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THE CONFORMATION OF THE BICYCLO(3,3,1)NONANE SYSTEM FROM X-RAY STUDIES†

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Abstract—X-ray data of eleven compounds containing the bicyclo(3,3,1)nonane system were analysed in order to study its conformation. From the available data, the structures have been subdivided into four major groups depending upon the conformation taken up in the crystal structure and also based on chemical classification of the bicyclo(3,3,1)nonane system. It was found that in the majority of the cases reported, the system exists in the 'chair–chair' form. However, in certain cases, especially when there are bulky substituents at positions 3 or 7, the system adopts the 'chair–boat' conformation. The interesting conformational features of the four major groups are discussed in terms of their bond lengths, bond angles and torsion angles.

The bicyclo(3,3,1)nonane system is of considerable stereochemical interest as this system may be constructed, using a ball and stick model, by the 1,3-fusion of the two cyclohexane chairs free of angular strain. However, construction of a scale model of the 'chair–chair' form shows that there is an intolerable transannular interaction between the axial hydrogens at C_3 and C_7 which are calculated to be about 1 Å apart. Owing to this short nonbonded interaction it has been predicted that the molecule should exist in a 'chair–boat' form even though this still has some fairly bad interactions.[1] Figure 1 shows the 'chair–chair' and 'chair–boat' conformations of the bicyclo(3,3,1)nonane system. This system may also be imagined to take up a 'boat–boat' (crown) conformation. However, the 'boat–boat' form is energetically very unstable compared to the other two and hence this is merely of theoretical interest and the possibility of structures existing in this conformation could be ruled out. IR spectra available on some of these compounds indicate that the 'chair–chair' form is preferred.[2] Analysis on this system using other techniques like C^{13}NMR[3] and electron diffraction[4] have also been reported. An interesting recent report on chair–boat equilibrium in the bicyclo(3,3,1)nonane system based on NMR and molecular mechanics study is available.[5]

Analysis of the data and discussion

Crystal structure data are available for eleven compounds from which interesting conclusions may be drawn regarding the conformation of the bicyclo(3,3,1)nonane system in the solid state. The structures could be divided into four groups as given in Table 1 which also gives the accuracy of the structure analysis (the mean estimated standard deviation in atomic coordinates (σ)), the conformation which the bicyclo(3,3,1)nonane system takes up in the crystal structure and the reference.[6–16] The structural formulae of the compounds are given in Fig. 2. Group I consists of structures that exist in the 'twin–chair' or 'chair–chair' form with all atoms as carbons in the bicyclo(3,3,1)nonane system. Group II deals with two azabicyclo(3,3,1)nonane compounds with nitrogen at position 3 in the ring and all the other ring atoms as carbons while group III deals with two tetrazabicyclo(3,3,1)nonane structures. Group IV contains compounds in the 'boat–chair' conformation, some of which have bulky substituents at positions 3 or 7 of the ring. Structure **9** of Group IV has a bulky substitution of a tertiarybutyl group attached to position 7 while structures **10** and **11** have a Br atom covalently bonded to position 3 of the ring which could cause a very serious short contact if the bicyclo(3,3,1)nonane system were to exist in the chair–chair conformation. It is interesting to note that compound **4**, which has a 5-membered ring attached to the bicyclo(3,3,1)nonane system, exists in both the 'chair–chair' and 'boat–chair' conformations with the methylene carbon at position 7 having alternate sites in the lattice, the 'chair–chair' form having a probability of occurrence of 70% and the 'chair–boat' form having 30% probability. Hence, this structure is referred to in Groups I and IV in Table 1. Figure 1(a) gives the nomenclature adopted in this paper for equivalent bond lengths and angles of the bicyclo(3,3,1)nonane system to facilitate discussion on the structures.

The bond lengths, bond angles and torsion angles observed for the eleven crystal structures are given in Tables 2, 3 and 4 respectively together with the mean bond lengths, bond angles and torsion angles of individual structures while Table 5 gives the overall averages of the four groups of structures. In taking the overall averages of the structures in Group IV, the structure **4b** is excluded (due to its inherent inaccuracy on account of the disordered position). There are not many structures in each of the different groups to draw more meaningful estimates of average parameters. However, one may

