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A Neutron Study on the Structure of DL-Aspartic Acid

BY A. SEQUEIRA, H. RAJAGOPAL AND M. RAMANADHAM

Neutron Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay 400085, India

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Abstract. $C_4H_7NO_4$, $NH_3^+CH(CH_2COOH)COO^-$, $M_r = 133.1$, monoclinic, $C2/c$, $a = 18.96$ (1), $b = 7.43$ (1), $c = 9.20$ (2) Å, $\beta = 124.1$ (1)°, $V = 1073$ Å³, $Z = 8$, $D_x = 1.65$ g cm⁻³, neutrons, $\lambda = 1.036$ (1) Å, $\mu = 2.004$ cm⁻¹, $F(000) = 263$ fm, room temperature. For all 648 independent observations with $(\sin\theta)/\lambda \leq 0.51$ Å⁻¹ $R(F^2)$ is 0.042. The C-atom skeleton is nearly fully extended, with a C–C–C torsion angle of 174.2 (2)°. There is a near-perfect staggered conformation across the C–NH₃⁺ bond. One of the three N⁺–H...O hydrogen bonds is bifurcated with an intramolecular component. The crystal contains chains of aspartic acid molecules in alternately L and D configurations linked through a short and straight O–H...O hydrogen bond between –COOH and –COO groups.

Introduction. The present neutron diffraction study on the structure of DL-aspartic acid is part of an ongoing programme aimed at obtaining high-precision data on the H-atom stereochemistry and hydrogen-bonding interactions in amino acids and small peptides [for reviews, see Koetzle & Lehmann (1976) and Ramanadham & Chidambaram (1978)]. A high-precision X-ray study of the structure of DL-aspartic acid was reported earlier by Rao (1973).

Experimental. Tiny crystals of DL-aspartic acid were grown by slow evaporation from an aqueous solution of a commercial grade sample. Large crystals suitable for the neutron experiment were subsequently obtained by seeding a saturated solution with these crystals. A prism-shaped crystal with dimensions 1.8 × 2.3 × 2.9 mm was mounted on the computer-controlled four-circle neutron diffractometer, D4 (Sequeira *et al.*, 1978) at the CIRUS reactor, Trombay, with the prism axis (c axis) coincident with the φ axis of the diffractometer. The cell constants were refined against 2θ values of 30 observations, with $2\theta \leq 26^\circ$, manually

centred on the diffractometer. Integrated intensities of 1174 observations with $(\sin\theta)/\lambda \leq 0.51$ Å⁻¹ were recorded in the $\theta:2\theta$ (=1:2) step-scan mode with a 2θ step of 0.1°, at a neutron wavelength of 1.036 (1) Å, obtained by using a germanium-(111) monochromator. Two reflections, 400 and 113, were recorded at regular intervals to monitor the consistency of the experimental conditions. The raw data were reduced to a set of F_o^2 values by using the program *TRABS* (Rajagopal & Chidambaram, unpublished), in which absorption corrections were computed by a numerical method (Chidambaram, 1980). Transmission factors were in the range 0.96 to 0.98. The (F_o^2) values were initially computed as $[\sigma^2(\text{count}) + 0.04 |F_o^2|]^{1/2}$. Finally, a set of 648 unique F_o^2 values was obtained by averaging over the repeated ($R_{int} = 0.015$) observations. The ranges of h , k and l for the data set were –19 to 16, 0 to 7 and 0 to 9, respectively.

The X-ray positions of the H atoms were confirmed by relocating them in a neutron F_o Fourier map, phases for which were computed from X-ray positions of the nine non-H atoms. The model, consisting of 16 atoms, was then subjected to full-matrix least-squares refinement, using the Trombay version *TRXFLS* (Rajagopal & Sequeira, unpublished) of the program *ORFLS* (Busing, Martin & Levy, 1962). A scale factor, K , and an isotropic secondary-extinction parameter, G (Zachariasen, 1967), were refined. The quantity minimized was $\sum w(F_o^2 - KF_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$. The neutron scattering lengths used were 6.63 for C, 9.4 for N, 5.75 for O and –3.72 fm for H atoms (*International Tables for X-ray Crystallography*, 1974). All the observations, including the negative F_o^2 values, were considered for inclusion in the refinement. This approach had led earlier to satisfactory results in the refinement of the neutron structure of L-threonine (Ramanadham, Sikka & Chidambaram, 1973). Observations with significantly large ΔF^2 values were carefully excluded at every stage in order to avoid their

