C(2), C(4) and C(5) is near to the tetrahedral value. The bond valency angles of 113·6° and 114·2° at C(6) and C(7) are a little greater than the tetrahedral value.

All the other distances and bond angles are normal and in good agreement with those obtained by Dobler & Dunitz (1964) for 3-azabicyclo[3,3,1]nonane hydrobromide. The bond lengths and angles of the hydrogen atoms are shown in Table 5.

The arrangement of the molecules in the crystal as seen in projection along the b axis is shown in Fig. 2.

The nearest contacts between the molecule and the unattached Br⁻ ion are shown in Fig 3.

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The Crystal Structures of Azabicyclo Compounds. II. The Crystal and Molecular Structure of 1,2,4,4,5,8-Hexamethyl-8-N-acetamidobicyclo[3,3,1]-3-azanonane (ANA)

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The title compound (ANA) crystallizes in the monoclinic space group $C2/c$ with $Z = 8$. The cell dimensions are $a = 19·409$ (2), $b = 18·368$ (1), $c = 10·258$ (3) Å, $\beta = 117·478$ (1)°. The phasing model was obtained using direct methods and the refinement was carried out by full-matrix least-squares methods. The final R value was 0·075. The positions of the hydrogen atoms were located from a difference Fourier synthesis.

Introduction

The compound ANA is the hydrogenated derivative of the compound BRANA (described in part I). Therefore the double bond between the N(3) and C(2) atoms is eliminated. The resolution of this structure was undertaken in order to ascertain the new conformation of the bicyclo compound.

Experimental

A crystalline sample of ANA was provided by Professor García-Muñoz. Crystals, obtained by slow evaporation from a solution in absolute ethanol, were colourless, belonging to the monoclinic system. Accurate values for the cell parameters were determined by least-

squares calculations on an automatic four-circle diffractometer with Mo $K\alpha$ radiation. The crystal data are given in Table 1.

The θ–2θ scan mode of the Philips PW 1100 diffrac-

Table 1. Crystal data

Standard deviations, given in parentheses, refer to the least significant digits.

Molecular formula	$C_{16}H_{30}N_2O$
Molecular weight	266·427
Space group	$C2/c$
$a = 19·409$ (2) Å	$d_x = 1·074$ g cm⁻³
$b = 18·368$ (1)	$Z = 8$
$c = 10·258$ (3)	$F(000) = 1168·00$
$\beta = 117·478$ (1)°	$V = 3244·48$ Å³
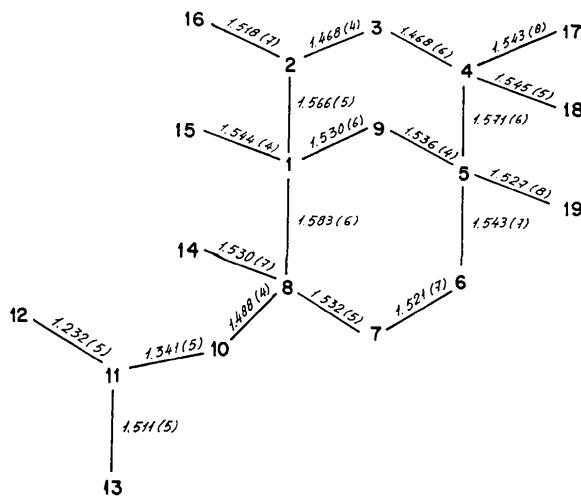
Fig. 1. Bond lengths (Å) with their estimated standard deviations in parentheses. Distances not shown on the diagram are N(3)–C(7) = 2·880, N(3)–C(9) = 2·542 and C(7)–C(9) = 2·920 Å.