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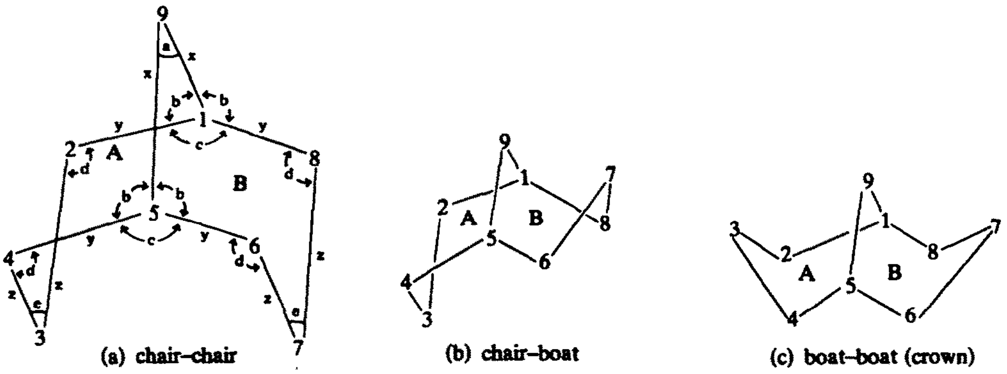


(a) chair–chair (b) chair–boat (c) boat–boat (crown)

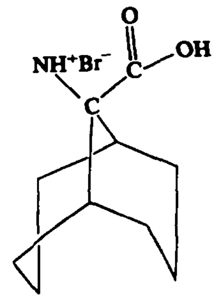
Fig. 1.

draw the following observations from the analysis of the averages. The mean C—C bond length of the 3-atom birdgehead, which does not involve the methine carbons at C_5 and C_1 (⟨z⟩) appears to have a lower value compared to the mean ⟨y⟩ bonds involving the methine carbons as is seen from values reported in Table 2 for Groups I and II. The overall mean values of ⟨z⟩ are 1.52(2) and 1.50(4) Å respectively for Group I and II structures (Table 5(a)). The mean C—C bond length of the one-atom bridgehead (⟨x⟩) has a value of 1.52(2) Å for Group I and 1.54(2) Å for Group II compounds while the mean bond length ⟨y⟩ is 1.54(2) Å for Group I and 1.52(2) Å for Group II. For Group IV structures, which exist in the 'boat–chair' conformation, the mean C—C bond length of the one-atom bridgehead of 1.51(1) Å is found to be smaller than the mean values of ⟨y⟩ and ⟨z⟩ which have values 1.54(3) Å and 1.53(2) Å respectively. The bond angles of the 3-atom bridgehead have been observed to have values larger than tetrahedral (109°28′) compared to the other bond angles in the structures belonging to Groups I, II and III. This is due to the considerable distortion of the two cyclohexane rings which exist in a 'distorted–chair' conformation in the crystal lattice. Thus, it is seen in Table 5(b) that ⟨d⟩ and ⟨e⟩ values of the bond angles of Groups I to III are, in general, observed to be significantly larger than tetrahedral except for the C—C—N angle ⟨d⟩ of Group II of 109(3)°. The mean angle ⟨a⟩ is observed to be slightly larger than tetrahedral except for 3-azabicyclo(3,3,1)nonanes (Group II) which has a low mean value of 104(3)°. The mean angle ⟨b⟩ is close to tetrahedral for compounds belonging to Groups I to IV with a minimum of 108.5(12)°, for Group IV and a maximum of 110.7(18)° for Group II. The mean angle ⟨c⟩ for Groups I to III is observed in general to be

Table 1. List of bicyclo(3,3,1)nonane structure

Group	Code	Compound name	Space group	R-factor	⟨e.s.d.⟩ Å	Conformation*	Ref.
I	1	9-Aminobicyclo(3,3,1)nonane-9-carboxylic acid hydrobromide monohydrate	$P2_1/c$	7.9%	0.006	c–c	6
	2	1-p-Bromobenzenesulphonyloxymethyl-5-methylbicyclo(3,3,1)nonan-9-ol	$P\bar{1}$	12.9%	0.017	c–c	7
	3	2-Chlorobicyclo(3,3,1)nonan-9-one	$P2_1/c$	8.8%	0.005	c–c	8
	4A	DL-1,7-dicarbomethoxy-3a-7-methano-3aH-decahydrocyclopentacyclooctane-2-10-dione	$P2_1/c$	5.6%	0.002	c–c	9
II	5	3-Azabicyclo(3,3,1)nonane hydrobromide	$P42_1/c$	8.9%	—†	c–c	10
	6A	1,5-Dinitro-3-methyl-3-azabicyclo(3,3,1)-nonane-7-one	$P3_1/c$	8.6%	0.009	c–c	11
	6B	1,5-Dinitro-3-methyl-3-azabicyclo(3,3,1)-nonane-7-one	Pccn	8.1%	0.005	c–c	11
III	7	3,7-Diacetyl-1,3,5,7-tetrazabicyclo-(3,3,1)nonane	$P2_1/c$	5.2%	0.002	c–c	12
	8	3,7-Dinitro-1,3,5,7-tetrazabicyclo-(3,3,1)nonane	$P2_1/c$	3.5%	0.002	c–c	13
IV	9	1-Methyl-7-exo-t-butylbicyclo(3,3,1)-nonane-2,9-dione	$P\bar{1}$	6.0%	0.004	b–c	14
	10	9-Benzoyl-3-α-bromo-2-β-hydroxy-9-azabicyclo(3,3,1)nonane	$P2_1/c$	11.2%	0.008	b–c	15
	11	9-Benzoyl-3-α-bromo-9-azabicyclo(3,3,1)-nonane-2-one	$P2_1/c$	10.1%	0.015	b–c	16
	4B	D,L-1,7-dicarbomethoxy-3a-7-methano-3aH-decahydrocyclopentacyclooctane-2,10-dione	$P2_1/c$	5.6%	0.003	b–c	9