Table 1. Fractional atomic parameters and equivalent isotropic B values with e.s.d.'s
$$B_{\text{eq}} = \frac{4}{3}a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}$$

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
N	0.6549 (1)	0.2989 (3)	0.4847 (2)	1.6 (1)
CA	0.6537 (1)	0.3690 (3)	0.6352 (3)	1.3 (1)
C	0.7449 (1)	0.3857 (3)	0.7981 (2)	1.3 (1)
O1	0.8029 (1)	0.3237 (4)	0.7865 (3)	2.2 (1)
O2	0.7544 (1)	0.4631 (3)	0.9285 (3)	1.8 (1)
CB	0.5991 (1)	0.2523 (4)	0.6717 (3)	1.6 (1)
CG	0.5069 (1)	0.2500 (3)	0.5185 (3)	1.5 (1)
OD1	0.4825 (1)	0.3266 (4)	0.3819 (3)	2.3 (1)
OD2	0.4570 (2)	0.1616 (4)	0.5486 (4)	2.3 (1)
H1	0.6891 (3)	0.3824 (8)	0.4578 (5)	2.8 (2)
H2	0.6820 (3)	0.1731 (9)	0.5092 (6)	2.9 (2)
H3	0.5944 (3)	0.2955 (6)	0.3748 (7)	3.0 (2)
HA	0.6273 (2)	0.5016 (7)	0.6002 (6)	2.8 (2)
HB1	0.6225 (3)	0.1162 (9)	0.7052 (7)	4.0 (2)
HB2	0.6021 (2)	0.3033 (8)	0.7837 (7)	3.9 (2)
HD2	0.3942 (3)	0.1669 (6)	0.4422 (6)	2.7 (2)

undue influence on the course of refinement. The model was taken through 12 cycles of refinement, the first six with individual isotropic, and the next six with individual anisotropic temperature parameters. The weights were reassigned as $w = [\sigma^2(\text{count}) + 0.05|F_o|^2]^{-1}$ on the basis of an error analysis carried out on the $|AF^2|$ values after the twelfth cycle, and the refinement was terminated after another six cycles, when no parameter shifts were more than 1% of the corresponding e.s.d.'s. The $R(F^2)$ and weighted $R(F^2)$ values for the 641 observations accepted during the final cycles of refinement were 0.040 and 0.041 respectively compared with 0.042 and 0.047 for all 648 observations; for the seven rejected reflections $\Delta F^2/\sigma(F^2)$ was 4–8. The refined value of the extinction parameter, G , was $0.191(10) \times 10^4$. The extreme values in the final ΔF synthesis were 0.582 and $-0.635 \text{ fm } \text{\AA}^{-3}$, less than 4% of the extreme values in the final F_o synthesis.

Discussion. The atomic coordinates in Table 1 correspond to an aspartic acid molecule in the L configuration shown in Fig. 1. Geometric parameters calculated using *ORFFE* (Busing, Martin & Levy, 1964) and *TORLSP* (Ramanadham, 1987) are presented in Tables 2 and 3.* The molecular packing is shown in Fig. 2. In producing Tables 2 and 3 and Figs. 1 and 2 the more precise X-ray unit-cell parameters [$a = 18.947(1)$, $b = 7.433(1)$, $c = 9.184(1) \text{ \AA}$ and $\beta = 123.75(2)^\circ$] were used.