Table 2. *The positional* ($\times 10^4$) *and thermal* ($\times 10^3$) *parameters for non-hydrogen atoms*

Standard deviations, given in parentheses, refer to the least significant digits. Thermal factors are those in the expression

$$\exp(-2\pi^2 \sum U_{ij} a_i^* a_j^* h_i h_j).$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2097 (2)	1510 (2)	6680 (3)	57 (2)	51 (2)	34 (2)	3 (2)	23 (2)	5 (1)
C(2)	2539 (2)	2247 (2)	7265 (4)	65 (3)	58 (2)	54 (2)	−15 (2)	29 (2)	−2 (2)
N(3)	3203 (2)	2154 (2)	8727 (3)	60 (2)	67 (2)	52 (2)	−12 (2)	23 (2)	−14 (2)
C(4)	3799 (2)	1621 (2)	8880 (4)	52 (2)	92 (3)	54 (2)	−7 (2)	24 (2)	−10 (2)
C(5)	3384 (2)	875 (2)	8240 (4)	54 (2)	77 (3)	48 (2)	8 (2)	23 (2)	−6 (2)
C(6)	3019 (3)	532 (3)	9149 (4)	75 (3)	76 (3)	40 (2)	2 (3)	13 (2)	12 (2)
C(7)	2356 (3)	970 (3)	9158 (4)	76 (3)	78 (3)	37 (2)	−17 (3)	29 (2)	−2 (2)
C(8)	1722 (2)	1155 (2)	7610 (3)	57 (2)	54 (2)	40 (2)	−5 (2)	29 (2)	−3 (2)
C(9)	2714 (2)	989 (2)	6688 (3)	58 (2)	70 (2)	39 (2)	8 (2)	27 (2)	−6 (2)
N(10)	1343 (2)	470 (2)	6842 (3)	58 (2)	50 (2)	40 (1)	−8 (2)	25 (1)	−7 (1)
C(11)	1034 (2)	−39 (2)	7353 (4)	54 (2)	53 (2)	45 (2)	2 (2)	23 (2)	−5 (2)
O(12)	1015 (2)	−4 (1)	8536 (3)	86 (2)	75 (2)	54 (1)	−13 (2)	44 (1)	3 (1)
C(13)	697 (2)	−688 (2)	6355 (4)	72 (3)	61 (3)	54 (2)	−9 (2)	27 (2)	2 (2)
C(14)	1101 (3)	1623 (2)	7728 (5)	86 (3)	68 (3)	93 (3)	0 (2)	64 (3)	−9 (2)
C(15)	1477 (2)	1643 (2)	5077 (4)	68 (3)	64 (2)	45 (2)	−7 (2)	24 (2)	8 (2)
C(16)	2087 (3)	2916 (2)	7291 (5)	89 (3)	52 (2)	84 (3)	−2 (2)	37 (3)	−6 (2,
C(17)	4281 (3)	1889 (3)	8128 (5)	66 (3)	139 (5)	86 (3)	−14 (3)	46 (3)	−3 (3)
C(18)	4355 (3)	1579 (3)	546 (5)	59 (3)	120 (4)	61 (3)	−9 (3)	14 (2)	−16 (3)
C(19)	3949 (3)	323 (3)	8149 (5)	76 (3)	121 (4)	85 (3)	32 (3)	19 (3)	−17 (3)
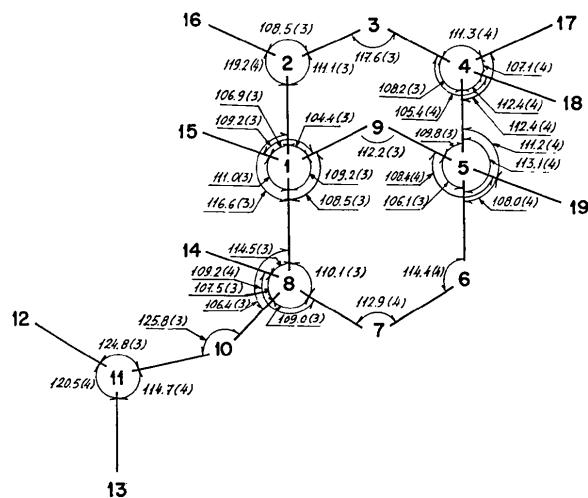
Fig. 2. Valency angles (°), with their estimated standard deviations in parentheses.

