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N-Carbamoyl-DL-aspartic Acid

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Abstract. $C_5H_8N_2O_5$, $P\bar{1}$, $a = 6{\cdot}438$ (2), $b = 7{\cdot}486$ (3), $c = 8{\cdot}048$ (4) Å, $\alpha = 72{\cdot}2$ (1), $\beta = 80{\cdot}8$ (1), $\gamma = 76{\cdot}4$ (1)°, $D_m = 1{\cdot}65$ (1) (flotation), $D_c = 1{\cdot}64$ Mg m^{-3}, $Z = 2$. Final $R = 0{\cdot}095$ for 1205 observed reflections. The molecule assumes the sterically least favourable conformation with the side chain carboxyl group staggered between the α-carboxyl group and the N atom attached to C^{α}. The ureido group takes part in two specific interactions involving two nearly parallel hydrogen bonds in one and two convergent hydrogen bonds in the other.

Introduction. Aspartate transcarbamylase is an allosteric enzyme which plays a key role in the regulation of pyrimidine biosynthesis. *N*-Carbamoyl-L-aspartic acid is one of the products of the reaction catalysed by this enzyme. It also inhibits the enzyme from several sources (Heyde, Nagabhushanam & Morrison, 1973; Chang & Jones, 1974; Savithri, Vaidyanathan & Appaji Rao, 1978). The structure determination of the racemate *N*-carbamoyl-DL-aspartic acid is reported here.

X-ray data were collected on a CAD-4 computer-controlled diffractometer from a specimen of dimensions 0·38 × 0·50 × 0·75 mm using graphite-monochromated Cu $K\alpha$ radiation up to a Bragg angle of 70°. Of the 1360 unique reflections in this range, 1205 had $I > 2\sigma(I)$ and were used for structure solution and refinement. The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971) and refined by the block-diagonal least-squares method to $R = 0{\cdot}095$. The non-H atoms and the H atoms were assigned anisotropic and isotropic thermal parameters respectively. The scattering factors for the heavy atoms were taken from Cromer & Waber (1965) and those for H atoms from Stewart, Davidson & Simpson (1965). The final positional coordinates and the equivalent isotropic temperature factors (Hamilton, 1959) of the non-H atoms are given in Table 1.† It may be mentioned that the final R factor and the e.s.d.'s are somewhat high although the structure analysis is accurate enough to provide an adequate description of the molecular geometry and the crystal structure.

Table 1. *Atomic coordinates* (×10^3) *and equivalent isotropic temperature factors* (×10) (*Hamilton*, 1959) *of the non*-H *atoms with e.s.d.'s in parentheses*

	x	y	z	B_{eq} (Å^2)
C(2)	686 (2)	437 (1)	768 (1)	18 (6)
C(1)	697 (2)	650 (1)	708 (1)	18 (6)
O(2)	637 (1)	731 (1)	837 (1)	28 (5)
O(1)	749 (1)	734 (1)	559 (1)	24 (5)
N(1)	731 (1)	371 (1)	612 (1)	19 (5)
C(3)	695 (2)	202 (1)	610 (1)	18 (6)
O(3)	604 (1)	99 (1)	743 (1)	22 (5)
N(2)	761 (2)	148 (1)	464 (1)	26 (6)
C(4)	834 (2)	324 (1)	908 (1)	20 (7)
C(5)	1070 (2)	319 (1)	838 (1)	18 (6)
O(4)	1135 (1)	467 (1)	765 (1)	24 (5)
O(5)	1184 (1)	150 (1)	860 (1)	31 (6)

Discussion. The crystal structure of the compound is given in Fig. 1 and the torsional angles which define the conformation of the molecule (IUPAC–IUB Commission on Biochemical Nomenclature, 1970) are listed in Table 2. The two carboxyl groups in the structure are not ionized and the ureido group attached to C^{α} is planar. The α-carboxyl group, C^{α} and the N atom attached to C^{α} lie approximately in a plane as observed in almost all α-amino acids (Vijayan, 1976). The ureido and the α-carboxyl groups are nearly coplanar with an angle between them of 14·8 (10)°. The side chain in the molecule assumes the sterically least favourable conformation (Bhat, Sasisekharan & Vijayan, 1979) with its carboxyl group staggered between the α-carboxyl

