SHORT STRUCTURAL PAPERS

Refinement of DL-Aspartic Acid

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Abstract. Crystals of DL-aspartic acid ($C_4NO_4H_7$) were grown at room temperature from an aqueous solution of the commercially available sample. The crystals belong to the monoclinic system with cell dimensions $a = 18 \cdot 947 \pm 0 \cdot 002$, $b = 7 \cdot 433 \pm 0 \cdot 001$, $c = 9 \cdot 184 \pm 0 \cdot 001$ Å and $\beta = 123 \cdot 75 \pm 0 \cdot 02°$. The systematic absences are: hkl, $h + k = 2n + 1$ and $h0l$, $l = 2n + 1$. The space group is $C2/c$ with eight molecules in the unit cell. The calculated density is $1 \cdot 563$ g cm^{-3} and the density observed by the method of flotation in a bromoform–benzene mixture is $1 \cdot 561$ g cm^{-3}.

Introduction. The crystal structure of DL-aspartic acid (DLASP) has already been determined using the symbolic addition procedure for centrosymmetric space groups (Rao, Srinivasan & Valambal, 1968) using visually estimated photographic data. The intensities of reflections out to $2\theta = 128°$ were measured on a Picker FACS-I diffractometer using Ni filtered Cu $K\alpha$

radiation in the θ–2θ scan mode with a scan rate of $2°$ per min for the 2θ. The crystal size was $0 \cdot 2 \times 0 \cdot 2 \times 0 \cdot 3$ mm. Both hkl and $h\bar{k}l$ reflections were measured. The data were corrected for Lorentz and polarization factors but not for absorption. The equivalent reflections were averaged and a set of 891 independent reflections was obtained. The R value [$= \sum|F_1 - F_2|/0 \cdot 5\sum(F_1 + F_2)$] between the two sets of amplitudes was $0 \cdot 018$.

The refinement was carried out by minimizing $\sum w(|F_o| - |F_c|)^2$ with the full-matrix least-squares program of Busing, Martin & Levy (1962), starting with the positional parameters of the heavy atoms determined in the earlier work. The positions of all the hydrogen atoms were determined from a difference electron density map. The heavy atoms were refined with anisotropic thermal parameters and the hydrogen atoms with isotropic thermal parameters. The final R value for the 851 observed reflections ($I > 1 \cdot 5\sigma$) used in the refinement was $0 \cdot 031$. The weighting scheme

Table 1. *Positional and thermal parameters of atoms in* DL-*aspartic acid*

Positional parameters of heavy atoms are $\times 10^5$ and those of hydrogen atoms, $\times 10^4$. Anisotropic thermal parameters are $\times 10^5$. Standard deviations refer to the least significant digits. The anisotropic temperature factor is of the form $\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)]$.

	x	y	z	β_{11} or β	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	25451 (7)	−3729 (15)	92871 (13)	200 (6)	1231 (28)	700 (23)	−13 (9)	185 (9)	−193 (18)
O(2)	30298 (7)	−17698 (17)	78597 (14)	139 (6)	1776 (32)	810 (25)	63 (9)	136 (9)	−228 (20)
O(3)	−1754 (7)	−17340 (18)	38142 (14)	172 (6)	2142 (35)	631 (24)	−30 (10)	139 (9)	265 (21)
O(4)	−4290 (7)	−33846 (18)	54931 (15)	161 (6)	2134 (35)	779 (25)	−127 (10)	173 (10)	214 (21)
N	15502 (8)	−20127 (20)	48174 (17)	147 (7)	1309 (31)	542 (31)	14 (11)	153 (12)	28 (24)
C(1)	24513 (9)	−11503 (19)	79835 (19)	156 (7)	809 (31)	635 (31)	−7 (11)	162 (12)	41 (24)
C(2)	15394 (9)	−13199 (21)	63580 (19)	142 (8)	1002 (35)	543 (30)	14 (12)	150 (12)	−18 (24)
C(3)	9873 (10)	−24731 (23)	67080 (19)	160 (8)	1295 (40)	543 (30)	−29 (14)	153 (13)	39 (26)
C(4)	719 (9)	−25005 (21)	51910 (19)	155 (7)	1199 (36)	581 (30)	−18 (12)	181 (12)	−104 (25)
H(1)	1009 (16)	−2055 (29)	3869 (31)	3·2 (6)					
H(2)	1887 (15)	−1172 (30)	4606 (29)	3·5 (5)					
H(3)	1797 (13)	−3164 (28)	5060 (25)	2·3 (5)					
H(4)	1311 (11)	−86 (25)	6036 (22)	1·5 (4)					
H(5)	1012 (12)	−2029 (25)	7706 (26)	2·3 (4)					
H(6)	1186 (14)	−3699 (29)	6956 (27)	3·0 (5)					
H(7)	−1013 (21)	−3337 (42)	4542 (41)	6·9 (10)					

