Structure of 9-Aminobicyclo[3.3.1]nonane-9-carboxylic Acid Dihydrate, $C_{10}H_{17}NO_2.2H_2O$

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Abstract. $M_r = 219.3$, $P2_1/c$, $a = 13.582$ (5), $b = 7.182$ (3), $c = 11.936$ (4) Å, $\beta = 105.5$ (1)°, $V = 1122.0$ (9) Å^3, $Z = 4$, $D_m = 1.35$, $D_x = 1.298$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å, $\mu = 1.108$ cm^{-1}, $F(000) = 480$, $T = 303$ K, $R = 0.068$ for 987 diffractometer reflections. The bicyclo[3.3.1]nonane system exists in the twin-chair conformation, with the two cyclohexane rings as slightly flattened chairs. The structure is stabilized by a network of N—H···O and O—H···O hydrogen bonds involving the ionized carboxyl and amino groups and the water molecules. The structure is compared with that of the hydrobromide.

Introduction. 9-Aminobicyclo[3.3.1]nonane-9-carboxylic acid dihydrate (ABN) is an amino-acid analogue, having the bicyclo[3.3.1]nonane system as its side group. The structural study of this compound forms part of a project on antagonists of amino acids, some of which were reported earlier from this laboratory (Chacko, Swaminathan & Bhattacharjee, 1980). The bicyclo[3.3.1]nonane system is of considerable stereochemical interest as it can be constructed by the 1,3-fusion of two cyclohexane ring systems and it has been predicted that this bicyclic molecule would prefer a boat-chair conformation (Eliel, 1962) instead of the twin-chair conformation to relieve the strong repulsion of the axial H atoms of C(3) and C(7). The conformational aspects of the bicyclo[3.3.1]nonane system, based on X-ray studies, have already been reported (Bhattacharjee & Chacko, 1979). The structure of ABN is reported here due to the interest in it as an amino-acid analogue and for the conformational aspects of its side group. The hydrobromide derivative of the same compound, namely 9-aminobicyclo[3.3.1]-nonane-9-carboxylic acid hydrobromide monohydrate (ABN.HBr), has already been reported (Bhattacharjee, Chacko & Zand, 1979). The title compound was synthesized and made available by Dr R. Zand of the Biophysics and Research Division, University of Michigan, USA.

Experimental. Needle-shaped crystal (from water), $0.2 \times 0.3 \times 0.3$ mm, Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation for collection of three-dimensional X-ray data, density measurement by flotation, cell constants and e.s.d.'s at 303 K from least-squares refinement of 13 reflections, $7 < \theta < 12°$, 987 independent reflections, $I > 2\sigma(I)$, corrected for Lorentz and polarization factors, 1517 unique reflections out of which 530 unobserved, limiting value for 2θ of 60°, $-14 < h < 14$, $0 < k < 7$, $0 < l < 13$, 2 standard reflections, intensity variation <4%; structure determination by *MULTAN*80 (Main *et al.*, 1980), 13 non-hydrogens and water molecules (two per asymmetric unit) located from difference map and confirmed by density measurement. Successive refinements on F of positions and B_{iso}, H from stereochemical considerations and confirmed by ΔF syntheses, block-diagonal anisotropic refinement (Shiono, 1968), max. height in final ΔF syntheses <0.4 e Å^{-3}, final full-matrix refinement with overall scale factor, Hughes-type weighting scheme (Hughes, 1941), $w = 1/\sigma^2$, $\sigma = |F_o|$ for $|F_o| \geq 25.0$ and $\sigma = 25.0$ for $|F_o| < 25.0$, *UCLALS*1 (Gantzel, Sparks & Trueblood, 1961), final $R = 0.068$,‡ $wR = 0.072$, $S = 4.8$, ratio of $\Delta/\sigma < 0.6$, H included in structure-factors calculations with isotropic temperature factors but not refined, atomic scattering factors from *International Tables for X-ray Crystallography* (1962).

Discussion. The bond lengths and bond angles are shown in Fig. 1. Fractional atomic coordinates of the non-hydrogens and their equivalent isotropic thermal parameters are listed in Table 1. The molecule exists as a zwitterion. The ionized carboxyl group is planar and the nitrogen atom is out of its plane by 1.414 (5) Å in contrast to the structure of ABN.HBr, where the nitrogen is nearly coplanar with the un-ionized carboxyl group.

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‡ Lists of structure factors, anisotropic thermal parameters, hydrogen-atom coordinates, bond lengths and bond angles and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39321 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The dimensions of the bicyclo[3.3.1]nonane system of ABN compare well with those of ABN.HBr. The C(9)—N and C(9)—C(10) distances, 1·525 (6) and 1·576 (7) Å, in ABN agree fairly well with the corresponding values of 1·507 (8) and 1·566 (8) Å in ABN.HBr. However, these values differ significantly from the corresponding C^α—N and C^α—C' distances of 1·487 (6) and 1·531 (5) Å observed in amino acids (Ramanathan & Chidambaram, 1975). The C(10)—C(9)—N angle, 101·9 (3)°, which is close to 102·6 (4)° observed in ABN.HBr, is significantly smaller than the tetrahedral value. The mean C—C bond length, 1·540 (8) Å, of ABN agrees fairly well with corresponding values of 1·533 (10) Å observed in ABN.HBr. The C—C—C bond angle of the one-atom bridge in ABN is nearly tetrahedral [108·9 (4)°] as it is for ABN.HBr. The mean C—C—C bond angle of the three-atom bridgeheads [114·2 (4)°] in ABN is significantly larger than the tetrahedral value and compares well with 114·7 (6)° in ABN.HBr.

