

## L-Arginine L-Aspartate\*

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(Received 31 July 1981; accepted 26 October 1981)

**Abstract.**  $C_6H_{15}N_4O_2^+ \cdot C_4H_6NO_4^-$ , monoclinic,  $P2_1$ ,  $a = 5.511$  (3),  $b = 8.438$  (4),  $c = 15.265$  (9) Å,  $\beta = 97.9$  (1)°,  $D_m = 1.467$  (8) (floatation),  $D_c = 1.452$  Mg  $m^{-3}$ ,  $Z = 2$ . The structure has been refined to a final  $R$  value of 0.044 for 1226 independent counter-measured reflections. The conformation of the arginine molecule is different from those previously observed, whereas the conformation of the aspartate ion is similar to that found in L-aspartic acid, DL-aspartic acid and L-lysine L-aspartate. The unlike molecules aggregate into separate alternating layers and the  $\alpha$ -amino and  $\alpha$ -carboxylate groups in the arginine layer are periodically brought into close proximity in a 'head-to-tail' arrangement. There exist a specific ion-pair interaction involving electrostatic attraction and two nearly parallel N—H...O hydrogen bonds between the guanidyl group and the  $\alpha$ -carboxylate group of the aspartate ion.

**Introduction.** The crystal structures of a number of complexes of amino acids, among themselves as well as with other biomolecules, have been determined in this laboratory in an attempt to elucidate, at atomic resolution, the structural features of the possible non-covalent interactions involving amino acids (Salunke & Vijayan, 1982; Sudhakar, Bhat & Vijayan, 1980, and references therein). We have now determined the structure of a 1:1 crystalline complex between arginine and aspartic acid.

Needle-shaped crystals of the complex were grown by the slow diffusion of 1-propanol into an aqueous solution of the compound (obtained commercially). The data were collected on a CAD-4 computer-controlled diffractometer from a specimen of approximate dimensions 0.38 × 0.25 × 0.25 mm using graphite-monochromated Cu  $K\alpha$  radiation up to a Bragg angle of 70°. Of the 1379 reflections recorded in this range, 1226 had  $I > 2\sigma_I$  and were subsequently used for structure determination and refinement. The structure was solved using *MULTAN* (Germain, Main & Woolfson, 1971) and refined by the block-diagonal

least-squares method using the modified version of a program originally written by R. Shiono. The heavy atoms and the H atoms were given anisotropic and isotropic temperature factors respectively. The refinement converged at  $R = 0.044$ . The weighting scheme was of the form  $1/(a + bF_o + cF_o^2)$  where  $a = 0.945$ ,  $b = 0.047$  and  $c = 0.007$ . The scattering factors for the non-hydrogen atoms and the H atoms were taken from Cromer & Waber (1965) and Stewart, Davidson & Simpson (1965) respectively. The final coordinates of the non-hydrogen atoms are given in Table 1.†

† Lists of structure factors, anisotropic temperature factors and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36504 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters ( $\times 10^4$ ) and equivalent isotropic temperature factors (Hamilton, 1959) for the non-hydrogen atoms

Estimated standard deviations are given in parentheses.

	$x$	$y$	$z$	$B_{eq}$ (Å <sup>2</sup> )
N(1)	13605 (4)	10000	5922 (2)	1.6 (1)
O(1)	8709 (4)	9724 (3)	5940 (2)	2.4 (1)
O(2)	8273 (4)	7934 (4)	4857 (1)	2.4 (1)
C(1)	9526 (5)	8774 (4)	5424 (2)	1.5 (1)
C(2)	12317 (5)	8638 (4)	5474 (2)	1.6 (1)
C(3)	13253 (5)	7106 (4)	5956 (2)	1.7 (1)
C(4)	12907 (6)	7024 (4)	6936 (2)	2.0 (1)
C(5)	13414 (5)	5351 (4)	7297 (2)	2.0 (1)
N(6)	11552 (5)	4205 (4)	6941 (2)	2.2 (1)
C(7)	9794 (5)	3620 (4)	7375 (2)	1.7 (1)
N(8)	9414 (5)	4163 (4)	8161 (2)	2.4 (1)
N(9)	8326 (5)	2499 (4)	6979 (2)	2.4 (1)
N(11)	4342 (4)	256 (3)	10008 (2)	1.9 (1)
C(11)	4546 (5)	1272 (4)	8494 (2)	1.6 (1)
C(12)	3621 (5)	-75 (4)	9038 (2)	1.6 (1)
O(11)	5620 (5)	2420 (3)	8884 (1)	2.3 (1)
O(12)	4232 (5)	1063 (3)	7674 (1)	2.7 (1)
C(13)	866 (6)	-388 (4)	8854 (2)	2.0 (1)
C(14)	170 (5)	-2037 (4)	9167 (2)	1.8 (1)
O(15)	1572 (4)	-3175 (3)	9066 (2)	2.5 (1)
O(16)	-1783 (6)	-2157 (5)	9501 (3)	5.5 (2)

\* X-ray Studies on Crystalline Complexes Involving Amino Acids and Peptides. VII. Part VI: Salunke & Vijayan (1982).

