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Molecular structures and conformations of three 3-azabicyclononanes

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Abstract

The structure, conformation, molecular geometry and the mode of packing of 7-*tert*-butyl-*N*-methyl-2,4-diphenyl-3-azabicyclo[3.3.1]nonane ($C_{25}H_{33}N$; MTABN), *N*-acetyl-2,4-diphenyl-3-azabicyclo[3.3.1]nonane ($C_{22}H_{25}NO$; AABN) and *N*-methyl-2,4-bis(2-methylphenyl)-3-azabicyclo[3.3.1]nonan-9-ol ($C_{23}H_{29}NO$; MHABN) are presented. The compounds MTABN and MHABN crystallize in monoclinic space groups, whereas AABN is orthorhombic. In each of the three structures, the bicyclic ring system adopts a chair–chair conformation and the phenyl rings are in equatorial orientation with respect to the piperidine ring. In AABN, apart from the van der Waals forces, weak intermolecular C—H···O type interactions are involved in the packing.

1. Introduction

Many derivatives of 3-azabicyclononanes have been found to possess useful medicinal and biological activities, including analgesic (Kobayashi *et al.*, 1970), anti-inflammatory (Ohki *et al.*, 1970), hypotensive (Rossi, 1960), sedative, antipyretic, psycholeptic and hypoglycemic activities (Takeuchi *et al.*, 1971). The azabicyclononanes derived from primary amines and aldehydes are found to be potential antitumour agents (Jeyaraman & Avila, 1981). In order to throw some more light on these antitumour agents, a series of aza bicyclic ring compounds have been synthesized (Jeyaraman & Ponnuswamy, 1997) and studied by using crystallographic methods. The crystal and molecular structures of 7-*tert*-butyl-*N*-methyl-2,4-diphenyl-3-azabicyclo[3.3.1]nonane (MTABN), *N*-acetyl-2,4-diphenyl-3-aza- bicyclo[3.3.1]nonane (AABN) and *N*-methyl-2,4-bis(2-methylphenyl)-3-azabicyclo[3.3.1]nonan-9-ol (MHABN) are reported herein. The chemical structures of these compounds are depicted in Fig. 1.

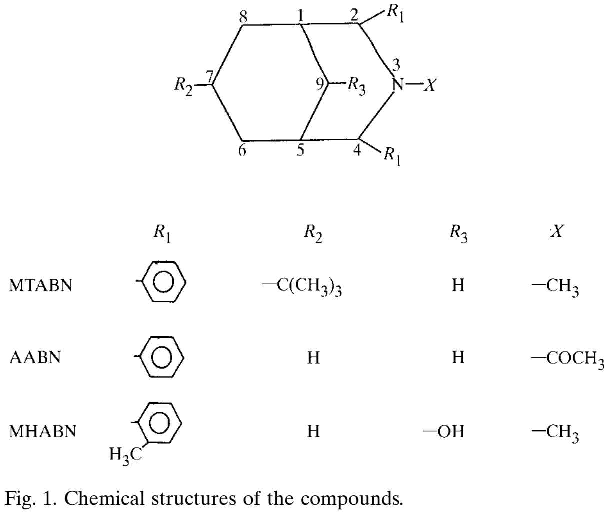

Fig. 1. Chemical structures of the compounds.

2. Experimental

The samples were crystallized in different solvent media using slow-evaporation methods at room temperature. The intensity data were collected on a Siemens *P*4 diffractometer with graphite-monochromated Mo *Kα* radiation ($\lambda = 0.7107$ Å). The structures were solved by direct methods using the program *SHELXS*86 (Sheldrick, 1985) and refined by full-matrix least-squares procedures using *SHELXL*93 (Sheldrick, 1993). The geometrical parameters were obtained using the program *PARST* (Nardelli, 1983*a*, 1995) and plots were drawn using *ZORTEP* (Zsolnai, 1997) and *PLUTO* (Motherwell & Clegg, 1978). The energy of each crystal structure was minimized by using the *DISCOVER* module in the program *Insight*II (Biosym Technologies, 1993) by keeping the dielectric constant at unity. The steepest-descent algorithm and consistent valence force field (CVFF91) were used for the minimization.