The bicyclo[3.3.1]nonane system exists in the twin-chair conformation, as in ABN.HBr, with structural features nearly agreeing with the features of the twin-chair conformation of the system reported by
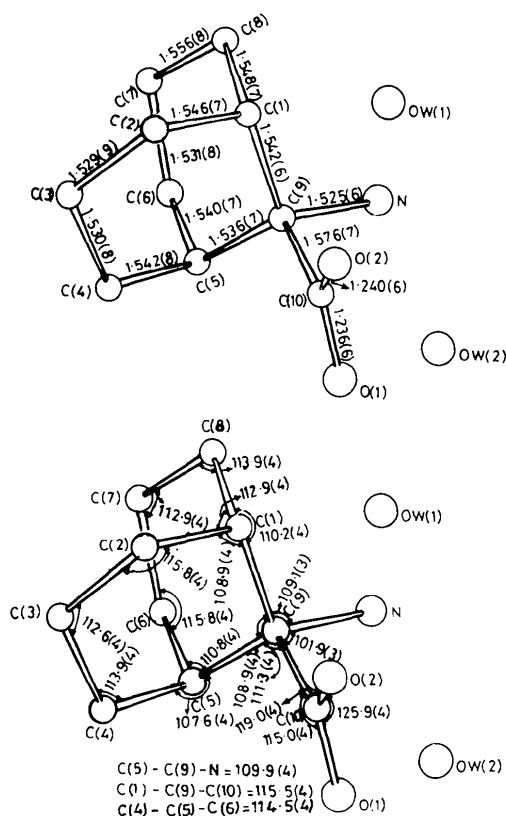
Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and their equivalent isotropic thermal parameters* ($\times 10^2$) *with e.s.d.'s in parentheses*

	x	y	z	$B_{eq}(Å^2)^*$
C(1)	2358 (3)	11362 (7)	1214 (4)	282
C(2)	1507 (4)	12629 (7)	1430 (5)	367
C(3)	865 (4)	11792 (8)	2179 (5)	416
C(4)	1510 (4)	10718 (8)	3227 (5)	392
C(5)	2306 (4)	9408 (7)	2935 (4)	284
C(6)	1847 (4)	7764 (7)	2137 (5)	326
C(7)	1331 (4)	8261 (7)	868 (5)	397
C(8)	1936 (4)	9739 (7)	368 (4)	364
C(9)	2998 (3)	10594 (6)	2390 (4)	270
C(10)	3600 (4)	12096 (7)	3274 (5)	304
O(1)	4025 (3)	11497 (5)	4255 (3)	485
O(2)	3646 (3)	13716 (5)	2932 (3)	454
N	3864 (3)	9402 (5)	2188 (3)	271
OW(1)	3682 (3)	5913 (5)	1024 (3)	493
OW(2)	4878 (3)	6690 (5)	3864 (3)	365

* $B_{eq} = \frac{4}{3}[b_{11}a^2 + b_{22}b^2 + b_{33}c^2 + ab b_{12}\cos\gamma + bc b_{23}\cos\alpha + ac \times b_{13}\cos\beta]$.

Bhattacharjee & Chacko (1979) (under group I structures). ABN prefers a twin-chair conformation owing to the absence of bulky substituents at C(3) and C(7), whereas with bulky substituents the predicted conformation is chair-boat (Bhattacharjee & Chacko, 1979). The two cyclohexane rings exist as slightly flattened chairs. This is due to the non-bonded interaction between the axial hydrogens H2C(3)–H2C(7) = 1·87 (8) Å of the methylene groups C(3) and C(7) and is reflected in the increase of the C(3)···C(7) separation from the ideal twin-chair value of 2·5 Å (Brown, Martin & Sim, 1965) to 3·132 (8) Å and the concomitant flattening of the rings. This value closely agrees with the value of 3·12 (5) Å observed in ABN.HBr. The slightly flattened chair conformation of the cyclohexane rings is also evident from the average value of the torsion angles observed for the system about the C—C bonds with respect to the one-atom and three-atom bridgeheads, which indicates more flattening of the cyclohexane rings at the three-atom bridgehead. The average value of the torsion angles in ABN about the one-atom bridgehead is ±62·6 (4)°, that about the three-atom bridgehead involving methine carbons [C(1) and C(5)] is ±53·2 (5)° and that about the three-atom bridgehead involving the methylene carbons [C(3) and C(7)] is ±42·8 (6)°. These values closely agree with the average values of 62 (2), 52 (2) and 44 (3)° respectively reported for bicyclo[3.3.1]-nonanes under group I structures (Bhattacharjee & Chacko, 1979). The theoretical value of the torsion angle about C—C bonds for the cyclohexane chair conformation is ±54·7° (Bixon & Lifson, 1967).