Table 3. *Positional* ($\times 10^3$) *and thermal parameters for hydrogen atoms*

Standard deviations, given in parentheses, refer to the least significant digits.

	x	y	z	B
H(2)	2755 (3)	2360 (3)	6519 (6)	6·350
H(3)	3441 (3)	2607 (3)	9070 (6)	6·569
H(6,1)	2163 (3)	4923 (3)	1247 (7)	7·637
H(6,2)	3420 (3)	452 (3)	162 (6)	7·637
H(7,1)	2560 (3)	1434 (3)	9678 (7)	7·177
H(7,2)	2105 (3)	683 (3)	9670 (6)	7·177
H(9,1)	2494 (3)	495 (3)	6274 (5)	6·103
H(9,2)	2914 (3)	1192 (3)	6060 (5)	6·103
H(10)	1300 (3)	385 (3)	5939 (5)	5·357
H(13,1)	648 (3)	9360 (3)	5383 (5)	5·487
H(13,2)	1016 (3)	8888 (3)	6799 (5)	5·487
H(13,3)	168 (3)	9197 (2)	6298 (5)	5·487
H(14,1)	824 (3)	1327 (3)	8129 (7)	8·336
H(14,2)	692 (3)	1820 (3)	6758 (7)	8·336
H(14,3)	1294 (4)	2047 (3)	8343 (7)	8·336
H(15,1)	1036 (3)	1939 (3)	5045 (6)	7·077
H(15,2)	1724 (3)	1901 (3)	4612 (6)	7·077
H(15,3)	1240 (3)	1156 (3)	4523 (6)	7·077
H(16,1)	2457 (4)	3350 (3)	7426 (7)	8·194
H(16,2)	1955 (3)	2918 (3)	8123 (7)	8·194
H(16,3)	1552 (4)	2978 (3)	6378 (6)	8·194
H(17,1)	3992 (4)	1867 (3)	7033 (7)	8·822
H(17,2)	4717 (4)	1530 (3)	8457 (7)	8·822
H(17,3)	4533 (4)	2423 (3)	8545 (7)	8·822
H(18,1)	4737 (3)	1201 (3)	722 (6)	7·248
H(18,2)	4050 (3)	1443 (3)	1097 (6)	7·248
H(18,3)	4656 (3)	2034 (3)	891 (6)	7·248
H(19,1)	3696 (4)	9837 (4)	7890 (8)	10·968
H(19,2)	4168 (4)	489 (4)	7477 (8)	10·968
H(19,3)	4374 (4)	244 (4)	9089 (8)	10·968

tometer, monochromated with a graphite crystal, was used for the recording of intensity data. Three reflexions were monitored after every 22 measurements and showed good stability. A total of 2078 independent reflexions were collected in the range $6° < 2\theta < 60°$. Of these 1768 were directly observed, and 310 were considered as unobserved according to the criterion $I < 2\sigma(I)$ where $I = Cp - Cb_1 - Cb_2$ and $\sigma^2(I) = Cp + Cp_1 + Cp_2 + (0.04 \times I)^2$, I being the integrated intensity and $\sigma(I)$ its estimated standard deviation.

The structure amplitudes were obtained after the usual Lorentz and polarization reduction. No correction for absorption was applied.

Structure determination and refinement

Atomic scattering factors for carbon and oxygen were those from *International Tables for X-ray Crystallography* (1974).

An overall temperature factor ($B = 4.086$) and scale factor were calculated (Wilson, 1942) and used to compute normalized structure factors (E) (Karle & Hauptman, 1956). The statistics of the E's confirmed a centrosymmetric structure. Direct methods were applied with the *MULTAN* program (Main, Woolfson & Germain, 1971). The 205 E values greater than 1·90 were used to generate a starting set of phases ($R_{\text{Karle}} = 21.39$,

absolute figure of merit of 1·18). An E map based on these phases showed the two ring fragments and six more atoms. A structure factor Fourier synthesis revealed the four remaining heavy atoms. Four cycles of least-squares calculations with isotropic temperature factors converged to an R of 0·172. Anisotropic

temperature factors were included in the next least-squares refinement and R decreased to 0·099. A difference map was computed and all hydrogen atoms were located. Three cycles of full-matrix least-squares refinement including the heavy atoms with anisotropic temperature factors and the hydrogen atoms with iso-