* c–c refers to Chair–chair; b–c refers to Boat–chair conformations.
† e.s.d.'s not available in the reference[10].



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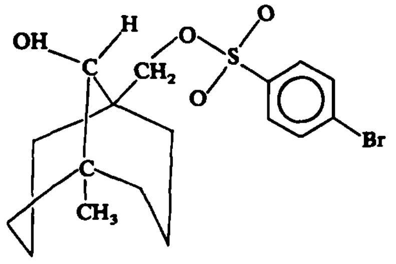

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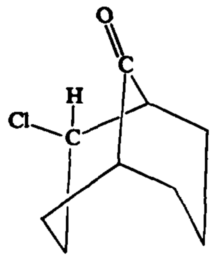

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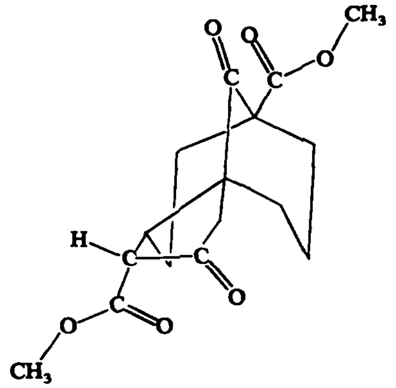
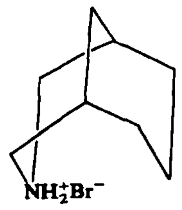
Group I



4a



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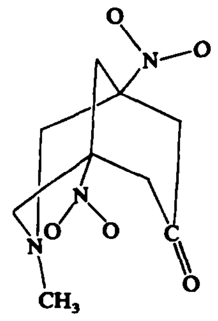

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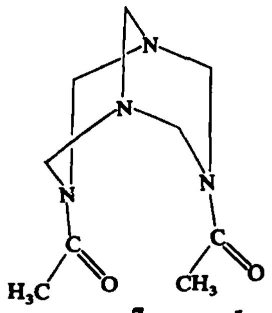
Group II



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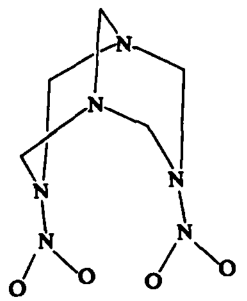

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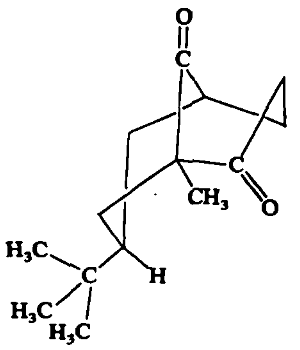

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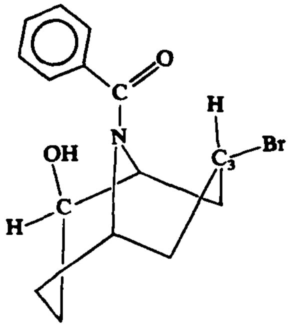
Group III



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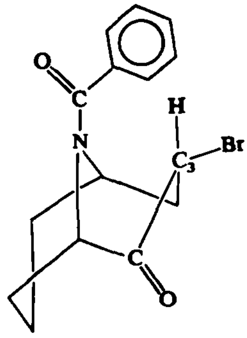

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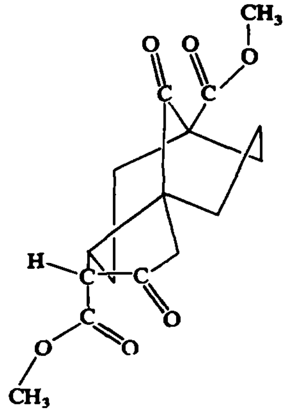

4b

Group IV

Fig. 2.