The molecular packing viewed down the *b* axis is shown in Fig. 2 with hydrogen bonds indicated. The hydrogen-bonding scheme is given in Table 2. It is interesting to note that there exist broad similarities in the packing features of this molecule and ABN.HBr.
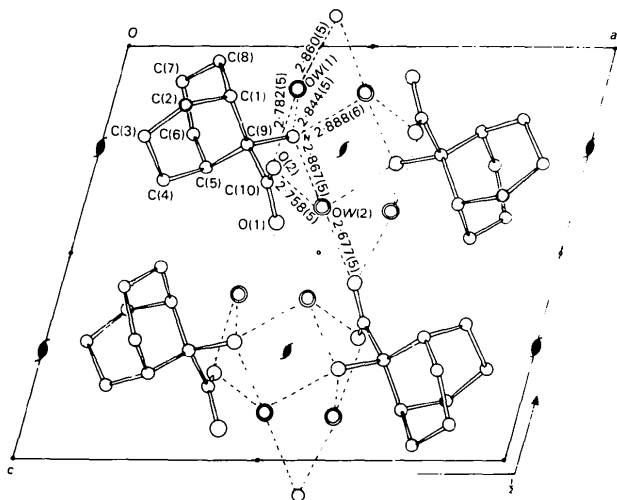

Fig. 1. Bond lengths (Å) and bond angles (°).

Fig. 2. Projection of the structure down the *b* axis.

Table 2. *Hydrogen-bonding scheme of ABN*

$D–H\cdots A$	$D\cdots A$ (Å)	$H\cdots A$ (Å)	$D–H\cdots A$ (°)
N–H1N$\cdots$O*W*(2)	2·867 (5)	1·92 (4)	152 (3)
N–H3N$\cdots$O*W*(2^{ii})	2·888 (6)	1·85 (4)	175 (3)
N–H2N$\cdots$O*W*(1)	2·844 (5)	1·89 (4)	150 (3)
O*W*(1)–H1*W*(1)$\cdots$O(1^{iv})	2·860 (5)	1·85 (4)	179 (3)
O*W*(1)–H2*W*(1)$\cdots$O(2^{i})	2·782 (5)	1·77 (4)	179 (3)
O*W*(2)–H1*W*(2)$\cdots$O(2^{i})	2·758 (5)	1·94 (4)	136 (3)
O*W*(2)–H2*W*(2)$\cdots$O(1^{iii})	2·677 (5)	1·79 (4)	162 (3)

Symmetry code: (i) x, $y-1$, z; (ii) $1-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; (iii) $1-x$, $2-y$, $1-z$; (iv) x, $\frac{3}{2}-y$, $z-\frac{1}{2}$.

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The amino nitrogen (NH$_3^+$) forms three N–H$\cdots$O hydrogen bonds with the water oxygens O*W*(1), O*W*(2) and symmetry-related O*W*(2). The two water molecules in the asymmetric unit form an extensive O–H$\cdots$O hydrogen-bonded network with the symmetry-related carboxyl oxygen atoms. While O*W*(2) acts as acceptor of two N–H$\cdots$O hydrogen bonds, O*W*(1) acts as acceptor of only one N–H$\cdots$O hydrogen bond.

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Structures of a Hydrocarbon $C_{58}H_{40}$ and its Photo-oxidation Products.
II. 4'5'-Dihydro-1',2,2',3,4,4,4'-heptaphenylspiro[cyclopent-2-ene-5,5'-naphtho[2,1-*b*]furan]-1-one, $C_{58}H_{40}O_2$

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Abstract. $M_r = 768\cdot95$, triclinic, $P\bar{1}$, $a = 12\cdot030$ (3), $b = 13\cdot196$ (3), $c = 13\cdot754$ (3) Å, $\alpha = 93\cdot27$ (2), $\beta = 100\cdot56$ (2), $\gamma = 109\cdot20$ (2)°, $V = 2010\cdot9$ (8) Å^3, $Z = 2$, $\lambda(\text{Mo } K\alpha_1) = 0\cdot709300$ Å, $T = 295$ (2) K, $F(000) = 808$, $D_x = 1\cdot270$ Mg m^{-3}, $\mu = 0\cdot070$ mm^{-1}, final $R = 0\cdot039$ for 4171 observed data $[I > 3\sigma(I)]$, $0\cdot115$ for all 7867 data. The sample was provided by M. J. Gallagher and I. D. Jenkins of the School of Chemistry, The University of New South Wales. The solution by direct methods was facilitated by the fortunate inclusion of a pair of Friedel equivalents in the reflection data. Photo-oxidation of the parent hydrocarbon was found