estimated standard devations are given in parentheses.

A···*B*	*A*···B (Å)	*A*···*B*	*A*···B (Å)
N1···O12^{a}	2·811 (6)	N1···O67^{h}	2·820 (7)
N1···O21^{c}	2·780 (5)	N7···O22^{d}	2·766 (10)
N7···O57^{h}	2·915 (10)	N7···O48^{h}	2·969 (11)
N11···O2^{h}	2·775 (10)	N11···O77^{h}	2·872 (10)
N11···O31^{c}	2·823 (10)	N17···O32^{d}	2·759 (9)
N17···O47^{e}	2·842 (10)	N17···O57^{h}	2·906 (11)
N21···O32^{d}	2·800 (11)	N21···O42^{h}	2·873 (10)
N21···O1^{g}	2·904 (9)	N27···O51^{d}	2·796 (10)
N27···O12^{h}	2·776 (11)	N27···O41^{c}	2·836 (12)
N31···O22^{h}	2·789 (10)	N31···O61^{h}	2·910 (8)
N31···O11^{g}	2·847 (8)	N37···O52^{c}	2·958 (10)
N37···O41^{c}	2·845 (10)	N37···O2^{c}	2·787 (11)
O48···O78^{h}	2·445 (10)	O52···O62^{h}	2·477 (8)
O58···O68^{d}	2·464 (9)	O72···O42^{c}	2·533 (9)

Symmetry code: (*a*) $x+1$, *y*, *z*; (*b*) *x*, *y*, *z*; (*c*) *x*, $y+1$, $z+1$; (*d*) *x*, *y*, $z+1$; (*e*) $x-1$, *y*, *z*; (*f*) $x+1$, $y+1$, *z*; (*g*) *x*, $y-1$, $z-1$; (*h*) $x+1$, *y*, $z-1$; (*i*) *x*, $y+1$, *z*; (*j*) *x*, *y*, $z-1$; (*k*) *x*, $y-1$, *z*.

inversion centres through hydrogen bonds involving α-amino and α-carboxylate groups to form what may be described as double head-to-tail sequences. The double sequences are then interconnected in the layer through hydrogen bonds between side-chain amino and α-carboxylate groups of adjacent layers. The aggregation pattern in the amino-acid layer in form II of the L-lysine complex is basically similar to that in the DL-lysine complex in that in both complexes it is based on *S*2 type head-to-tail double sequence interconnected through interactions involving side-chain amino groups. However, in the L-lysine complex, the individual sequences in the



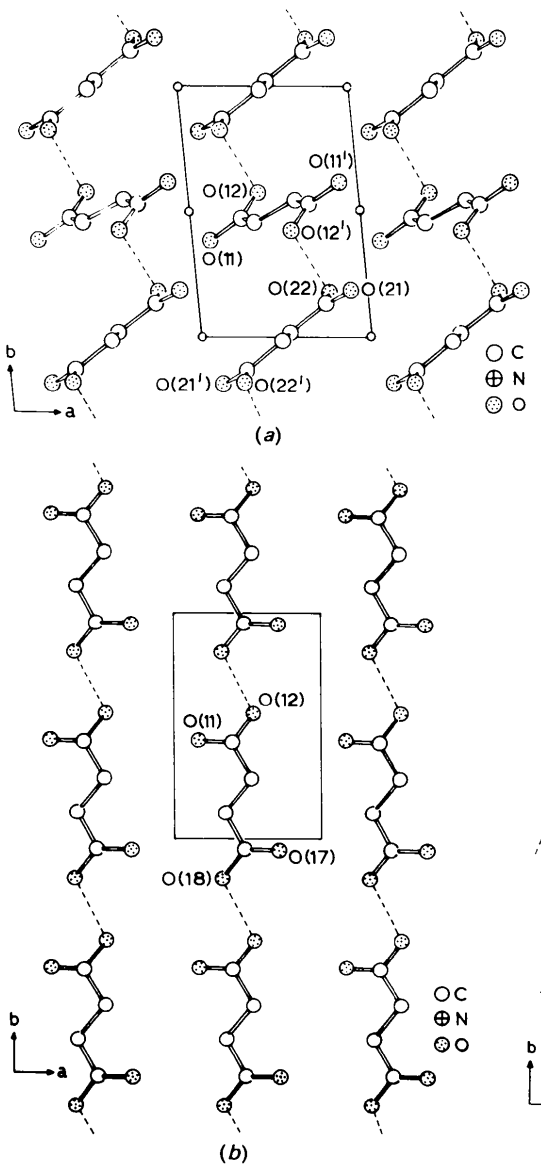
(*a*) (*b*) (*c*)

Fig. 5. The arrangement of molecules in the lysine layer in (*a*) the DL-lysine complex, (*b*) form I of the L-lysine complex and (*c*) form II of the L-lysine complex.

double sequence are related by pseudo twofold axes instead of inversion centres. Furthermore, the hydrogen bonds connecting adjacent double sequences involve the α-carboxylate oxygen *cis* to the α-amino group in the DL-lysine complex whereas they involve the oxygen *trans* to the amino group in the L-lysine complex. Thus the basic element of aggregation in the layers in the three complexes is an *S*2 type head-to-tail sequence. This basic element is combined in different ways to give the different aggregation patterns observed in the three complexes.