Table 2. Bond lengths (Å)

Code →		1	2	3	4a	5[α]	6a[α]	6b[α]	7[β]	8[β]	9	10[γ]	11[γ]	4b
Group → Category ↓		I				II			III		IV			
RING A														
y	1–2	1.534	1.57	1.52	1.57	1.47	1.530	1.510	1.453*	1.45*	1.54	1.52	1.53	1.57
y	4–5	1.538	1.58	1.52	1.57	1.52	1.525	1.540	1.449*	1.45*	1.55	1.51	1.50	1.57
z	2–3	1.541	1.52	1.50	1.53	1.52*	1.464*	1.457*	1.469*	1.49*	1.53	1.54	1.51	1.53
z	3–4	1.509	1.48	1.54	1.51	1.44*	1.458*	1.433*	1.472*	1.49*	1.53	1.55	1.54	1.51
RING B														
y	5–6	1.545	1.54	1.53	1.55	1.51	1.508	1.508	1.447*	1.45*	1.53	1.54	1.60	1.55
y	8–1	1.534	1.55	1.52	1.54	1.56	1.534	1.516	1.449*	1.45*	1.55	1.55	1.56	1.54
z	6–7	1.533	1.51	1.53	1.50	1.43	1.525	1.496	1.475*	1.49*	1.51	1.51	1.49	1.51
z	7–8	1.532	1.57	1.55	1.50	1.54	1.477	1.510	1.472*	1.49*	1.53	1.52	1.56	1.40
COMMON TO A & B														
x	5–9	1.544	1.53	1.49	1.52	1.56	1.529	1.498	1.464*	1.47*	1.52	1.48*	1.48*	1.52
x	9–1	1.542	1.51	1.52	1.53	1.56	1.520	1.544	1.451*	1.47*	1.50	1.49*	1.49*	1.53
	⟨c–c⟩	1.535(10)	1.54(3)	1.52(2)	1.53(3)	1.52(5)	1.519(19)	1.52(2)	1.46(1)*	1.47(2)*	1.53(2)	1.53(2)	1.54(4)	1.52(5)
	⟨z⟩	1.529(14)	1.52(4)	1.53(2)	1.51(1)	1.49(8)	1.50 (3)	1.50(1)	1.472(2)*	1.49(6)*	1.525(10)	1.53(2)	1.53(3)	1.49(6)
	⟨y⟩	1.538(5)	1.56(2)	1.523(5)	1.56(2)	1.52(4)	1.52 (1)	1.52(2)	1.450(3)*	1.45(0)*	1.543(10)	1.53(2)	1.55(4)	1.56(2)
	⟨x⟩	1.543(1)	1.52(1)	1.51 (2)	1.525(7)	1.56(0)	1.525(6)	1.52(3)	1.458(9)*	1.47(0)*	1.51 (1)	1.485(7)*	1.485(7)*	1.525(7)
	3 . . . 7	3.12	3.06	3.11	3.097	3.02	2.76	2.69	2.846*	2.87*	—	—	—	—

* C—N distance

[α] Atom 3 is N.

[β] Atoms 1, 3, 5 and 7 are N.

[γ] Atom 9 is N.

Note: Only C—C bonds are averaged in Group II compounds.

Table 3. Bond angles (°)