The experimental data for MTABN, AABN and MHABN and the atomic coordinates and equivalent displacement parameters of the non-H atoms are presented in Tables 1 and 2, respectively.†

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† Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0088). Services for accessing these data are described at the back of the journal.

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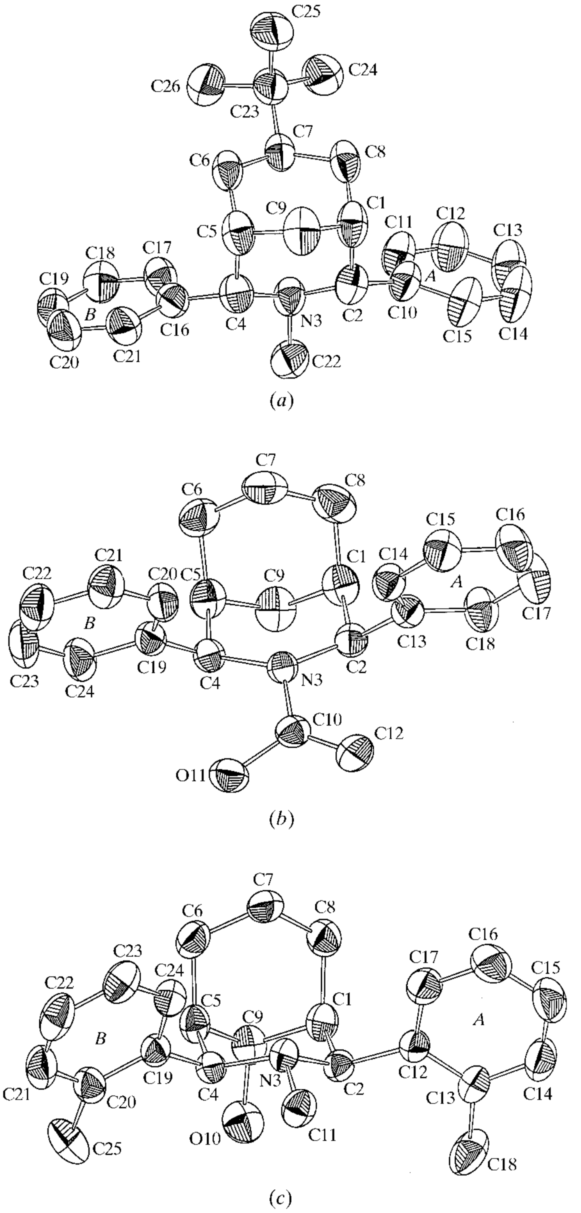
Table 1. *Experimental details*