The neutron (DLASP-N) and the X-ray (DLASP-X, Rao, 1973) structures of DL-aspartic acid agree very

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51646 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances and angles with e.s.d.'s

Bond distances (\AA)			
N-CA	1.490 (4)	N-H1	1.021 (7)
CA-C	1.538 (2)	N-H2	1.030 (7)
C-O1	1.250 (4)	N-H3	1.024 (5)
C-O2	1.248 (4)	CA-HA	1.071 (6)
CA-CB	1.524 (4)	CB-HB1	1.079 (7)
CB-CG	1.517 (2)	CB-HB2	1.068 (7)
CG-OD1	1.211 (4)	OD2-HD2	1.039 (5)
CG-OD2	1.300 (5)		
Bond angles ($^\circ$)			
CA-N-H1	110.5 (4)	CA-C-O1	116.9 (2)
CA-N-H2	112.2 (4)	CA-C-O2	117.1 (2)
CA-N-H3	109.6 (5)	O1-C-O2	126.0 (2)
H1-N-H2	107.4 (6)	CA-CB-CG	112.1 (2)
H1-N-H3	106.9 (5)	CA-CB-HB1	112.0 (4)
H2-N-H3	110.1 (4)	CA-CB-HB2	109.3 (4)
N-CA-C	110.0 (2)	CG-CB-HB1	109.5 (3)
N-CA-CB	111.6 (2)	CG-CB-HB2	108.4 (3)
C-CA-CB	111.4 (2)	HB1-CB-HB2	105.3 (5)
N-CA-HA	106.8 (4)	CB-CG-OD1	122.4 (2)
C-CA-HA	107.7 (3)	CB-CG-OD2	114.0 (2)
CB-CA-HA	109.2 (4)	OD1-CG-OD2	123.6 (2)
		CG-OD2-HD2	111.7 (5)

Hydrogen-bond parameters

$X-H \cdots Y$	$H \cdots Y(\text{\AA})$	$X \cdots Y(\text{\AA})$	$HXY(^\circ)$
N-H1...O2 ⁱ	1.814 (7)	2.833 (4)	3.0 (3)
N-H2...O2 ⁱⁱ	1.857 (6)	2.880 (3)	5.2 (3)
N-H3...OD1 ⁱⁱⁱ	1.980 (5)	2.901 (3)	21.0 (4)
N-H3...OD1	2.169 (8)	2.861 (4)	39.4 (4)
OD2-HD2...O1 ^{iv}	1.515 (4)	2.554 (3)	0.3 (5)

Symmetry-equivalent positions of acceptor atoms: (i) $x, 1.0-y, -0.5+z$; (ii) $1.5-x, -0.5+y, 1.5-z$; (iii) $1.0-x, y, 0.5-z$; (iv) $-0.5+x, 0.5-y, -0.5+z$.

Table 3. Torsion angles ($^\circ$) in various forms of aspartic acid

	DLASP-N ^a	DLASP-X ^b	LASP ^c	DLASP-HCl ^d
$\phi^1(\text{C-CA-N-H1})$	-59.0 (4)			
$\phi^2(\text{C-CA-N-H2})$	60.9 (4)			
$\phi^3(\text{C-CA-N-H3})$	-176.5 (4)			
$\psi^1(\text{N-CA-C-O1})$	-7.0 (3)	-7.3 (2)	-37.8 (3)	-137 (1)
$\psi^2(\text{N-CA-C-O2})$	171.6 (2)	171.2 (1)	144.8 (3)	41 (1)
$\chi^{1,1}(\text{N-CA-CB-CG})$	-62.4 (3)	-61.8 (2)	-61.9 (3)	-64 (1)
$\chi^{1,2}(\text{N-CA-CB-HB1})$	61.1 (4)			
$\chi^{1,3}(\text{N-CA-CB-HB2})$	177.4 (3)			
$\chi^{2,1}(\text{CA-CB-CG-OD1})$	3.2 (4)	3.1 (3)	131.4 (4)	-7 (2)
$\chi^{2,2}(\text{CA-CB-CG-OD2})$	-175.7 (3)	-175.8 (2)	-51.3 (4)	174 (1)
$\chi^{2,3}(\text{CB-CG-OD2-HD2})$	178.0 (4)			
(C-CA-CB-CG)	174.2 (2)	174.2 (2)	178.2 (2)	-178 (2)