used was

$$\frac{1}{\sqrt{w}} = 0.87 \ (|F_o| < 21.3)$$

$$= 0.87 + 0.096 \ (|F_o| - |21.3|)|F_o| > 21.3 \ .$$

The R value ($= \sum ||F_o| - |F_c||/\sum |F_o|$) for all the 891 reflections was 0·034. The scattering factors used were those of Cromer & Waber (1965) for C, N and O and those of Stewart, Davidson & Simpson (1965) for hydrogen. The atomic coordinates are given in Table 1.*

Discussion. The crystal and molecular structure of aspartic acid has been studied as a part of a program to obtain accurate values for the bond lengths and bond angles of amino acids and peptides and to understand the conformational and hydrogen bonding properties of these biologically important molecules. The crystal

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* A table of observed and calculated structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30080. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
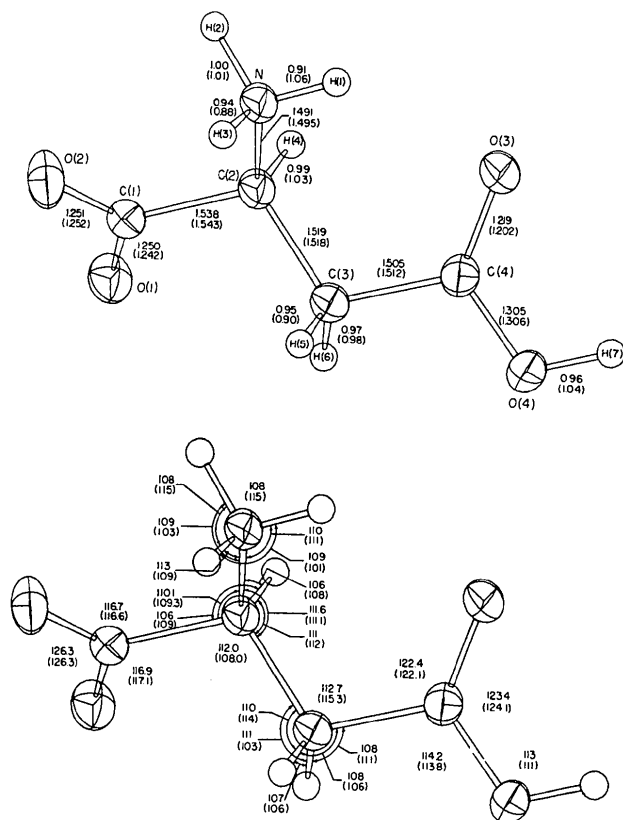

Fig. 1. Bond lengths and bond angles in DL-aspartic acid. The corresponding values for L-aspartic acid are given in parentheses. The molecular plot was made by ORTEP (Johnson, 1965) and the thermal ellipsoids correspond to 50% probability.