	MTABN	AABN	MHABN
Crystal data			
Chemical formula	$C_{25}H_{33}N$	$C_{22}H_{25}NO$	$C_{23}H_{29}NO$
Chemical formula weight	347.52	319.43	335.47
Cell setting	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	*Pbca*	$P2_1/n$
a (Å)	13.667 (1)	14.687 (1)	7.638 (1)
b (Å)	16.414 (2)	12.931 (1)	13.188 (1)
c (Å)	9.409 (1)	18.564 (1)	18.865 (2)
β (°)	94.54 (1)	90	97.94 (1)
V (Å^3)	2104.1 (4)	3525.6 (4)	1882.1 (3)
Z	4	8	4
D_x (Mg m^{-3})	1.097	1.204	1.184
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073
No. of reflections for cell parameters	40	42	45
θ range (°)	6.20–13.0	7.0–14.0	7–15
μ (mm^{-1})	0.062	0.073	0.071
Temperature (K)	293 (2)	293 (2)	293 (2)
Crystal form	Plate	Needle	Plate
Crystal size (mm)	0.67 × 0.58 × 0.45	0.59 × 0.47 × 0.30	0.68 × 0.59 × 0.31
Crystal colour	Pale yellow	Pale yellow	Pale yellow
Data collection			
Diffractometer	Siemens *P*4	Siemens *P*4	Siemens *P*4
Data collection method	$\theta/2\theta$ scans	$\theta/2\theta$ scans	$\theta/2\theta$ scans
Absorption correction	None	None	None
No. of measured reflections	4714	4946	5655
No. of independent reflections	3669	4005	4270
No. of observed reflections	2255	2454	3062
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0339	0.0178	0.0284
θ_{max} (°)	25.00	27.49	27.50
Range of h, k, l	$-16 \rightarrow h \rightarrow 16$ $-19 \rightarrow k \rightarrow 1$ $-1 \rightarrow l \rightarrow 11$	$-1 \rightarrow h \rightarrow 19$ $-1 \rightarrow k \rightarrow 16$ $-24 \rightarrow l \rightarrow 1$	$-1 \rightarrow h \rightarrow 9$ $-1 \rightarrow k \rightarrow 17$ $-24 \rightarrow l \rightarrow 24$
No. of standard reflections	3	3	3
Frequency of standard reflections	Every 100 reflections	Every 100 reflections	Every 100 reflections
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0592	0.0431	0.0426
$wR(F^2)$	0.1537	0.0994	0.1220
S	1.076	1.035	1.207
No. of reflections used in refinement	3649	4005	4269
No. of parameters used	368	317	343
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1151P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0619P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0705P)^2 + 0.0381P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}}$	0.013	0.000	0.002
$\Delta\rho_{\text{max}}$ (e Å^{-3})	0.172	0.127	0.231
$\Delta\rho_{\text{min}}$ (e Å^{-3})	−0.168	−0.181	−0.148
Extinction method	None	None	*SHELXL*93 (Sheldrick, 1993)
Extinction coefficient	–	–	0.0022 (16)
Source of atomic scattering factors	*International Tables for Crystallography* (Vol. C)	*International Tables for Crystallography* (Vol. C)	*International Tables for Crystallography* (Vol. C)
Computer programs			
Data collection	*XSCANS* (Siemens, 1994)	*XSCANS* (Siemens, 1994)	*XSCANS* (Siemens, 1994)
Cell refinement	*XSCANS* (Siemens, 1994)	*XSCANS* (Siemens, 1994)	*XSCANS* (Siemens, 1994)
Data reduction	*XSCANS* (Siemens, 1994)	*XSCANS* (Siemens, 1994)	*XSCANS* (Siemens, 1994)
Structure solution	*SHELXS*86 (Sheldrick, 1985)	*SHELXS*86 (Sheldrick, 1985)	*SHELXS*86 (Sheldrick, 1985)
Structure refinement	*SHELXL*93 (Sheldrick, 1993)	*SHELXL*93 (Sheldrick, 1993)	*SHELXL*93 (Sheldrick, 1993)
Preparation of material for publication	*PARST* (Nardelli, 1983*a*, 1995)	*PARST* (Nardelli, 1983*a*, 1995)	*PARST* (Nardelli, 1983*a*, 1995)

3. Results and discussion

Perspective views of the molecules of MTABN, AABN and MHABN are presented in Fig. 2. The bicyclo[3.3.1]nonane ring system offers a wide range of conformational flexibility, being able to adopt chair–chair (CC), chair–boat (CB) and boat–boat (BB) conformations. However, the chair–chair conformation, with various degrees of distortion of the cyclohexane ring, has been found to be the most favoured (Zefirov & Palyulin, 1990; Jeyaraman *et al.*, 1982; Cox *et al.*, 1985).