**Discussion.** The two amino groups and the guanidyl group are protonated and all three carboxyl groups are deprotonated. Thus the crystal structure is made up of positively charged arginine and negatively charged aspartate ions. The bond lengths and angles involving the non-hydrogen atoms are shown in Fig. 1. These dimensions are comparable to those in similar structures (Vijayan, 1976).

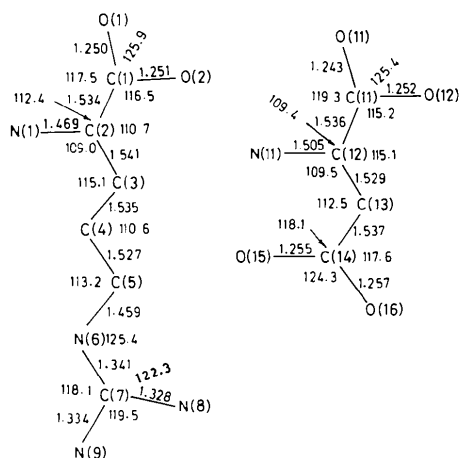


Fig. 1. Bond lengths (Å) and angles (°). The standard deviations in bond lengths and angles range from 0.003 to 0.005 Å and from 0.2 to 0.4° respectively.

Table 2. Torsional angles and hydrogen-bond parameters

Arginine			
$\psi_1$	O(1)–C(1)–C(2)–N(1)		–18.3 (4)°
$\psi_2$	O(2)–C(1)–C(2)–N(1)		160.7 (3)
$\chi^1$	N(1)–C(2)–C(3)–C(4)		59.1 (3)
$\chi^2$	C(2)–C(3)–C(4)–C(5)		168.7 (3)
$\chi^3$	C(3)–C(4)–C(5)–N(6)		–69.9 (3)
$\chi^4$	C(4)–C(5)–N(6)–C(7)		–104.0 (4)
$\chi^{51}$	C(5)–N(6)–C(7)–N(8)		7.2 (5)
$\chi^{52}$	C(5)–N(6)–C(7)–N(9)		–175.6 (3)
Aspartate			
$\psi_1$	N(11)–C(12)–C(11)–O(11)		–2.4 (4)
$\psi_2$	N(11)–C(12)–C(11)–O(12)		174.3 (3)
$\chi^2$	N(11)–C(12)–C(13)–C(14)		–75.2 (3)
$\chi^{21}$	C(12)–C(13)–C(14)–O(15)		–38.5 (4)
$\chi^{22}$	C(12)–C(13)–C(14)–O(16)		142.1 (3)
N(1)···O(1) <sup>b</sup>	2.819 (3) Å	H1(N1)–N(1)···O(1)	3 (3)°
N(1)···O(3) <sup>e</sup>	2.877 (3)	H2(N1)–N(1)···O(2)	1 (3)
N(1)···O(12) <sup>c</sup>	2.797 (3)	H3(N1)–N(1)···O(12)	17 (3)
N(6)···O(2) <sup>f</sup>	2.960 (4)	H1(N6)–N(6)···O(2)	1 (2)
N(8)···O(15) <sup>e</sup>	2.814 (4)	H1(N8)–N(8)···O(15)	9 (3)
N(8)···O(11) <sup>d</sup>	2.896 (4)	H2(N8)–N(8)···O(11)	3 (2)
N(9)···O(1) <sup>d</sup>	2.852 (4)	H1(N9)–N(9)···O(1)	28 (3)
N(9)···O(12) <sup>d</sup>	2.889 (4)	H2(N9)–N(9)···O(12)	4 (3)
N(11)···O(16) <sup>h</sup>	2.758 (5)	H1(N11)–N(11)···O(16)	10 (2)
N(11)···O(11) <sup>i</sup>	2.928 (4)	H2(N11)–N(11)···O(11)	6 (3)
N(11)···O(15) <sup>f</sup>	2.819 (3)	H3(N11)–N(11)···O(15)	24 (3)

Symmetry code: (a)  $x, y, z$ ; (b)  $x + 1, y, z$ ; (c)  $x + 1, y + 1, z$ ; (d)  $x, y - 1, z$ ; (e)  $2 - x, y + \frac{1}{2}, 1 - z$ ; (f)  $2 - x, y - \frac{1}{2}, 1 - z$ ; (g)  $1 - x, y + \frac{1}{2}, 2 - z$ ; (h)  $-x, y + \frac{1}{2}, 2 - z$ ; (i)  $1 - x, y - \frac{1}{2}, 2 - z$ .

The torsional angles (IUPAC–IUB Commission on Biochemical Nomenclature, 1970) which define the conformations of the molecules are given in Table 2. The side chain of the aspartate ion assumes the sterically most favourable conformation with the side-chain carboxylate group *trans* to the  $\alpha$ -carboxylate group, as in L-aspartic acid (Derissen, Endeman & Peerdeman, 1968), DL-aspartic acid (Rao, 1973) and L-lysine L-aspartate (Bhat & Vijayan, 1976). Indeed, if metal complexes are excluded, the only example reported so far in which the two groups are *gauche* to each other is that of histidine–aspartic acid monohydrate (Bhat & Vijayan, 1978). The arginine molecule can assume a number of different conformations as its side chain is relatively long and flexible. Nine unique conformations of arginine have been observed so far (Bhat & Vijayan, 1977, and references therein; Sudhakar & Vijayan, 1980); that observed here represents a tenth.