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† Lists of structure factors, thermal parameters, H-atom parameters and bond lengths and angles involving heavy atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36666 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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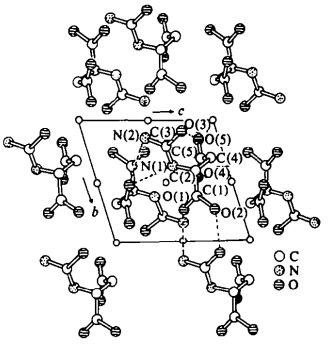

Fig. 1. Crystal structure as viewed along the *a* axis. The broken lines indicate a set of crystallographically non-equivalent hydrogen bonds.

Table 2. *Torsional angles and hydrogen-bond parameters*

φ	C(3)–N(1)–C(2)–C(1)	−166·9 (6)°
ψ_1	N(1)–C(2)–C(1)–O(1)	−4·6 (13)
ψ_2	N(1)–C(2)–C(1)–O(2)	173·5 (8)
χ^1	N(1)–C(2)–C(4)–C(5)	55·0 (11)
χ^{21}	C(2)–C(4)–C(5)–O(4)	54·0 (12)
χ^{22}	C(2)–C(4)–C(5)–O(5)	−124·5 (9)

Hydrogen-bond distances (Å)

O(2)···O(3^{i})	2·59 (1)	H2(N2)···O(4^{ii})	2·5 (1)
H(O2)···O(3^{i})	1·6 (1)	N(2)···O(1^{iii})	2·98 (1)
N(1)···O(4^{ii})	2·98 (1)	H1(N2)···O(1^{iii})	2·0 (1)
H(N1)···O(4^{ii})	2·3 (1)	O(5)···O(3^{iv})	2·69 (1)
N(2)···O(4^{ii})	3·07 (1)	H(O5)···O(3^{iv})	2·0 (1)

Hydrogen-bond angles (°)

H(O2)–O(2)···O(3^{i})	9 (8)	H1(N2)–N(2)···O(1^{iii})	14 (8)
H(N1)–N(1)···O(4^{ii})	34 (10)	H(O5)–O(5)···O(3^{iv})	21 (14)
H2(N2)–N(2)···O(4^{ii})	30 (12)		

Symmetry code: (i) x, $1+y$, z; (ii) $2-x$, $1-y$, $1-z$; (iii) x, $y-1$, z; (iv) $1+x$, y, z.

group and the N atom attached to C$^{\alpha}$. Excluding metal complexes in which the requirement of metal coordination introduces severe steric constraints, such a conformation for the aspartic acid side chain has so far been observed only in the crystal structure of histidine–aspartic acid (Bhat & Vijayan, 1978).

The parameters of the hydrogen bonds which stabilize the crystal structure are given in Table 2. It is interesting to note that the ureido O atom and the unprotonated O atom in the side-chain carboxyl group accept two hydrogen bonds each. Such hydrogen bonds are rare and according to Kuleshova & Zorkii (1981) only 31 such cases (with a common acceptor for two hydrogen bonds) were observed among the 2220 hydrogen bonds in organic homomolecular crystals examined by them. It might also be noted that the O···O distances in the two hydrogen bonds accepted

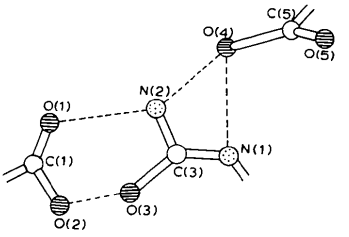

Fig. 2. Specific interactions involving the ureido group.

by the ureido O atom are considerably shorter than the mean of the O···O hydrogen-bonded distances observed in crystal structures (Mitra & Ramakrishnan, 1977; Ceccarelli, Jeffrey & Taylor, 1981) indicating that this O atom is a strong hydrogen-bond acceptor. Such short hydrogen bonds involving a chemically similar O atom are found also in the crystal structures containing urea (Fritchie & McMullan, 1981; Weber, Ruble, Craven & McMullan, 1980).