structure of L-aspartic acid (LASP) has been determined (Derissen, Endeman & Peerdeman, 1968) and in this paper the two structures are compared. In both cases the α-carboxyl group is ionized and the proton is transferred to the amino group. The bond lengths and bond angles observed in DLASP are given in Fig. 1. The corresponding values in LASP are also given in parentheses in the same figure. In DLASP the average standard deviation in the bond length between heavy atoms is 0·0025 and 0·025 Å for bonds involving the hydrogen atoms. The average standard deviation in bond angles involving heavy atoms is 0·1°. The bond lengths and bond angles in the two structures generally agree well with each other. It is interesting that the C(1)–C(2) bond length to the ionized β-carboxyl group (1·538 Å) is significantly longer than the C(3)–C(4) bond to the un-ionized β-carboxyl group (1·505 Å). The latter value is very close to the value of 1·50 Å usually associated with a Csp^2–Csp^3 bond. The C(2)–sp^3–C(3)sp^3 bond lengths (1·519 Å) lies between these two values. A similar trend is also found in LASP.

The molecule may be considered to be made up of three four-atom planes: C(1), C(2), C(3) and C(4) (plane I), O(1), O(2), C(1), C(2) (plane II) and C(3), C(4), O(3), O(4) (plane III). The mean deviation of the carbon skeleton from plane I in DLASP is 0·03 Å and is larger than the corresponding value of 0·01 Å for LASP. The view of the two molecules (DLASP and LASP) projected on the least-squares plane containing the carbon atoms is given in Fig. 2. The mean deviation of the four atoms in plane II is 0·005 Å and the deviation of the atom N from this plane is 0·201 Å. The corresponding values for LASP are 0·008 and 0·831 Å respectively. The four atoms in the β-carboxyl group are less planar (mean deviation 0·036 Å) in this case than in LASP (0·011 Å). The atom H(7) lies essentially in this plane, the deviation being 0·05 Å in DLASP and 0·03 Å in LASP. It is interesting to note that the β-carboxyl group is twisted in opposite directions about the bond C(3)–C(4) in the two structures. The dihedral angles between the planes (I, II), (II, III), (I, III) are 64·2, 61·8 and 3·9° in DLASP and 95·6, 34·8 and 50·7° in LASP respectively. The NH_3^+ group is in the staggered conformation about the bond C(2)–N. Some torsional angles in the molecule in DLASP and LASP are listed in Table 2. The four available hydrogen atoms participate in four hydrogen bonds. The distances and angles are given in Table 3. In DLASP the atom O(3) of the β-carboxyl group is close to the hydrogen atom H(1) of the amino group. The intramolecular distance between H(1) and O(3) is 2·27 Å and between N and O(3) is 2·862 Å. The angles are C(2)–N···O(3) = 125·7° and H(1)–N···O(3) = 39·2°. In view of these values it appears that there is an interaction between the two atoms but not an intramolecular hydrogen bond. This interaction may be responsible for reducing the bond angle C(2)–C(3)–C(4) to 112·7° in DLASP from 115·3° in LASP, where such an interaction does not exist. It is interesting to note that the normal

hydrogen bond formed by H(1) with O(3) of a neigh-
boring molecule in DLASP has the largest non-linear-
ity, *i.e.* (N–H1)$\cdots$O(3)=21·3°.

Table 2. *Torsion angles*

	DLASP	LASP
O(1)–C(1)–C(2)–N	+171·3°	+144·8°
O(2)–C(1)–C(2)–N	−7·3°	−37·8
O(1)–C(1)–C(2)–C(3)	−64·0	−94·2
O(2)–C(1)–C(2)–C(3)	+117·6	+83·2
C(1)–C(2)–C(3)–C(4)	+174·2	+178·2
C(2)–C(3)–C(4)–O(3)	+3·1	+131·4
C(2)–C(3)–C(4)–O(4)	−175·8	−51·3
N—–C(2)–C(3)–C(4)	−61·9	−61·9
H(1)–N—–C(2)–C(1)	−177	−173
H(2)–N—–C(2)–C(1)	−59	−50
H(3)–N—–C(2)–C(1)	+61	+75
C(3)–C(4)–O(4)–H(7)	+177	+179
O(3)–C(4)–O(4)–H(7)	−2	−4