(*a*)

(*b*)

(*c*)

Fig. 2. *ZORTEP* (Zsolnai, 1997) plots of (*a*) MTABN, (*b*) AABN and (*c*) MHABN. Ellipsoids are drawn at the 50% probability level

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($\AA^2$)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
(*a*) MTABN				
C1	0.11854 (11)	0.45720 (10)	0.2068 (2)	0.0636 (5)
C2	0.19282 (12)	0.51444 (10)	0.1427 (2)	0.0594 (4)
N3	0.29617 (9)	0.49279 (8)	0.1848 (2)	0.0588 (4)
C4	0.31556 (12)	0.40523 (10)	0.1638 (2)	0.0605 (5)
C5	0.24034 (12)	0.34913 (10)	0.2269 (2)	0.0648 (5)
C6	0.24121 (12)	0.34877 (10)	0.3881 (2)	0.0636 (5)
C7	0.20941 (11)	0.42982 (9)	0.4516 (2)	0.0551 (4)
C8	0.11627 (11)	0.46092 (10)	0.3680 (2)	0.0609 (5)
C9	0.13846 (13)	0.37053 (12)	0.1597 (2)	0.0733 (6)
C10	0.17040 (11)	0.60231 (10)	0.1769 (2)	0.0553 (4)
C11	0.21512 (12)	0.64257 (11)	0.2941 (2)	0.0632 (5)
C12	0.18830 (13)	0.72145 (11)	0.3242 (2)	0.0691 (5)
C13	0.11632 (13)	0.76033 (12)	0.2392 (2)	0.0758 (6)
C14	0.07042 (14)	0.72073 (12)	0.1246 (2)	0.0775 (6)
C15	0.09753 (14)	0.64204 (12)	0.0942 (2)	0.0697 (5)
C16	0.41887 (12)	0.38136 (10)	0.2197 (2)	0.0600 (5)
C17	0.46496 (12)	0.41270 (12)	0.3422 (2)	0.0696 (5)
C18	0.55508 (14)	0.38407 (13)	0.3977 (3)	0.0834 (6)
C19	0.60096 (15)	0.32262 (14)	0.3291 (3)	0.0943 (7)
C20	0.5565 (2)	0.29156 (14)	0.2076 (3)	0.0995 (8)
C21	0.46592 (14)	0.31970 (13)	0.1507 (3)	0.0834 (6)
C22	0.36094 (15)	0.54133 (13)	0.1018 (3)	0.0788 (6)
C23	0.20254 (13)	0.42777 (10)	0.6145 (2)	0.0659 (5)
C24	0.1785 (2)	0.51353 (13)	0.6671 (3)	0.0833 (6)
C25	0.3014 (2)	0.40214 (15)	0.6888 (2)	0.0833 (6)
C26	0.1228 (2)	0.36937 (15)	0.6594 (3)	0.0900 (7)
(*b*) AABN				
C1	1.01007 (11)	−0.01440 (13)	0.86986 (8)	0.0475 (4)
C2	0.91554 (10)	0.02789 (11)	0.84692 (7)	0.0398 (3)
N3	0.89455 (8)	0.01638 (8)	0.76856 (6)	0.0362 (3)
C4	0.96464 (9)	−0.01304 (11)	0.71401 (7)	0.0383 (3)
C5	1.05542 (10)	−0.05195 (13)	0.74545 (9)	0.0489 (4)
C6	1.06025 (13)	−0.16735 (14)	0.76229 (11)	0.0597 (5)
C7	0.99810 (14)	−0.19791 (14)	0.82338 (10)	0.0597 (5)
C8	1.01328 (14)	−0.12905 (14)	0.88846 (9)	0.0564 (4)
C9	1.07897 (12)	0.0118 (2)	0.81177 (9)	0.0554 (4)
C10	0.82807 (10)	0.07946 (10)	0.73987 (7)	0.0411 (3)
O11	0.82232 (8)	0.09191 (9)	0.67475 (5)	0.0567 (3)
C12	0.76209 (13)	0.13388 (14)	0.78858 (10)	0.0522 (4)
C13	0.84082 (10)	−0.01299 (11)	0.89586 (7)	0.0413 (3)
C14	0.78392 (11)	−0.09435 (12)	0.87867 (8)	0.0467 (4)
C15	0.71867 (12)	−0.1294 (2)	0.92690 (9)	0.0575 (4)
C16	0.70969 (13)	−0.0838 (2)	0.99332 (9)	0.0635 (5)
C17	0.76487 (14)	−0.0028 (2)	1.01111 (9)	0.0678 (5)
C18	0.82954 (13)	0.0331 (2)	0.96321 (8)	0.0565 (4)
C19	0.92943 (9)	−0.08596 (10)	0.65658 (7)	0.0387 (3)
C20	0.85792 (11)	−0.15441 (11)	0.66670 (8)	0.0441 (3)
C21	0.83427 (12)	−0.22551 (13)	0.61398 (9)	0.0541 (4)
C22	0.88165 (13)	−0.22872 (15)	0.55048 (9)	0.0639 (5)
C23	0.95165 (14)	−0.1598 (2)	0.53879 (9)	0.0667 (5)
C24	0.97504 (12)	−0.08899 (14)	0.59118 (8)	0.0539 (4)
(*c*) MHABN				
C1	0.1049 (2)	0.19893 (10)	0.19455 (7)	0.0414 (3)
C2	0.1187 (2)	0.08792 (9)	0.22148 (6)	0.0357 (3)
N3	0.00113 (14)	0.06656 (8)	0.27590 (5)	0.0355 (2)
C4	0.0204 (2)	0.14188 (10)	0.33440 (6)	0.0359 (3)
C5	0.0073 (2)	0.25244 (10)	0.30711 (7)	0.0411 (3)
C6	−0.1727 (2)	0.28536 (12)	0.26755 (8)	0.0487 (3)
C7	−0.2241 (2)	0.23019 (12)	0.19654 (8)	0.0495 (4)
C8	−0.0732 (2)	0.22895 (12)	0.15165 (7)	0.0497 (4)