CODE		1	2	3	4a	5	6a	6b	7	8	9	10	11	4b
CATEGORY GROUP		I				II			III		IV			
RING A														
b	4–5–9	111.0	109.0	108.7	106.3	107.0	110.5	109.7	109.0*	109.9*	107.2	108.3	111.5	106.3
b	9–1–2	111.0	109.0	108.4	109.3	109.0	110.0	110.8	109.8*	109.8*	107.9	108.5	108.8	109.3
d	1–2–3	115.4	113.0	115.2	116.1	112.0†	107.6†	106.9†	112.9‡	109.2‡	113.1	112.6	111.5	116.1
d	3–4–5	115.2	115.0	114.6	113.8	114.0†	105.9†	106.2†	113.4‡	110.4‡	113.5	110.3	109.6	123.1
e	2–3–4	114.4	116.0	113.4	109.7	111.0*	110.5*	112.2*	112.8*	118.0*	109.4	111.6	111.7	109.7
RING B														
b	8–1–9	109.2	110.0	108.1	106.0	114.0	111.6	110.0	108.7*	110.3*	109.6	110.1‡	107.3‡	106.0
b	9–5–6	107.6	109.0	107.9	107.3	112.0	111.5	112.7	108.5*	109.3*	108.9	108.7‡	107.9‡	107.3
d	5–6–7	116.1	115.0	113.5	116.5	118.0	112.4	112.6	112.9‡	113.4‡	116.7	110.9	112.0	118.4
d	7–8–1	113.8	112.0	114.0	114.6	112.0	113.0	111.8	113.2‡	113.9‡	114.6	108.9	112.7	114.6
e	6–7–8	113.3	114.0	112.7	114.7	112.0	118.0	117.7	114.1*	113.2*	112.3	113.3	110.2	120.1
COMMON TO A & B														
c	4–5–6	112.1	112.0	114.9	115.7	115.0	113.1	110.2	114.4*	114.1*	108.3	113.1	110.4	115.7
c	8–1–2	112.5	113.0	115.8	113.2	115.0	110.9	111.5	113.2*	114.2*	113.3	112.6	111.9	113.2
a	5–9–1	108.9	111.0	112.3	111.9	101.0	105.2	106.1	110.7	110.4	112.5	112.9*	112.9*	111.9
	⟨b⟩	109.7(16)	109.3(5)	108.3(4)	107.2(15)	111(3)	110.9(8)	110.8(13)	109.0(6)*	109.8(4)*	108.4(1)	108.4(1)	110(2)	107(1)
	⟨c⟩	112.3(4)	112.5(7)	115.4(6)	114.5(18)	115(0)	112(2)	110.9(9)	113.8(1)*	114.15(7)*	111(4)	112.9(4)	111(1)	114.5(18)
	⟨d⟩	115.1(10)	113.8(13)	114.3(7)	115.3(13)	115(4)	112.7(4)	112.2(7)	113.1(2)‡	112(2)‡	114.5(16)	110.7(15)	111.5(13)	118(4)
	⟨e⟩	113.9(8)	115.0(10)	113.1(5)	112(4)	112(0)	118.0(0)	117.7(0)	113.5(9)*	116(3)*	111(2)	112.5(12)	111(1)	115(7)

* C—N—C bond angle.
† C—C—N bond angle.
‡ N—C—N bond angle.
Note: All C—C—N bond angles and the C—N—C bond angles in Groups II and IV are not averaged.

Table 4. Torsion angles (°)

CODE		1	2	3	4a	5	6a	6b	7	8	9	10	11	4b
CATEGORY	GROUP	I				II			III		IV			
RING A														
x	4–5–9–1	60.0	60.2	61.9	−62.7	−66.8	61.4	59.9	61.3	57	−60.9	−64.7	−59.7	−62.7
x	5–9–1–2	−59.2	−61.9	−62.1	56.9	69.4	−59.4	−58.8	−61.0	−59	61.9	61.4	58.1	56.9
y	3–4–5–9	−51.3	−50.3	−50.8	61.6	61.9	−64.2	−63.6	−54.5	−47	55.7	58.2	55.2	61.6
y	9–1–2–3	49.5	52.2	51.6	−48.5	−61.9	61.9	59.4	63.2	50	−57.6	−52.9	−55.2	−48.5
z	1–2–3–4	−39.5	−44.1	−42.7	46.7	49.9	−64.9	−64.4	47.2	−43	53.2	49.9	54.4	46.7
z	2–3–4–5	40.2	43.6	42.0	−53.4	−50.4	65.2	65.7	48.1	38	−52.7	−52.2	−53.5	−53.4
RING B														
x	8–1–9–5	65.4	62.7	63.0	−65.4	−60.9	64.1	64.9	63.3	55	−68.1	−62.5	−63.3	−65.4
x	1–9–5–6	−62.9	−61.6	−64.4	61.6	59.8	−65.3	−63.3	−63.9	−57	56.1	58.8	61.7	61.6
y	7–8–1–9	−54.4	−52.5	−51.6	54.7	54.7	−50.8	−53.6	−52.9	−47	11.4	5.3	4.3	19.7
y	9–5–6–7	52.0	52.4	54.9	−47.7	−57.6	52.0	50.1	53.8	48	−0.6	0.5	−0.4	−13.5
z	5–6–7–8	−41.9	−44.5	−46.0	40.1	44.6	−37.4	−37.9	−45.6	−41	−46.3	−55.8	−53.3	−29.7
z	6–7–8–1	42.3	43.9	44.8	−43.8	−41.5	36.4	40.6	45.1	39	40.0	52.0	51.8	26.0
COMMON TO A & B														
yy	3–4–5–6	69.0	69.9	70.8	−57.3	−72.6	59.9	61.1	67.2	72.4	−62.3	−62.5	−64.7	57.3
yy	4–5–6–7	−70.4	−67.7	−67.1	70.7	68.0	−72.4	−72.8	−68.1	−69.0	114.4	121.0	121.7	104.8
yy	7–8–1–2	69.3	69.9	69.6	−64.9	−63.1	72.2	69.7	69.3	73.0	−109.2	−116.1	−115.1	−100.0
yy	8–1–2–3	−73.2	−70.4	−69.4	69.2	64.5	−62.0	−63.4	−78.2	−70.0	64.0	69.2	63.2	69.2
	$\phi_{A_{av}}$	50(9)	52(8)	52(9)	55(7)	60(8)	63(2)	62(3)	54(6)	49(8)	57(4)	57(6)	56(2)	55(7)
	$\phi_{B_{av}}$	53(10)	53(8)	54(8)	52(10)	53(8)	51(13)	52(11)	54(8)	48(7)				
	⟨x⟩	62(3)	61.6(10)	62.9(11)	62(4)	64(5)	63(3)	62(3)	62.4(14)	57.0(16)				
	⟨y⟩	52(2)	51.9(10)	52(2)	53(7)	59(4)	57(7)	57(6)	53.7(7)	48.0(14)				
	⟨z⟩	41.0(10)	44.0(4)	44(2)	46(6)	47(4)	51(16)	52(15)	46.5(14)	40.3(22)				
	⟨yy⟩	71(2)	69.5(12)	69.2(15)	66(6)	67(4)	67(7)	67(5)	68.2(9)	71.1(19)				