Table 4. *Least-squares planes, torsion angles and dihedral angles*

	Key to planes		Equations of the planes
1	C(1), C(2), C(4), C(5)	1	$0.6600X + 0.0451Y - 0.7499Z + 3.8120 = 0$
2	C(1), C(5), C(6), C(8)	2	$0.0160X + 0.7833Y + 0.6215Z - 5.9632 = 0$
3	C(1), C(5), C(6), C(7), C(8), C(9)	3	$0.2305X + 0.8760Y + 0.4236Z - 4.9470 = 0$
4	C(1), C(2), N(3), C(4), C(5), C(9)	4	$0.7234X + 0.3082Y - 0.6179Z + 1.9713 = 0$
5	C(8), N(10), C(11), O(12), C(13)	5	$0.7613X - 0.4659Y + 0.4510Z - 1.9322 = 0$
6	C(8), N(10), C(14)	6	$-0.2147X - 0.4247Y + 0.8795Z - 5.2463 = 0$
7	C(4), C(17), C(18)	7	$-0.3043X + 0.9466Y + 0.1062Z - 2.7114 = 0$

Distances (Å) of atoms from the planes. Italicized values belong to atoms forming the planes.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
C(1)	*−0·0222*	*0·0012*	*0·2664*	*−0·2729*	0·2095	−1·2720	0·2824
C(2)	*0·0225*	1·4019	1·8119	*0·2352*	0·2613	−1·5029	1·4437
N(3)	−0·5886	2·1056	2·3646	*−0·2069*	1·3944	−0·3895	1·2431
C(4)	*−0·0224*	1·4419	1·8147	*0·1885*	2·7392	−0·0828	*−0·0000*
C(5)	*0·0221*	*−0·0012*	0·2525	*−0·2361*	2·7330	0·0939	−1·2060
C(6)	−1·3791	*0·0012*	*−0·2119*	−1·7661	2·5323	1·3342	−1·3680
C(7)	−2·1999	0·6161	*0·1996*	−2·4558	1·1781	1·2757	−0·2119
C(8)	−1·4575	*−0·0012*	*−0·2144*	−1·8417	*0·0054*	*−0·0000*	0·1116
C(9)	0·7176	−0·7234	*−0·2921*	*0·2923*	1·5672	−1·1164	−0·9848
N(10)	−1·2362	−1·4277	−1·6995	−2·0676	*−0·0071*	*0·0000*	−1·0411
C(11)	−2·1820	−1·8840	−2·5148	−3·2511	*−0·0024*	0·9861	−1·6201
O(12)	−3·3800	−1·1745	−2·1404	−4·3279	*−0·0004*	2·0340	−1·2640
C(13)	−1·6753	−3·3855	−3·9864	−3·1897	*0·0045*	0·7330	−2·7900
C(14)	−2·3317	0·7181	0·2927	−2·5557	−1·3073	*0·0000*	1·3203
C(15)	0·7893	−0·7212	−0·2389	0·3824	−0·9008	−2·5636	0·4950
C(16)	−0·5263	2·3653	2·6940	−0·0435	−0·9784	−1·8140	2·8811
C(17)	1·3658	1·4223	2·2534	1·6976	3·1843	−1·1715	*0·0000*
C(18)	−0·9708	2·3286	2·4568	−0·5614	3·6799	1·2206	*−0·0000*
C(19)	0·7899	−0·8285	−0·4083	0·3262	4·0345	0·2071	−2·5209