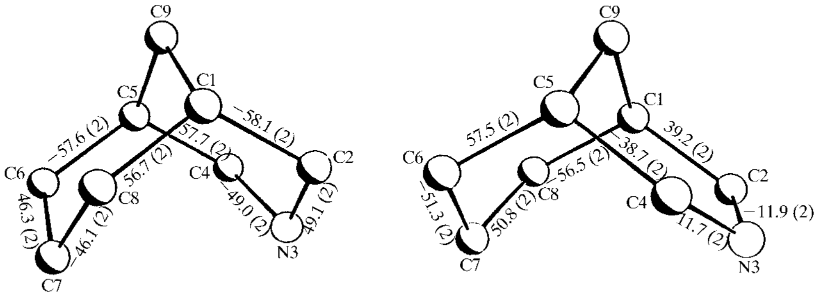
Table 2 (*cont.*)

	x	y	z	U_{eq}
C9	0.1468 (2)	0.27018 (11)	0.25812 (8)	0.0455 (3)
O10	0.32288 (14)	0.24968 (9)	0.29126 (7)	0.0576 (3)
C11	0.0464 (2)	−0.03323 (11)	0.30766 (8)	0.0457 (3)
C12	0.0850 (2)	0.01491 (9)	0.15865 (6)	0.0375 (3)
C13	0.2193 (2)	−0.00942 (11)	0.11756 (7)	0.0461 (3)
C14	0.1804 (2)	−0.07659 (12)	0.06059 (8)	0.0560 (4)
C15	0.0167 (3)	−0.12087 (12)	0.04425 (8)	0.0593 (4)
C16	−0.1152 (2)	−0.09646 (12)	0.08400 (8)	0.0540 (4)
C17	−0.0811 (2)	−0.02858 (11)	0.14029 (7)	0.0436 (3)
C18	0.4029 (2)	0.0345 (2)	0.13244 (13)	0.0691 (5)
C19	−0.1133 (2)	0.12445 (10)	0.38627 (6)	0.0376 (3)
C20	−0.0693 (2)	0.14465 (11)	0.45961 (7)	0.0448 (3)
C21	−0.2010 (2)	0.13675 (13)	0.50363 (8)	0.0573 (4)
C22	−0.3697 (2)	0.10757 (15)	0.47766 (10)	0.0652 (5)
C23	−0.4124 (2)	0.0855 (2)	0.40616 (10)	0.0654 (5)
C24	−0.2849 (2)	0.09382 (13)	0.36106 (9)	0.0536 (4)
C25	0.1156 (3)	0.1715 (2)	0.49312 (10)	0.0703 (6)