Table 5(a). Mean bond lengths (Å)

Mean bond length		Group I	Group II	Group III	Group IV
⟨x⟩	(i)	1.52(2)	1.54(2)	—	1.51(1)
	(ii)	—	—	1.464(9)	1.485(6)
⟨y⟩	(i)	1.54(2)	1.52(2)	—	1.54(3)
	(ii)	—	—	1.450(2)	—
⟨z⟩	(i)	1.52(2)	1.50(4)	—	1.53(2)
	(ii)	—	1.46(3)	1.474(15)	—

Note: (i) C—C bond
(ii) C—N bond

Table 5(b). Mean bond angles (°)

Mean bond angle		Group I	Group II	Group III	Group IV
⟨a⟩	(i)	111(2)	104(3)	—	112.5(0)
	(ii)	—	—	—	112.9(0)
	(iv)	—	—	110.6(2)	—
⟨b⟩	(i)	108.6(14)	110.7(18)	—	109(1)
	(ii)	—	—	109.4(6)	—
	(iii)	—	—	—	108.5(12)
⟨c⟩	(i)	113.7(16)	112.6(21)	—	111(4)
	(ii)	—	—	114.0(5)	—
⟨d⟩	(i)	114.6(12)	113(2)	—	112(2)
	(iii)	—	109(3)	—	—
	(iv)	—	—	112.4(7)	—
⟨e⟩	(i)	113.5(18)	116(3)	—	111(1)
	(ii)	—	111.2(9)	114.5(24)	—

Note: (i) C—C—C bond angle
(ii) C—N—C bond angle
(iii) C—C—N bond angle
(iv) N—C—N bond angle

Table 5(c). Mean torsion angles (°)

Mean torsion angle	Group I	Group II		Group III	Group IV	
		Ring A	Ring B		Chair-ring (A)	Boat-ring (B)
⟨x⟩	62(2)	63(4)	63(2)	60(3)	61(2)	62(4)
⟨y⟩	52(3)	62(2)	53(2)	51(3)	56(2)	4(4)
⟨z⟩	44(3)	61(8)	40(3)	44(4)	53(2)	50(6)
⟨yy⟩	69(4)	67(5)	67(5)	70(2)		

significantly larger than tetrahedral with a minimum of 112.6(21)° for Group II and a maximum of 114.0(5)° for Group III structures. It is worthwhile to note that the mean C—C—C bond-angle for a theoretically expected chair conformation of cyclohexane ring is larger than tetrahedral having the value of 111°.[17,18]

Conformational details of ring structures are best understood in terms of torsion angles which are given in Table 4† for all the structures. The Table also gives the mean torsion angles (ϕ_{av}) of the A and B cyclohexane rings for Groups I to IV along with the mean torsion angles about equivalent bonds for individual structures. The theoretical values of the torsion angles for the cyclohexane chair conformation are ±56.[17,18] The ϕ_{av} of individual structures with the two cyclohexane rings in the chair conformation, i.e., Groups I and III, have values close to each other. The small variations in ϕ_{av} may be due to the substituents attached to the A and B rings and to general packing features. However, in Group II, which deals with the azabicyclo(3,3,1)nonane system, the A ring containing nitrogen is seen to be more puckered and hence has a larger ϕ_{av} compared to the B ring. In Group IV structures the A and B rings have the chair and boat conformation respectively. The ϕ_{av} of the chair ring is generally larger than the ϕ_{av} in Groups I and III (except for ring A of Group II) which shows that the cyclohexane chair is less distorted in Group IV than structures having the chair–chair conformation. The broad general features already discussed on the conformation of the bicyclo(3,3,1)nonane system can be clearly visualised by considering the overall mean torsion angles

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† The torsion angles for the compound **7** reported in ref. 12 are found to be in error. The values reported here are correct values computed by us.