Table 3. *Hydrogen bond lengths and angles*

	Code	Distance		Angle
N$\cdots\cdots$O(3)	III	2·899 Å	C(2)–N$\cdots\cdots$O(3)	125·9°
H(1)$\cdots$O(3)		2·07	H(1)–N$\cdots\cdots$O(3)	21·3
			N—–H(1)$\cdots$O(3)	149·4
N$\cdots\cdots$O(1)	IV	2·837	C(2)–N$\cdots\cdots$O(1)	107·8
H(2)$\cdots$O(1)		1·84	H(2)–N$\cdots\cdots$O(1)	2·0
			N—–H(2)$\cdots$O(1)	177·0
N$\cdots\cdots$O(1)	VI	2·883	C(2)–N$\cdots\cdots$O(1)	110·9
H(3)$\cdots$O(1)		1·95	H(3)–N$\cdots\cdots$O(1)	5·3
			N—–H(3)$\cdots$O(1)	172·1
O(4)$\cdots$O(2)	VIII	2·558	C(4)–O(4)$\cdots$O(2)	111·1
H(7)$\cdots$O(2)		1·60	H(7)–O(4)$\cdots$O(2)	2·6
			O(4)–H(7)$\cdots$O(2)	175·9

Symmetry code

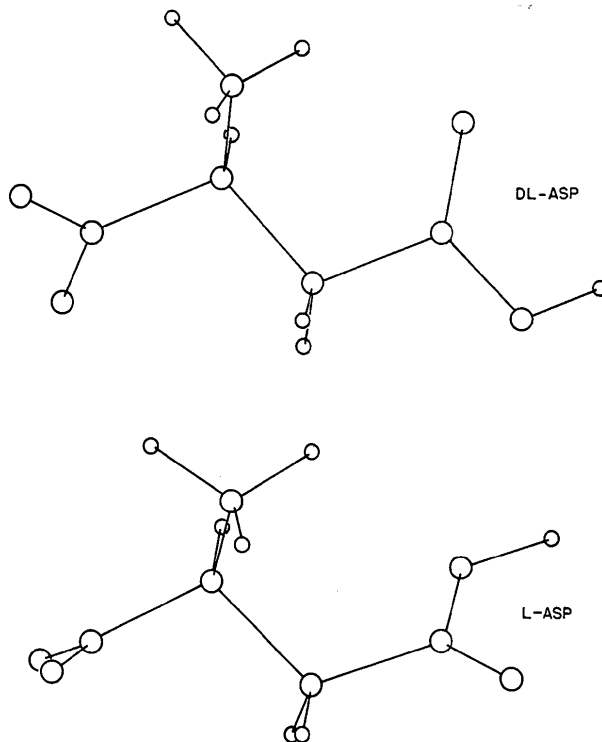| III	$\bar{x}$,	y, $\frac{1}{2}-z$
IV	x,	$\bar{y}$, $\frac{1}{2}+z$
VI	$\frac{1}{2}-x$,	$\frac{1}{2}+y$, $\frac{1}{2}-z$
VIII	$\frac{1}{2}+x$,	$\frac{1}{2}-y$, $\frac{1}{2}+z$

Fig. 2. Projection of the two aspartic acid molecules in the two
different crystal structures on the mean plane containing the
carbon chain.

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Structure Cristalline du Nitroxyde 1,5-Diméthyl-8-aza Bicyclo-[3,2,1]octane-3-one-8-oxyle ou 'NDAO'

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Abstract. $C_9H_{14}NO_2$ ('NDAO') is a stable organic
radical nitroxide. Space group $P2_1/c$, $a=10·05$ (1), $b=$
11·13 (1), $c=14·94$ (1) Å, $\beta=146·1$ (1)° and $Z=4$.

Introduction. Ce composé (Fig. 1) a été synthétise au
Laboratoire de chimie organique physique du C.E.N.G.
(Ronzaud & Rassat, 1970). Des mesures magnétiques