Examination of the torsion angles (Fig. 3) and asymmetry parameters of MTABN, AABN and MHABN shows that the bicyclic ring system in each adopts a chair–chair (CC) conformation; this is the most favoured conformation for the azabicyclo[3.3.1]nonane ring systems (Chakrabarthy *et al.*, 1970; Priya *et al.*, 1993).

The endocyclic bond angles observed at C2, C4, C6 and C8 are, respectively, 113.2 (1), 113.5 (1), 113.9 (1) and 114.7 (1)° in MTABN, 114.6 (1), 115.0 (1), 112.5 (1) and 112.7 (1)° in AABN, and 112.8 (1), 113.0 (1), 113.4 (1) and 113.2 (1)° in MHABN. The deviations of these bond angles from the normal tetrahedral value shows that the rings are slightly flattened.

In AABN, the bond lengths N3—C10 = 1.379 (2) Å and C10—O11 = 1.223 (2) Å and the sum of the bond angles around N3 [352.6 (2)°] show that the atom N3 is in an sp^2-hybridized state due to delocalization between the lone pair of electrons and the hetero π-electrons of the carbonyl group. This is also indicated by the displacement of the N3 atom from the base of the pyramid: 0.230 (1) Å in AABN, 0.469 (2) and 0.486 (1) Å in MTABN and MHABN, respectively. In MTABN and MHABN, the N3 atom has sp^3 character, the sums of angles around it being 331.0 (2) and 329.0 (2)°, respectively.

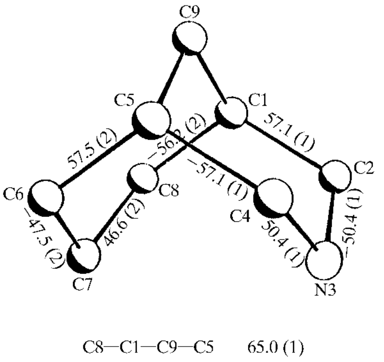


C8—C1—C9—C5	−63.0 (2)
C1—C9—C5—C6	63.9 (2)
C4—C5—C9—C1	−64.4 (2)
C5—C9—C1—C2	64.5 (2)

MTABN

C8—C1—C9—C5	60.0 (2)
C1—C9—C5—C6	−60.4 (2)
C4—C5—C9—C1	68.3 (2)
C5—C9—C1—C2	−68.4 (2)

AABN



C8—C1—C9—C5	65.0 (1)
C1—C9—C5—C6	−65.3 (1)
C4—C5—C9—C1	62.3 (1)
C5—C9—C1—C2	−62.3 (1)

MHABN

Fig. 3. The conformations of the bicyclic rings along with associated torsion angles.

In the cyclohexane ring, the displacements of atoms C7 and C9 from the best plane (C1, C5, C6 and C8) are, respectively, −0.580 (1) and 0.770 (2) Å in MTABN, 0.616 (2) and −0.728 (1) Å in AABN, and −0.575 (1) and 0.776 (1) Å in MHABN. In the piperidine ring, the displacements of N3 and C9 from the best plane formed by C1, C2, C4 and C5 are, respectively, −0.573 (1) and 0.784 (2) Å in MTABN, −0.133 (1) and 0.790 (1) Å in AABN and 0.584 (1) and −0.756 (1) Å in MHABN. This reflects the deviation of the piperidine rings from the ideal chair conformation. The displacement of N3 from the best plane in AABN indicates that the chair conformation of the piperidine ring is flattened at the N3 end. The non-bonded N3···C7 distances observed in MTABN, AABN and MHABN are 3.041 (1), 3.321 (1) and 3.024 (1) Å, respectively; the larger distance in AABN is due to the flattening of the piperidine ring.