References: (a) this work; (b) Rao (1973); (c) Derissen, Endeman & Peerdeman (1968); (d) Dawson (1977).

well with each other except for the CB-CG distance and the C-CA-CB and CA-CB-CG angles, which differ by a little over 2σ . In Table 3 the torsion angles for DLASP-N and DLASP-X are compared with those of the X-ray studies on L-aspartic acid [LASP by Derissen *et al.* (1968)] and DL-aspartic acid hydrochloride [DLASP.HCl by Dawson (1977)]. It is worth noting that the atomic coordinates reported for LASP by Derissen *et al.* (1968) correspond to the D

configuration. As indicated by a non-standard torsion angle, $C-CA-CB-CG$, the four C atoms are approximately planar in all three structures. However, there are differences in the relative orientations of the two carboxyl groups with respect to each other and with respect to the C-atom planes. Similar C-atom planes were also observed in the neutron structures of L-glutamic acid (Lehmann, Koetzle & Hamilton, 1972) and L-glutamic acid hydrochloride (Sequeira, Rajagopal & Chidambaram, 1972). In the latter structure, the fifth C atom, CD, and the side-chain carboxyl group are also in the extended conformation along with the first four C atoms.

A decisively more accurate description of the H-atom stereochemistry in DL-aspartic acid is provided by the present study. All the geometrical parameters involving the H-atom positions are in good agreement with those found in other neutron studies (Koetzle & Lehmann, 1976; Ramanadham & Chidambaram, 1978). The α -amino group is in near-perfect staggered conformation around the $CA-N$ bond. The amino group hydrogen atom H3 is involved in a bifurcated hydrogen bond with an intramolecular component to OD1. As is expected in such cases, both branches of the bifurcated hydrogen bond have large bending angles. The $O-H\cdots O$ hydrogen bond between the two carboxyl groups is quite short and straight. Such a short hydrogen bond is also seen in the crystal structure of L-glutamic acid (Lehmann *et al.*, 1972). A strong

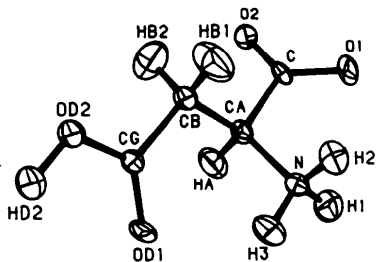


Fig. 1. ORTEPII (Johnson, 1976) drawing of the L-aspartic acid molecule. Atoms are represented by 50% probability ellipsoids.

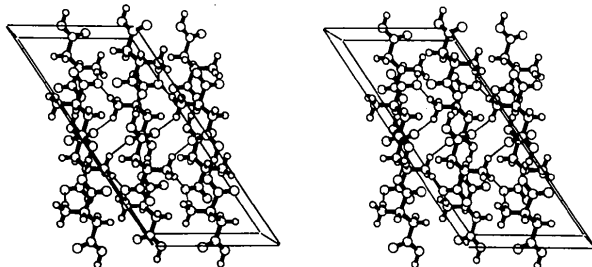


Fig. 2. ORTEPII stereoscopic drawing of the packing of D- and L-aspartic acid molecules in the crystal structure. The drawing is in the ca plane with the c axis horizontal, and the b axis pointing towards the viewer.

involvement of one of the two lone pairs of the sp^2 -hybridized O atom of the α -carboxyl group in this interaction is clearly indicated by a bond angle of $120.0(3)^\circ$ between $C-O1$ and $HD2\cdots O1$ bonds and a dihedral angle of $2.4(5)^\circ$ between $O2-C-O1$ and $C-O1\cdots HD2$ planes. The crystal structure is made up of chains of aspartic acid molecules, alternately in L and D configurations and linked by $O-H\cdots O$ hydrogen bonds, approximately parallel to the a^* axis. The interchain interactions are provided mainly by the three $N^+-H\cdots O$ hydrogen bonds. As observed by Ramanadham & Chidambaram (1978), the hydroxyl O atom in the neutral carboxyl group participates in the hydrogen-bond interaction only as a proton donor. A similar situation is indicated in the X-ray structures LASP and DLASP.HCl.

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