The arrangements of molecules (ions) in the succinic acid layers in the three structures are illustrated in Fig. 6. The basic elements of aggregation in all three are hydrogen-bonded ribbons. The structure of the ribbon is simplest in form I of the L-lysine complex (Fig. 6*b*). The semisuccinate ion, connected by hydrogen bonds between carboxyl and carboxylate groups, is repeated by the *b* translation with all the hydrogen bonds pointing in the same direction. Neutral succinic acid molecules and doubly charged succinate ions alternate in the ribbon in the DL-lysine complex (Fig. 6*a*), and alternate hydrogen bonds along the ribbons point in opposite directions. The ribbons in form II of the L-lysine complex (Fig. 6*c*) are remarkably similar to those in the DL-lysine complex. They propagate along the [110] direction. There are two crystallographically independent ribbons. In the one involving Succ 2 and Succ 3, succinic acid molecules and succinate ions alternate along the ribbon, with alternate hydrogen bonds pointing in opposite directions. In the other, Succ 1 has one carboxylate group and a partially ionized carboxyl group while Succ 4 has a neutral carboxyl group and a partially ionized carboxyl group. The partially ionized groups point towards each other and are connected by what appears to be a symmetrical O···H···O hydrogen bond. This hydrogen bond alternates with a normal O—H···O hydrogen bond between the neutral carboxyl group of Succ 4 and the carboxylate group of Succ 1. None of the complexes have interactions between ribbons in the layer. They are only interconnected indirectly through amino groups in the lysine layer.

Not surprisingly (Vijayan, 1988), no specificity is apparent in lysine–succinic acid interactions, unlike the case in the corresponding arginine complexes (Prasad & Vijayan, 1990). In the lysine complexes, both main-chain and side-chain amino groups are involved in interactions with the carboxyl and carboxylate groups of succinic acid molecules or succinate ions.



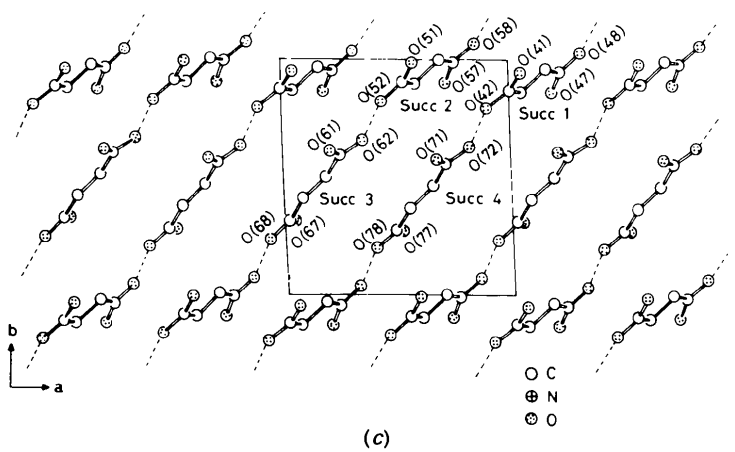


Fig. 6. The arrangement of molecules (ions) in the succinic acid/succinate layer in (*a*) the DL-lysine complex, (*b*) form I of the L-lysine complex and (*c*) form II of the L-lysine complex.

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Structural Phase Transition in Polyphenyls. X. Potential Barrier Heights in Crystalline Polyphenyls and in Gaseous Biphenyl Determined Uniquely from Diffraction Data

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Abstract

The analysis from X-ray or neutron diffraction data, of the librational motion around the long molecular axis of the *p*-terphenyl central ring permits resolution of its disorder: the phenyl rotation angle on either side of the average molecular plane is $\varphi = \pm 13{\cdot}3^\circ$. This disorder is associated with a double-well potential between two twisted conformations, and the overall libration on each site, at the bottoms of the double well, has the mean-square amplitude $\langle\theta^2\rangle = 52{\cdot}5\ \text{deg}^2$ at room temperature. The analysis also permits separation in $\langle\theta^2\rangle$ of the mean-square amplitude of the torsional *g* mode $\langle\theta_i^2\rangle = 35\ \text{deg}^2$ from that of the external mode $\langle\theta_e^2\rangle = 17{\cdot}5\ \text{deg}^2$. Thus it becomes possible to scale the parameters of a simple model describing inter- and intramolecular interactions in the whole family of polyphenyls. It is shown that the intramolecular potential between two adjacent phenyl rings cannot be described by a simple sinusoidal function but exhibits a steeper gradient near the planar conformation. This double potential well model accounts for disorder and libration in crystalline *p*-terphenyl and *p*-quaterphenyl. It gives

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