This flattening is attributed to the presence of allylic or $A_{1,3}$ strain (Johnson & Malhotra, 1965) between the acetyl and phenyl groups. This is also evidenced by the dihedral angle of 169.3 (1)° formed between the best plane through C1, C2, C4 and C5 and the plane through the atoms C2, N3 and C4.

The relative flattening of the piperidine ring in AABN is clearly indicated by the values of the total puckering amplitudes (Cremer & Pople, 1975): Q_T = 0.602 (2), 0.572 (2) and 0.590 (2) Å in MTABN, AABN and MHABN, respectively. The cyclooctane ring (N3, C2, C1, C8, C7, C6, C5 and C4) has a boat conformation, which is again more flattened in AABN than the other two compounds, as shown by the values of the total puckering amplitudes: Q_T = 1.635 (2), 1.50 (7), 1.63 (4) Å in MTABN, AABN and MHABN, respectively. Two local pseudo-mirrors are observed in this ring, running along the N3···C7 and C1···C5 directions.

For the molecules MTABN, AABN and MHABN, the asymmetry parameters (Duax & Norton, 1975; Nardelli, 1983*b*) of the piperidine ring for the pseudo-twofold axis passing through C1—C9 and N3—C4 are, respectively, Δ_2 = 0.0367 (6), 0.1132 (5) and 0.0297 (4), and the asymmetry parameters for the pseudo-mirror passing through the atoms N3 and C9 are, respectively, Δ_s = 0.0023 (8), 0.0026 (6) and 0.0007 (7). The high value of Δ_2 [0.1132 (5)] implies that the piperidine ring is more distorted in AABN than in the other two structures.

The dihedral angles formed between the best plane through C1, C8, C5 and C6 and that through C1, C2, C4 and C5 are 115.8 (1), 115.9 (1) and 115.9 (1)° in MTABN, AABN and MHABN, respectively. This indicates that the substitution at different positions of the piperidine ring does not influence the values of these intersecting planes.

In all the structures, the aryl rings have equatorial orientations. The corresponding torsion angles are C9—C1—C2—*X* = 175.4 (1), 169.5 (1) and −177.6(1)°, C9—C5—C4—*Y* = −175.6 (1), −169.5 (1) and 177.5 (1)° for MTABN (*X* = C10, *Y* = C16), AABN (*X* = C13, *Y* = C19) and MHABN (*X* = C12, *Y* = C19), respectively.

In MTABN, the methyl group at N3 and the tertiary butyl group at C7 are in *exo* positions; the corresponding torsion angles are C1—C2—N3—C22 = 170.9 (2) and C5—C6—C7—C23 = 175.6 (1)°, respectively. The phenyl rings *A* and *B* form a dihedral angle of 23.5 (1)°. The angles between the best plane through C1, C2, C4 and C5 and the aryl rings *A* and *B* are 75.9 (1) and 81.0 (1)°, respectively.

In AABN, the acetyl group is planar with a maximum deviation of 0.005 (2) Å observed for C12. C10—O11 is +*antiperiplanar* to C2—N3, as indicated by the value [162.6 (1)°] of the torsion angle C2—N3—C10—O11 and +*synperiplanar* to C4—N3, the C4—N3—C10—O11 torsion angle being 11.6 (2)° as a consequence of the planarity of the group. The corresponding values for the compounds MTABN and MHABN are C5—C4—N3—