All the hydrogen bonds in the structure involve the ureido group as either acceptor or donor. The topology of the two specific interactions involving the ureido group, shown in Fig. 2, is of particular interest and is similar to those of two of the specific interactions in which the guanidyl group is known to take part (Salunke & Vijayan, 1981). In one of them, the terminal O and N atoms of this group are connected to the α-carboxyl group of a neighbouring molecule through a pair of nearly parallel hydrogen bonds. The other interaction involves a pair of converging N–H···O hydrogen bonds with the N atoms in the ureido group as the donors and an O atom in the side-chain carboxyl group of an adjacent molecule as the common acceptor.

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Structure of Benz[*a*]anthracene-7,12-dione

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Abstract. $C_{18}H_{10}O_2$, monoclinic, $C2/c$, $a = 10{\cdot}918$ (1), $b = 11{\cdot}369$ (1), $c = 19{\cdot}850$ (1) Å, $\beta = 97{\cdot}224$ (7)°, $U = 2444{\cdot}4$ Å^3, $Z = 8$, $D_m = 1{\cdot}41$ (2), $D_c = 1{\cdot}403$ Mg m^{-3}, $F(000) = 1072$, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0{\cdot}742$ mm^{-1}. 2253 reflections were measured, of which 1039 had significant intensities. Refinement converged to a final R of 0·045. The molecule is approximately planar. Ring C is significantly non-delocalized. Bonds C(3)–C(4) and C(5)–C(6) are short, and indicate pronounced olefinic character for these bonds.

Introduction. The polycyclic aromatic hydrocarbon benz[*a*]anthracene is a well established weak carcinogen (Searle, 1976). Its biological activity results from metabolic activation to reactive species, such as the 9,10-diol 11,12-epoxide or the 5,6-epoxide (Harvey, 1981). Particular regions of reactivity of the benz[*a*]anthracene molecule, such as '*K*' and 'bay' regions, are therefore especially susceptible to electrophilic attack. This is seen, for example, by the olefinic character of the *K* region in various methyl-substituted benz[*a*]anthracene structures.

In this study, we describe the structure of a non-carcinogenic derivative of benz[*a*]anthracene, and compare its geometry with that of various other benz[*a*]anthracene derivatives, all of which show at least some carcinogenic activity. The structure described in this paper is that of the 7,12-dione derivative (BA dione), which appears to have little or no tumorogenic activity following injection into mice (*Survey of Compounds which have been Tested for Carcinogenic Activity*, 1971–1972).

Experimental. Prismatic crystals of BA dione were grown from alcoholic solution, which showed monoclinic symmetry when examined by oscillation and Weissenberg photography. Accurate cell dimensions were obtained by measurement of 25 θ values on an Enraf–Nonius CAD-4 diffractometer. Intensity data were collected on the diffractometer using graphite-monochromated Cu $K\alpha$ radiation and an ω–2θ scan technique ($1{\cdot}5 < \theta < 65{\cdot}0°$). Only 1039 of the 2253 unique reflections measured had significant intensity [$I > 2{\cdot}0\sigma(I)$]. No crystal decomposition was recorded during data collection.

The structure was routinely solved by direct methods and refined by full-matrix least-squares techniques to a final R of 0·045 and a weighted R_w of 0·049. Weights used were of the form $1/[\sigma^2(F_o^2) + (0{\cdot}03F_o^2)^2]^{1/2}$. H-atom positions were located in a difference Fourier synthesis; these, together with individual H-atom isotropic thermal parameters, were included in the refinement. All calculations were performed on a PDP 11/34A computer using the Enraf–Nonius SDP program system, together with others written by S. Islam. Coordinates and thermal parameters are given in Table 1.*

* Lists of structure factors and anisotropic thermal parameters, together with Table 4, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36670 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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