The crystal structure is stabilized by ionic interactions and hydrogen bonds (Fig. 2). The parameters of the hydrogen bonds are given in Table 2. As in the case of the other crystalline complexes involving lysine or arginine (Bhat & Vijayan, 1976, 1977, 1978; Sudhakar & Vijayan, 1980), the unlike molecules aggregate into separate alternating layers and the  $\alpha$ -amino and  $\alpha$ -carboxylate groups are periodically brought into close proximity in a ‘head-to-tail’ arrangement, a feature shared by the structures referred to above. Such an arrangement may have been important in the prebiotic polymerization of amino acids (Vijayan, 1980).

The interactions involving the guanidyl group are of interest in relation to the possible topological features of guanidyl interactions. It has been suggested, on the

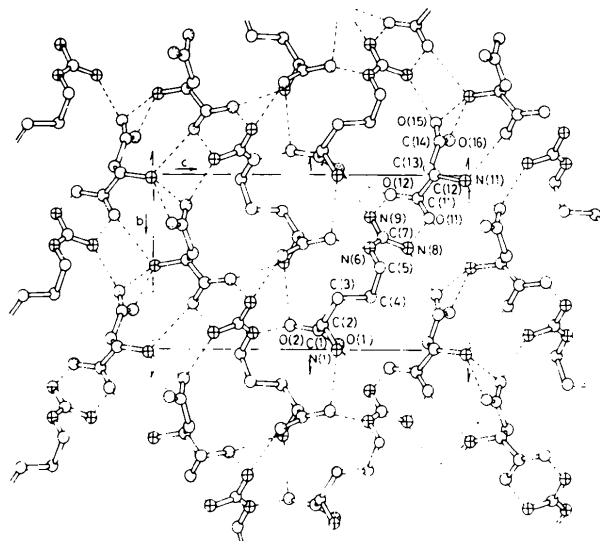


Fig. 2. Crystal structure as viewed along the  $a$  axis. The broken lines indicate hydrogen bonds.

basis of a careful examination of several relevant crystal structures, that the guanidyl group can and does take part in four different types of specific (implying recognition) interactions, each involving a pair of nearly parallel or convergent hydrogen bonds (Salunke & Vijayan, 1981). The specific interaction observed here between the guanidyl group and the  $\alpha$ -carboxylate group of the aspartate ion is type *A* according to the classification of Salunke & Vijayan (1981), and is topologically similar to guanidyl carboxylate interactions in L-arginine dihydrate (Karle & Karle, 1966; Lehmann, Verbist, Hamilton & Koetzle, 1973) and L-arginine L-glutamate monohydrate (Bhat & Vijayan, 1977).

The authors thank SERC, Department of Science and Technology, India, for financial support. One of us (DMS) thanks the University Grants Commission, India, for the award of a junior research fellowship.

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## Structure of Bis{2-[(cyclooctatetraenyl)thio]-4,5-dimethylphenyl} Disulphide. The Product of an Attempted Preparation of a 1,4-Dithia[12]annulene

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(Received 4 August 1981; accepted 26 October 1981)

**Abstract.**  $C_{32}H_{30}S_4$ , orthorhombic, *Pbcn*,  $a = 22.972$ ,  $b = 5.788$ ,  $c = 20.909$  Å,  $V = 2780.1$  Å<sup>3</sup>,  $F(000) = 1152$ ,  $D_c = 1.297$  g cm<sup>-3</sup>,  $Z = 4$ ,  $\mu(\text{Cu } K\alpha) = 31.6$  cm<sup>-1</sup>;  $R = 0.0608$ ,  $R_w = 0.0631$  for 513 observations. The title compound was previously thought to be a 1,4-dithia[12]annulene but has now been shown to be a dimeric cyclooctatetraene derivative.

**Introduction.** 1,4-Dithiaannulenes are heteroanalogues of multi- $\pi$ -electron hydrocarbons and should show the corresponding properties, particularly aromatic charac-

ter in special cases. The preparation and investigation of these and other related thia heterocycles have been examined in a series of papers which include the preparation and crystal structures of 8,9-dimethyl-1,6-benzodithiocin (I) (Schroth & Moegel, 1977; Barnes, Schroth & Moegel, 1979) and of 2,3-dimethyl-5a,11a-dihydro-*trans*-cycloocta[1,4]benzodithiin (II) (Kaiser, Richter, Moegel & Schroth, 1979). The latter was reported (Moegel, Schroth & Werner, 1978) to isomerize on reaction with  $\text{KO}^t\text{Bu}-\text{Me}_2\text{SO}$  at 313 K to give a product (20%, m.p. 416 K) which