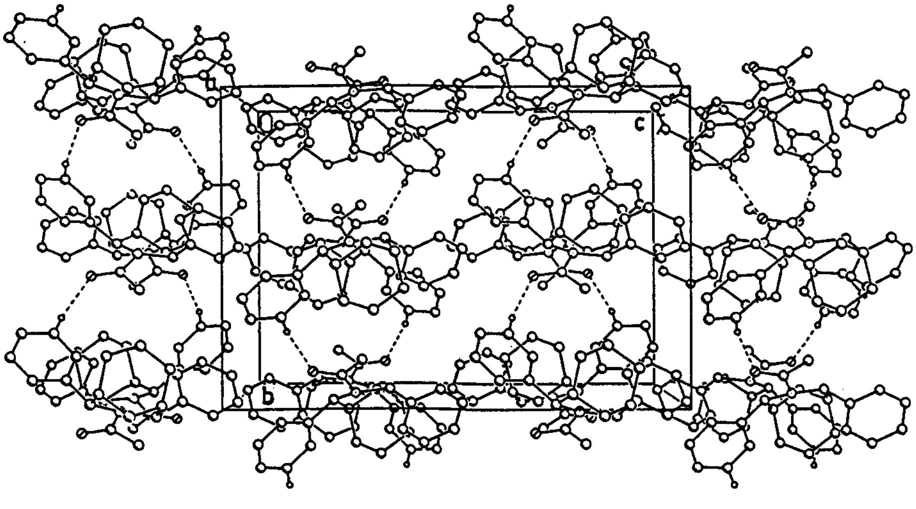


Fig. 4. Packing of molecules of AABN viewed down the *a* axis (dashed lines indicate the hydrogen bond).

C22 = −170.7 (2) and C1—C2—N3—C11 = −169.6 (1)°, respectively. The phenyl rings are approximately perpendicular to the acetyl group [86.3 (1) and 84.5 (1)° for rings *A* and *B*, respectively]. The phenyl rings *A* and *B* almost lie in the same plane and are oriented at an angle of 1.9 (1)° to each other. The dihedral angles formed by the best plane through C1, C2, C4 and C5 and the aryl rings *A* and *B* are 68.7 (1) and 66.9 (1)°, respectively.

In MHABN, the methyl group at N3 is in an *exo* position and the C1—C2—N3—C11 torsion angle is −169.6 (1)°. The hydroxyl group at C9 is *exo* to the cyclohexane ring [C6—C5—C9—O10 = 175.4 (1)°] and *endo* to the piperidine ring [C4—C5—C9—O10 = −57.1 (1)°]. The phenyl rings *A* and *B* form a dihedral angle of 27.7 (1)°. The angles between the best plane through C1, C2, C4 and C5 and the aryl rings *A* and *B* are 72.5 (1) and 82.6 (1)°, respectively.

The minimum energies obtained for the isolated molecules MTABN, AABN and MHABN are −54.392, 11.924 and −9.330 kJ mol^{-1}, respectively. Higher energy is expected for MTABN because of the bulky tertiary butyl group, but the energies were found to follow the reverse order, *i.e.* MTABN < MHABN < AABN. AABN has the highest energy when compared to the other two structures because of the presence of $A_{1,3}$ strain between the lone pair of electrons and the aryl rings.

4. Intermolecular features

In all the structures, the primary interactions between the molecules are van der Waals in nature. It is interesting to note that the hydroxyl substituent (O10) of MHABN is not involved as a donor in hydrogen bonding, in contrast to what is usually found with structures containing hydroxyl groups. In AABN, the lone oxygen atom O11 acts as an acceptor and forms a hydrogen bond with C21 [C21···O11 $(-x + \frac{3}{2}, y - \frac{1}{2}, z)$ = 3.484 (2), C21—H21 = 0.99 (2), H21···O11 = 2.52 (2) Å, C21—H21···O11 = 165 (1)°]. The layers of AABN lie parallel to the *ac* plane and are stacked along the **b** direction (Fig. 4). The layers are connected one over the other by this C—H···O hydrogen bonding.

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