Dihedral angles

| Planes	Angle	Planes	Angle	Planes	Angle	Planes	Angle
1–2	65·2	1–5	81·8	1–6	34·9	1–7	76·2
1–3	82·8	2–5	85·8	2–6	77·8	2–7	36·6
2–3	17·6	3–5	87·6	3–6	87·2	3–7	36·5
1–4	17·3	4–5	82·6	4–6	33·9	4–7	89·7
2–4	82·5			5–6	64·5	5–7	51·3
3–4	79·9					6–7	75·9
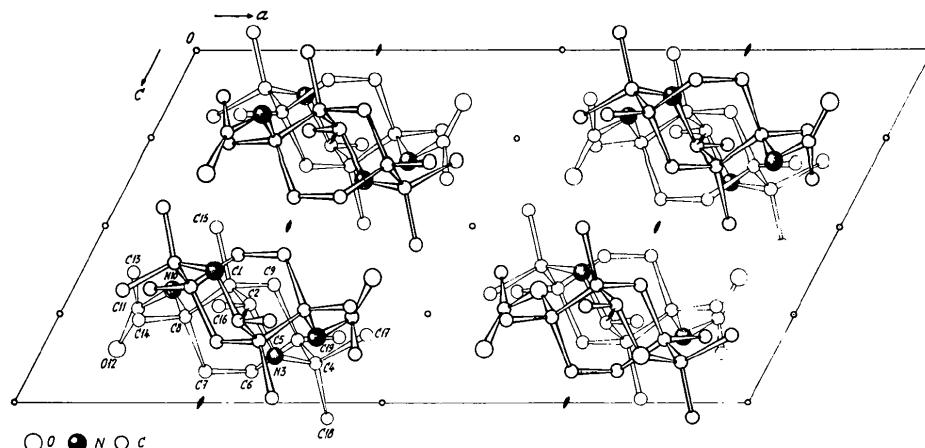
Fig. 3. Projection of the crystal structure along the b axis and the atom numbering.

Table 5. *Bond lengths (Å) and valence angles (°) concerning the hydrogen atoms*

C(2)—H(2)	1·049	C(1)——C(2)—H(2)	102·9	H(14,1)-C(14)-H(14,3)	107·3
N(3)—H(3)	0·938	C(3)——C(2)—H(2)	108·1	H(14,2)-C(14)-H(14,3)	104·3
C(6)—H(6,1)	0·991	C(16)——C(2)—H(2)	106·3	C(1)——C(15)-H(15,1)	110·8
C(6)—H(6,2)	0·980	C(2)——N(3)—H(3)	109·3	C(1)——C(15)-H(15,2)	106·9
C(7)—H(7,1)	0·985	C(1)——N(3)—H(3)	108·9	C(1)——C(15)-H(15,3)	112·0
C(7)—H(7,2)	1·014	C(5)——C(6)—H(6,1)	107·6	H(15,1)-C(15)-H(15,2)	109·7
C(9)—H(9,1)	1·010	C(5)——C(6)—H(6,2)	109·8	H(15,1)-C(15)-H(15,3)	106·9
C(9)—H(9,2)	0·967	C(7)——C(6)—H(6,1)	110·2	H(15,2)-C(15)-H(15,3)	110·6
N(10)-H(10)	0·904	C(7)——C(6)—H(6,2)	109·5	C(2)——C(16)-H(16,1)	104·8
C(13)-H(13,1)	0·962	H(6,1)—C(6)—H(6,2)	104·9	C(2)——C(16)-H(16,2)	113·3
C(13)-H(13,2)	0·968	C(6)——C(7)—H(7,1)	109·7	C(2)——C(16)-H(16,3)	114·9
C(13)-H(13,3)	1·022	C(6)——C(7)—H(7,2)	109·4	H(16,1)-C(16)-H(16,2)	108·6
C(14)-H(14,1)	0·979	C(8)——C(7)—H(7,1)	107·4	H(16,1)-C(16)-H(16,3)	112·3
C(14)-H(14,2)	1·011	C(8)——C(7)—H(7,2)	107·7	H(16,2)-C(16)-H(16,3)	103·1
C(14)-H(14,3)	0·963	H(7,1)—C(7)—H(7,2)	109·7	C(4)——C(17)-H(17,1)	113·3
C(15)-H(15,1)	1·003	C(1)——C(9)—H(9,1)	112·3	C(4)——C(17)-H(17,2)	103·6
C(15)-H(15,2)	0·945	C(1)——C(9)—H(9,2)	108·1	C(4)——C(17)-H(17,3)	110·9
C(15)-H(15,3)	1·045	C(5)——C(9)—H(9,1)	107·7	H(17,1)-C(17)-H(17,2)	107·6
C(16)-H(16,1)	1·039	C(5)——C(9)—H(9,2)	109·6	H(17,1)-C(17)-H(17,3)	113·2
C(16)-H(16,2)	0·999	H(9,1)—C(9)—H(9,2)	106·8	H(17,2)-C(17)-H(17,3)	107·6
C(16)-H(16,3)	1·035	C(8)——N(10)-H(10)	118·5	C(4)——C(18)-H(18,1)	109·0
C(17)-H(17,1)	0·998	C(11)——N(10)-H(10)	115·7	C(4)——C(18)-H(18,2)	109·7
C(17)-H(17,2)	1·001	C(11)——C(13)—H(13,1)	115·8	C(4)——C(18)-H(18,3)	110·5
C(17)-H(17,3)	1·093	C(11)——C(13)—H(13,2)	109·4	H(18,1)-C(18)-H(18,2)	108·1
C(18)-H(18,1)	0·970	C(11)——C(13)—H(13,3)	108·2	H(18,1)-C(18)-H(18,3)	105·3
C(18)-H(18,2)	1·019	H(13,1)-C(13)—H(13,2)	107·3	H(18,2)-C(18)-H(18,3)	114·0
C(18)-H(18,3)	0·987	H(13,1)-C(13)—H(13,3)	110·1	C(5)——C(19)-H(19,1)	109·5
C(19)-H(19,1)	0·994	H(13,2)-C(13)—H(13,3)	105·6	C(5)——C(19)-H(19,2)	112·4
C(19)-H(19,2)	1·010	C(8)——C(14)—H(14,1)	109·1	C(5)——C(19)-H(19,3)	110·6
C(19)-H(19,3)	0·948	C(8)——C(14)—H(14,2)	114·4	H(19,1)-C(19)-H(19,2)	113·6
		C(8)——C(14)—H(14,3)	115·0	H(19,1)-C(19)-H(19,3)	103·1
		H(14,1)-C(14)—H(14,2)	106·2	H(19,2)-C(19)-H(19,3)	107·2