Table 6. Least squares plane deviations

Group	I	II	III	IV
Mean deviation of atom 3 from L.S. Plane through atoms 1, 2, 4, and 5 (Plane X)	−0.53 Å	−0.67 Å	−0.54 Å	−0.64 Å
Mean deviation of atom 9 from L.S. Plane through atoms 1, 2, 4, and 5 (Plane X)	+0.71	+0.79	+0.70	+0.69
Mean deviation of atom 7 from L.S. Plane through atoms 5, 6, 8 and 1 (Plane Y)	−0.52	−0.46	−0.53	+0.60
Mean deviation of atom 9 from L.S. Plane through atoms 5, 6, 8 and 1 (Plane Y)	+0.73	+0.78	+0.70	+0.68
⟨3 . . . 7⟩ distance	3.09	2.82	2.86	—

about various bonds as given in Table 5(c). Thus, for Group I structures the mean torsion angles starting from the 3-atom bridgehead show a gradual increase in value from 44(3)° (⟨z⟩) to 62(2)° (⟨x⟩) at the one-atom bridgehead. It is observed that the mean torsion angle ⟨yy⟩ about bonds involving both A and B rings have the maximum puckering with a value of 69(4)° for Group I, 67(5)° for Group II and 70(2)° for Group III structures. The mean torsion angles about various bonds of the B ring of Group II resemble structures in Groups I and III. However, the torsion angles about bonds of the A ring involving nitrogen are found to have torsion angles close to each other and this suggests that the A ring involving N is particularly less distorted. However, the large values of torsion angles (greater than 60°) show that the A ring is more puckered than a pure cyclohexane chair conformation in which the expected torsion angle is close to ±56°.[17,18] The mean torsion angles of the tetrazabicyclo(3,3,1)nonane system (Group III) appears to have the same pattern that is observed in Group I structures. In Group IV, the A ring, which has the chair conformation, has mean torsion angles about the x, y and z bonds agreeing more closely with one another unlike the structures in Groups I and III and this shows that the chair conformation is less distorted in 'chair–boat' structures. The torsion angles about the bonds of ring B shows that these values correspond to a slightly distorted boat conformation.[19]

The overall general discussion on the conformation of the bicyclo(3,3,1)nonane system could also be visualised in terms of least squares plane calculations through different groups of atoms and some characteristic features have been tabulated (Table 6). The deviations of atoms 3 and 9 from the best plane through the atoms 1, 2, 4 and 5 (referred to as Plane X) and of 7 and 9 from the best plane through atoms 5, 6, 8 and 1 (referred to as Plane Y) should, in the ideal case, have the same expected value of 0.73 Å. However, the deviations of atoms 3 and 7 of the 3-atom bridgeheads from Planes X and Y for Group I are found to have mean values of −0.53 and −0.52 Å respectively while atom 9 of one-atom bridgehead deviates from these planes by significantly larger distances, i.e., +0.71 and +0.73 Å respectively and the latter are found to be close to the ideal value for the chair conformation. This feature again shows that the ring is flattened near the 3-atom bridgehead and more puckered at the one-atom bridgehead of the bicyclo(3,3,1)nonane system. The mean deviations of atoms 3 and 9 in Group II from Plane X (corresponding to ring A involving nitrogen) are −0.67 and +0.79 Å showing that it is considerably less distorted than Group I. However, the mean deviations of atoms 7 and 9 of −0.46 and +0.78 Å respectively from Plane Y (corresponding to ring B with all C atoms) indicate that the ring is more distorted. Mean values of the Least squares plane deviations of atoms in the tetrazabicyclo(3,3,1)nonanes of Group III agreee well with the values of Group I structures. In Group IV the mean deviations of −0.64 and +0.69 Å with respect to ring A (which exists in the chair conformation) clearly show that the ring is less distorted than Group I and III structures already described. The deviations from Plane Y (with respect to ring B which exists in the boat conformation) show that the mean deviations reported are on the same side of the plane and the boat conformation is less distorted as these have nearly the same values of +0.60 and +0.68 Å respectively. Table 6 also gives the non-bonded $C_3 \ldots C_7$ distances for Groups I to III which exist in the 'twin–chair' conformation and the mean values are 3.09, 2.82 and 2.86 Å respectively. These values are larger than the expected non-bonded separation of 2.52 Å[7]† when both the