tropic thermal parameters (the value of the adjacent heavy atom) were carried out. The final R index was 0·075. In all refinements unit weight was assigned for each reflexion. Final parameters are listed in Tables 2 and 3.*

Discussion

Figs. 1 and 2 show the bond lengths and bond angles with their standard deviations. In Table 2 some of the least-squares planes through several parts of the molecule, the deviation of the atoms from this plane and some dihedral and torsional angles are listed.

In this compound the only H atom attached to the N atom is located in the *exo* position. The displacement of the N(3) atom from the plane through C(1), C(2), C(4) and C(5) is −0·589 Å (Table 4). The deviation of the bridge atom C(9) from the same plane is 0·718 Å. Consequently the cyclohexane ring C(1),C(2), N(3),C(4), C(5), C(9) presents a slightly flattened chair conformation. The bond length C(2)–N(3) 1·468 Å is normal for a single bond. In the other ring the deviations of the C(7) and C(9) atoms from the plane through C(1), C(5), C(6) and C(8) are 0·616 and −0·723 Å respectively. Since in the ANA compound there is no interaction between the *endo* hydrogen atom at C(7) and

the H atom at N(3), the chair conformation is even closer to the ideal than the corresponding conformation exhibited by same ring in the BRANA compound. As a result the distance N(3)···C(7) is 2·880 Å, near to the value of 2·25 Å found in the ideal chair conformation. The distance N(3)···H(7,1) is 2·991 Å. The bond angles at C(6) and C(7) (Table 5) are greater than those in the BRANA compound.

The angles C(4)–C(5)–C(6) of 113·1° and C(2)–C(1)–C(8) of 116·6° are greater than the tetrahedral value. The angle between the two rings is 100·1°. All other bond lengths and angles are very similar to those found for the previous compound. A projection of the structure along the b axis is illustrated in Fig. 3. The approach distances appear to indicate normal van der Waals interactions.

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