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† This value is, however, based on a cyclohexane chair conformation with tetrahedral bond angles and +60° torsion angles. It might appear that if we assume the currently accepted smaller values of torsion angles (±56°) and bond angles slightly larger (111°)[17,18], this $C_3 \ldots C_7$ separations would increase. However, model building shows that this value actually slightly decreases to 2.39 Å. This is because the model building would result in the bond angles 'C' (see Fig. 1) on either side of the bridgehead to have a much smaller value of 101° which effectively causes the slight shortening of the $C_3 \ldots C_7$ distance. A correct theoretical approach for the above estimation of the distance would involve detailed potential energy calculations using minimization techniques allowing for variations in bond lengths, bond angles and torsion angles and particularly treating these to have unequal values about various bonds as is observed from the observations of the structural data reported in this paper.

chairs have the ideal chair conformation. It is to be noted that the abovementioned non-bonded distances for Group II of 2.82 Å gives the mean $N_3 \ldots C_7$ contact while for Group III structures it is a $N_3 \ldots N_7$ contact and hence these values are found to have mean values smaller than the $C_3 \ldots C_7$ contact of 3.09 Å of Group I.

The structural studies on the bicyclo(3,3,1)-nonane system thus reveal that the system prefers to adopt in general the 'chair–chair' conformation in the crystal lattice with considerable flattering at the 3-atom bridgeheads as revealed by the bond angles and torsion angles of the structures. It adopts a 'boat–chair' conformation mainly in situations of bulky substitutions at positions 3 or 7 as in the case of structures **9**, **10** and **11**. It is further seen that the 'boat–chair' conformation is considerably less distorted than the 'chair–chair' form. For the 3-azabicyclo(3,3,1)nonane system (Group II) it is seen that the 6-membered ring involving N is less distorted than the other ring having all C atoms. The tetrazabicyclo(3,3,1)nonane structures (**7** and **8**) exist in the 'chair–chair' form with distortions in the 6-membered ring system very nearly the same as in structures belonging to Group I.

REFERENCES

[1] E. L. Eliel, *Stereochemistry of Carbon Compounds* p. 295, McGraw-Hill, New York (1962).

[2] G. Englinton, J. Martin, and W. Parker, *J. Chem. Soc.* 1243 (1965).

[3] H. J. Schneider, and W. Ansorge, *Tetrahedron* **33**(2), 265 (1977).

[4] E. L. Osina, V. S. Mastryukov, L. V. Vilkov, and N. A. Belinkova, *J. Chem. Soc.* Chem. Commun. **1**, 12 (1976).

[5] J. A., Peters, J. M. A., Baas, B. van der Graaf, J. M. van der Toorn, and H. van Bekkum, *Tetrahedron* **34**, 3313 (1978).

[6] S. K. Bhattacharjee, K. K. Chacko and R. Zand, (1978).

[7] W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.* 1844 (1965).

[8] N. C. Webb and M. R. Becker, *Ibid.* (B), p. 1317 (1967).

[9] E. E. Abola, J. Pletcher and M. Sax, *Acta Cryst.* **B30**, 1555 (1974).

[10] M. Dobler and J. D. Dunitz, *Helv. Chim. Acta* **47**, 695 (1964).

[11] M. Kaftory and J. D. Dunitz, *Acta Cryst.* **B32**, 1 (1976).

[12] C. S. Choi, A. Santaro and J. E. Abel, *Ibid.* **B32**, 354 (1976).

[13] C. S. Choi and S. Bulusu, *Ibid.* **B30**, 1576 (1974).

[14] P. W. Hickmott, F. J. Cox and G. A. Sim, *J. Chem. Soc.* Perkins Trans-1, 2544 (1974).

[15] C. Tamura and G. A. Sim, *Ibid.* (B), 1241 (1968).

[16] P. D. Crawdwick and G. A. Sim, *Ibid.* (B), 2218 (1971).

[17] C. Altona and M. Sundaralingam, *Tetrahedron* **26**, 925 (1970).

[18] R. Bucourt, *Topics in Stereochemistry*, (Edited by E. L. Eliel and N. L. Allinger) Vol. 8, p. 165 (1974).

[19] M. Bixon and S. Lifson, *Tetrahedron* **23**, 769 (1967).